

Preparations of $[(^n\text{C}_3\text{H}_7)_2\text{NH}_2][\text{V}_7\text{MF}_8(\text{O}_2\text{CCMe}_3)_{16}]$ and $[(^n\text{C}_3\text{H}_7)_2\text{NH}_2][\text{Fe}_7\text{MF}_8(\text{O}_2\text{CCMe}_3)_{16}]$

All procedures were performed under nitrogen atmosphere. Acetonitrile was distilled over CaH_2 . Acetone was from Fluka. All other commercially available reagents and solvents were used without further treatment.

VF_3 was purchased from Alfa Aesar, $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, di-propylamine, $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, CdCO_3 were from Aldrich, pivalic acid, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ from Fluka, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ from Merck, $2 \cdot \text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ from Fisher and $[\text{Co}_2(\text{OH})_2(\text{O}_2\text{CMe}_3)_4(\text{HO}_2\text{CMe}_3)_4]$ 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. Winpenney Chem. Eur. J. 2003, 9, 5142 – 5161.

1. $[(\text{C}_3\text{H}_7)_2\text{NH}_2][\text{V}_7\text{ZnF}_8(\text{O}_2\text{CCMe}_3)_{16}]$

An intimate mixture of VF_3 (2 g, 0.019 moles), pivalic acid (27.5 g, 270 mmoles) and dipropylamine (1.6 g, 16.0 mmoles) was heated at 140°C for 0.5 hours. After which time Zn powder (0.65 g, 10.0 mmoles) was added and the mixture was heated at 160°C for 14.5 hours. On cooling MeCN (50 cm^3) was added and the mixture was refluxed for 30 minutes. Once cooled the crude product was collected by filtration, and extracted into hexane (20 cm^3) and the mixture was filtered. The solvent was removed and acetone (20 cm^3) was added and again the suspension was filtered. The green solid (4.14 g, 60 % yield) was dried *en vacuo* and could be recrystallised from EtOAc/MeCN or pentane/acetone mixtures. The acetone layer when left under a stream of nitrogen also yielded crystals of the product.

Elemental analysis calculated for $\text{V}_7\text{ZnC}_{86}\text{H}_{160}\text{O}_{32}\text{NF}_8$: C, 45.02; H, 7.03; N, 0.61; V, 15.54; Zn, 2.85; F, 6.64. Found: C44.78; H 7.25; N 0.49; V 15.42; Zn 2.85; F 6.38. Electrospray ES (sample dissolved in THF, run in MeCN) m/z : -2192 $[\text{M} - (\text{C}_3\text{H}_7)_2\text{NH}_2]^-$; +2314 $[\text{M} + \text{Na}]^+$

2. $[(\text{C}_3\text{H}_7)_2\text{NH}_2][\text{V}_7\text{NiF}_8(\text{O}_2\text{CCMe}_3)_{16}]$

An intimate mixture of VF_3 (2 g, 0.019 moles), pivalic acid (27.5 g, 270 mmoles), dipropylamine (1.6 g, 16.0 moles) and 'basic nickel carbonate', $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (0.50 g, 0.86 mmoles) was heated at 160°C for 6 hours. On cooling MeCN (50 cm^3) was added and the mixture was refluxed for 30 minutes. Once cooled the mixture was filtered and washed with acetone and dried *en vacuo*. The green solid could be recrystallised from hot EtOAc/MeCN mixture or heptane.

Elemental analysis calculated for $\text{V}_7\text{NiC}_{86}\text{H}_{160}\text{O}_{32}\text{NF}_8$: C, 45.16; H, 7.05; N, 0.61; V, 15.59; Ni, 2.57. Found: C43.91; H 6.95; N, 0.58; V, 16.01; Ni, 2.07.

Electrospray ES (THF) m/z : - 2185 $[\text{M} - \text{C}_3\text{H}_7)_2\text{NH}_2]^-$.

Preparations of $[(C_3H_7)_2NH_2][Fe_7M'F_8(O_2CCMe_3)_{16}]$

3. $[(C_3H_7)_2NH_2][Fe_7MnF_8(O_2CCMe_3)_{16}]$

Hydrated iron fluoride $FeF_3 \cdot 3H_2O$ (3.0 g, 18.0 mmol), dipropylamine $^n(C_3H_7)_2NH$ (1.3 g, 12.8 mmol) and pivalic acid Me_3CCOOH (27.0g 264 mmol) were stirred together at 140 °C for half hour, followed by addition of a reagent containing the second metal (for ex.) $MnCl_2 \cdot 4H_2O$ (1.25g, 6.3 mmol) followed by further heating for 7 hours. Cooling to room temperature and addition of acetonitrile (70 ml) with stirring causes formation of a precipitate. This precipitate was collected after 1h, washed with acetonitrile, acetone and dried under N_2 . It was then redissolved in pentane, the solution filtered and to this solution was added ethylacetate (EtOAc). Slow concentration of the solution under a N_2 flow at room temperature gives a light red-brown crystalline product, that was filtered washed with ethylacetate: acetonitrile (3:1) and dried in N_2 .

Yield 3.85 g, 65% calculated from $FeF_3 \cdot 3H_2O$.

Elemental analysis calculated for $C_{86}H_{160}F_8Fe_7Mn_1N_1O_{32}$: C, 44.56; H, 6.96; N, 0.60; Fe, 16.86; Mn, 2.37.

Found: C 43.96; H 6.83; N 0.56; Fe 16.38; Mn 2.13.

EI ES m/z : + 2317 $[M]^+$.

$[(C_3H_7)_2NH_2][Fe_7M'F_8(O_2CCMe_3)_{16}]$, where $M' = Ni, Cd, Zn, Fe, Co$, were prepared similarly approximate in the same yields by using the following salts as secondary metal source:

$2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$; $CdCO_3$ or $CdCl_2 \cdot H_2O$; $2ZnCO_3 \cdot 3Zn(OH)_2$; $FeCl_2 \cdot 4H_2O$ and $[Co_2(OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$

4. $[(C_3H_7)_2NH_2][Fe_7NiF_8(O_2CCMe_3)_{16}] \cdot EtOAc$,

Elemental analysis calculated for $C_{90}H_{168}F_8Fe_7Ni_1O_{34}$: C, 44.86; H, 7.03; N, 0.58; Fe, 16.22; Ni, 2.44, F 6.31. Found: C, 44.95; H 7.11; N 0.59; Fe 16.07; Ni 2.42; F 6.23.

5. $[(C_3H_7)_2NH_2][Fe_7CdF_8(O_2CCMe_3)_{16}]$,

Elemental analysis calculated for $C_{86}H_{160}Cd_1F_8Fe_7N_1O_{32}$: C, 43.48; H, 6.79; N, 0.59; Fe, 16.46; Cd, 4.73. Found: C 43.34; H 7.01; N 0.57; Fe 16.88; Cd 4.13.

6. $[(C_3H_7)_2NH_2][Fe_7FeF_8(O_2CCMe_3)_{16}] \cdot EtOAc$,

Elemental analysis calculated for $C_{90}H_{168}F_8Fe_8N_1O_{34}$: C, 44.91; H, 7.20; N, 0.56; Fe, 18.56; F, 6.31. Found: C 44.77; H 7.20; N 0.56; Fe 18.87; F 6.37.

7. $[(C_3H_7)_2NH_2][Fe_7CoF_8(O_2CCMe_3)_{16}] \cdot EtOAc$,

Elemental analysis calculated for $C_{86}H_{160}CoF_8Fe_7N_1O_{32}$: C, 44.85; H, 7.03; N, 0.58; Fe, 16.22; Co, 2.45, F 6.31. Found: C 44.72; H 6.72; N 0.58; Fe 16.04; Co 2.39; F 6.10.

8. $[(C_3H_7)_2NH_2][Fe_7ZnF_8(O_2CCMe_3)_{16}]$

Electrospray ES (THF) m/z : + 2328 $[M]^+$; - 2226 $[M - C_3H_7)_2NH_2]^+$,

Unit cell dimensions for $[(C_3H_7)_2NH_2][Fe_7M'F_8(O_2CMe_3)_{16}]$

Cryst. solvent	M'	a, Å	b, Å	c, Å	α	β	γ	V	T	SG	color
EtOAc	Mn	25.301(1)	16.334(1)	30.568(1)	90	110.180(1)	90	11857(1)	100	P2 ₁ /c	light red-brown
EtOAc	Cd	25.758(6)	16.624(4)	31.065(9)	90	110.73(2)	90	12441(3)	100	P	light yellow
Pentane/EtOAc	Ni	25.68(1)	20.199(7)	26.245(8)	90	109.17(3)	90	12858	100	P	light green
Pentane/EtOAc	Zn	25.995(7)	20.419(6)	26.346(7)	90	109.91(2)	90	13148(5)	220	C2	pale-green
Pentane/EtOAc	Fe ²⁺	26.041(3)	20.515(2)	26.199(3)	90	110.125(3)	90	13142	180	C2	green
Pentane/EtOAc	Co	26.794(8)	20.945(6)	26.516(6)	90	110.57(2)	90	13932	RT	C	light red-orange

Unit cell dimensions for $[(C_3H_7)_2NH_2][V_7M'F_8(O_2CMe_3)_{16}]$

Acetone	Zn	25.803(4)	16.903(3)	31.364(4)	90	110.396(10)	90	12822	240	P2 ₁ /c	emerald
EtOAc	Ni	25.533(9)	20.342(7)	26.137(10)	90	108.640(6)	90	12863	100	C2/c	emerald

Comment on the Fe₇M' structures. Crystals of these compounds have well defined morphology, nevertheless, they all diffract rather poorly. The molecular ring structure and the location of the amine molecule could in all cases be determined unequivocally, but the tert-butyl groups appear to be rather disordered and thus result in poor refinements with rather large residuals. Two structures, representatives for the two different types of unit cells are demonstrated by their cif files, namely the compound with Mn substituted for one of the Fe³⁺ and the one with an Fe²⁺ substitution.

Preparations of $[R'_2NH_2][Cr_7M'F_8(O_2CR)_{16}]$

9. $[(C_3H_7)_2NH_2][Cr_7Fe^II F_8(O_2CCH_2CMe_3)_{16}]$

CrF₃·4H₂O (5.0 g, 27.6 mmol), tert-butylacetic acid (20 g, 172.4 mmol) and dipropylamine (1.5 g, 14.9 mmol) were heated in a Teflon flask at 140 °C for 2 hours with stirring. During this period the chromium fluoride dissolved to produce a green solution. The flask was then heated for a further 15 min under nitrogen before the addition of Fe^{II}Cl₂·4H₂O (1.5 g, 7.5 mmol). The temperature was then increased to 160 °C and the flask heated for a further 5 hours. After this the flask was cooled to room temperature and acetonitrile (50 mL) was added with stirring. The green product was filtered and washed with a large quantity of acetonitrile. The product was purified by column chromatography on silica gel using as the eluent toluene with 2% ether and it is eluted as the second fraction. Yield 5.2 g (52.4 %). The product was recrystallised from toluene/MeCN.

Elemental analysis calculated (%) for Cr₇FeF₈O₃₂C₁₀₂H₁₉₂N: Cr, 14.46; Fe, 2.22; C, 48.68; H, 7.69; N, 0.56. Found: Cr, 14.32; Fe, 2.31; C, 48.66; H, 7.77; N, 0.49.

Electrospray-MS (MeOH) *m/z*: +2436 {[M – (C₃H₇)₂NH₂]+Na}⁺; +2538 [M+Na]⁺.

10. $[\text{Et}_2\text{NH}_2][\text{Cr}_7\text{Zn}^{\text{II}}\text{F}_8(\text{O}_2\text{CCH}_2\text{CMe}_3)_{16}]$ - was obtained by an analogous procedure to **9** but in air and replacing $\text{Fe}^{\text{II}}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ with $2 \cdot \text{ZnCO}_3 \cdot 3 \cdot \text{Zn}(\text{OH})_2$ (0.9 g,) and dipropylamine by diethylamine. The eluent for the silica column was a solution of toluene with 5% ether, and **10** elutes as the first fraction. Yield 7.1 g (72.1 %). The product was recrystallised from MeOH.

Elemental analysis calculated (%) for $\text{Cr}_7\text{ZnF}_8\text{O}_{32}\text{C}_{100}\text{H}_{188}\text{N}$: Cr, 14.57; Zn, 2.62; C, 48.08; H, 7.59; N, 0.56. Found: Cr, 14.63; Zn, 2.57; C, 48.04; H, 7.68; N, 0.44. Electrospray-MS (MeOH) m/z : -2422 $[\text{M} - (\text{C}_3\text{H}_7)_2\text{NH}_2]^-$; +2519 $[\text{M} + \text{Na}]^+$.

11. $[\text{Et}_2\text{NH}_2][\text{Cr}_7\text{Mn}^{\text{II}}\text{F}_8(\text{O}_2\text{CCH}_2\text{CMe}_3)_{16}]$ - was obtained by an analogous procedure to **9** but replacing $\text{Fe}^{\text{II}}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ with $\text{Mn}^{\text{II}}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (1.5 g, 7.6 mmol). The eluent for the silica column was a 20:1 solution of toluene:ethyl acetate, **11** elutes as the second fraction). Yield 5.4 g (55.0 %). The product was recrystallised from MeOH.

Elemental analysis calculated (%) for $\text{Cr}_7\text{MnF}_8\text{O}_{32}\text{C}_{100}\text{H}_{188}\text{N}$: Cr, 14.63; Mn, 2.21; C, 48.29; H, 7.62; N, 0.56. Found: Cr, 14.80; Mn, 2.22; C, 48.22; H, 7.84; N, 0.46. Electrospray-MS (MeOH) m/z : +2486 $[\text{M}]^+$; +2509 $[\text{M} + \text{Na}]^+$.

12. $[(\text{C}_3\text{H}_7)_2\text{NH}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C}_5\text{H}_3\text{S})_{16}]$. $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ (2.0 g, 11.0 mmol), thiophene-3-carboxylic acid (10 g, 78.0 mmol), dipropylamine (0.7 g, 9.6 mmol) and $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (0.2 g, 0.34 mmol) were heated in a Teflon flask at 150 °C for 1h with stirring. During this period a green solid was formed. After this the flask was cooled to 100°C and toluene (30 mL) was added with stirring. The obtained solution was refluxed for 5h, then toluene was removed by distillation and acetonitrile (20 ml) was added. The microcrystalline product was washed with a large quantity of acetonitrile and dried in air. The product was recrystallised from THF/toluene.

Yield 2.72g (63.6%)

Elemental analysis calculated (%) for $\text{C}_{86}\text{H}_{64}\text{Cr}_7\text{F}_8\text{N}_1\text{Ni}_1\text{O}_{32}\text{S}_{16}$: C, 38.10; H, 2.38; N, 0.52; Cr, 13.43; Ni, 2.16 Found: C, 38.42; H, 2.41; N, 0.52; Cr, 12.98; Ni, 2.21. Electrospray-MS (THF) m/z : +2813 $[\text{M} + (\text{C}_3\text{H}_7)_2\text{NH}_2]^+$.

13. $[(\text{C}_3\text{H}_7)_2\text{NH}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C}_5\text{H}_3\text{S})_{16}]$. $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ (2.0 g, 11.0 mmol), thiophene-2-carboxylic acid (10 g, 78.0 mmol), dipropylamine (0.7 g, 9.6 mmol) and $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (0.2 g, 0.34 mmol) were heated in a Teflon flask at 150 °C for 6h with stirring. During this period a green solid was formed. After this the flask was cooled to room temperature and acetone added (30 mL) with stirring. The precipitate was collected by filtration and washed with a large quantity of acetone and dried in air. The product was recrystallised from THF/acetonitrile. Yield 3.4g (79.5%) .Elemental analysis calculated (%) for $\text{C}_{86}\text{H}_{64}\text{Cr}_7\text{F}_8\text{N}_1\text{Ni}_1\text{O}_{32}\text{S}_{16}$: C, 38.10; H, 2.38; N, 0.52; S, 18.92; Cr, 13.43; Ni, 2.16 Found: C, 38.44; H, 2.55; N, 0.49; S, 19.14; Cr, 12.78; Ni, 2.35.

14. $[(\text{C}_3\text{H}_7)_2\text{NH}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C}_6\text{H}_4\text{CH}_3)_{16}]$ was obtained by an analogous reaction to **13** but using o-toluic acid . The reaction produced a green precipitate during heating, and after cooling THF (30 ml) was added to complete precipitation. The solid was collected by filtration, washed with THF (3x15 ml), dried in air and crystallized from toluene. Yield 3.1 g (56.7%). Elemental analysis calculated (%) for $\text{C}_{134}\text{H}_{128}\text{Cr}_7\text{F}_8\text{N}_1\text{Ni}_1\text{O}_{32}$: C,

56.69; H, 4.54; N, 0.49; Cr, 12.82; Ni, 2.07 Found: C, 57.7; H, 4.82; N, 0.44; Cr, 12.41; Ni, 2.08

15. $[(C_3H_7)_2NH_2][Cr_7NiF_8(O_2C_6H_2(OMe)_3)_{16}]$ was obtained by an analogous reaction to **13**, using 2,3,4-trimethoxybenzoic acid. The reaction produced a green precipitate during heating, and after cooling MeCN (30 ml) was added to complete precipitation. The solid was collected by filtration, washed with MeCN (3x15 ml), dried in air and crystallized from hot MeCN. Yield 2.7 g (42%). Elemental analysis calculated (%) for $C_{166}H_{192}Cr_7F_8N_1Ni_1O_{80}$: C, 49.16; H, 4.77; N, 0.35; Cr, 8.97; Ni, 1.45 Found: C, 49.20; H, 4.76; N, 0.31; Cr, 9.24; Ni, 1.43.

16. $[(C_3H_7)_2NH_2][Cr_7NiF_8(O_2CCH_2Cl)_{16}]$ $CrF_3 \cdot 4H_2O$ (5.0 g), chloroacetic acid (12 g, 127 mmol) and dipropylamine (0.7 g, 9.6 mmol) and $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ (1.2 g, 2.0 mmol) were heated in a Teflon flask at 140 °C for 2.5 hours with stirring. After this the flask was cooled to room temperature and THF (50 mL) was added with stirring. The green product was collected by filtration, washed with THF, dried over $CaCl_2$ and then dissolved in MeCN in presence of small amount of chloroacetic acid, filtered and finally precipitated by Et_2O . Yield 4.2 g (49%).

Elemental analysis calculated (%) for $C_{38}H_{48}Cl_{16}Cr_7F_8N_1Ni_1O_{32}$: C, 21.01; H, 2.23; N, 0.64; Cr, 16.75; Ni, 2.70 Found: C, 20.94; H, 2.22; N, 0.63; Cr, 16.11; Ni, 2.93.

Electrospray-MS (THF) m/z : +2195 $[M+Na]^+$, - 2070 $[M - (C_3H_7)_2NH_2]^+$.