The Acid Test: the chemistry of carboxylic acid functionalised {Cr_7Ni} rings

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1. General Experimental Section

All reagents and solvents were commercially available and used as received. Green $[^{n}Pr_2NH_2][Cr_7NiF_8(O_2C^{t}Bu)_{16}]$ was prepared by the modification of the published method,[1] using basic nickel carbonate and a reaction time of 24 h at 160 °C. Column chromatography was carried out using Silica 60A (particle size 35-70 µm, Fisher, UK) as the stationary phase, and TLC was performed on pre-coated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany). ESI mass spectrometry and elemental analyses were performed by departmental services at The University of Manchester. Carbon, nitrogen and hydrogen analysis was performed using a Flash 200 elemental analyser. Metal analysis was performed by Thermo iCap 6300 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The crystal data for compounds **2**, **3** and **5** were collected on a Bruker X8 Prospector 3-circle diffractometer with a copper microfocus source and an APEX II CCD detector. The crystal data for compound **4** was collected in-house on an Agilent Technologies SuperNova 4-circle diffractometer with a molybdenum microfocus source and an EOS CCD detector. The crystal data for Compound **5** was collected on Diamond light source beamline I19 equipped with a 4-circle κ goniometer using a Rigaku Saturn 724+ CCD detector.

2. Synthesis and Experimental Section

2.1 Synthesis of $[^{n}Pr_2NH_2][Cr_7NiF_8(O_2C^{t}Bu)_{15}(O_2CC_6H_4CO_2H)]$ 2

$[^{n}Pr_2NH_2][Cr_7NiF_8(O_2C^{t}Bu)_{16}]$ (3.46 g, 1.51 mmol), *iso*-phthalic acid (0.6 g, 3.61 mmol), toluene (25 mL) and 1,2-dichlorobenzene (25mL) were heated with constant stirring at 180°C for 2.5 hrs, with a condenser attached to remove the toluene. The solution was allowed to cool to room temperature, upon which a precipitate formed. The solution was filtered and collected and the solid, mainly starting material, was re-reacted with the above conditions. The process was repeated three times, after which all filtered solutions were combined and solvent removed under reduced pressure. The resulting residue was purified by column chromatography on 40-63 µm mesh silica gel (BDH). First toluene followed by 40:1 toluene:ethyl acetate was used, which allowed un-reacted $[^{n}Pr_2NH_2][Cr_7NiF_8(O_2C^{t}Bu)_{16}]$ to be eluted, leaving the products of the reaction at the top of the column. Thereafter 15:1 toluene:ethyl acetate elution was used, eluting **2**. The solvent was removed under reduced pressure and the resulting residue recrystallized from slow evaporation of diethyl ether and acetonitrile, yielding dark green crystals suitable for single crystal XRD. Yield 1.02 g, 28.6 % (based on $[^{n}Pr_2NH_2][Cr_7NiF_8(O_2C^{t}Bu)_{16}]$) ES-MS *m/z*: +2358 $[M+H]^+$, +2380 $[M+Na]^+$ Elemental anal. calculated (%) for $C_{89}H_{156}N_1O_{34}F_8Cr_7Ni$: C 45.323, H 6.67, N 0.59, Cr 15.43, Ni 2.49; Found: C 44.95, H 6.89, N 0.60, Cr 15.67, Ni 2.52

2.2 Synthesis of $\{[C_5H_{10}NH_2][^{n}Pr_2NH_2][Cr_7NiF_8(O_2C^{t}Bu)_{15}(O_2CC_6H_4CO_2)]\}$ 3

Compound **2** (0.52 g, 0.211 mmol), was dissolved in acetone (15 mL) and diethyl ether (15 mL). To this 10 mL of 0.021 M solution of piperidine in acetone (0.212 mmol) was added and the mixture stirred for 5 minutes. The solution was left to slowly evaporate yielding small dark green crystals suitable for single crystal XRD. These were analysed and the remaining

crystals collected by filtration. Yield 0.53 g (97.8 % based on **1**) Elemental anal. calculated (%) for $C_{94}H_{295}Cr_7F_8N_2NiO_{34}$: C 43.88, H 11.56, N 1.09, Cr 14.15, Ni 2.28; Found: C 44.02, H 11.46, N 1.05, Cr 14.23, Ni 2.26

2.3 Synthesis of {[$C_9H_{18}NH_2$][$^n Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_6H_4CO_2)$]} 4

Compound **2** (0.52 g, 0.211 mmol), was dissolved in acetone (15 mL) and diethyl ether (15 mL). To this 10 mL of 0.021 M solution of piperidine in acetone (0.212 mmol) was added and the mixture stirred for 5 minutes. The solution was left to slowly evaporate yielding small dark green crystals suitable for single crystal XRD. These were analysed and the remaining crystals collected by filtration. Yield 0.50 g (95.7 % based on **1**) Elemental anal. calculated (%) for $C_{98}H_{175}Cr_7F_8N_2NiO_{34}$: C 47.08, H 7.06, N 1.12, Cr 14.56, Ni 2.35; Found: C 46.85, H 7.33, N 1.24, Cr 14.32, Ni 2.12

2.4 Synthesis of {{[$^n Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_6H_4CO_2)$]}$_4$[$Cu_4(OH)_4(OC_3H_6)$]} 5

Compound **2** (0.52 g, 0.211 mmol), was dissolved in acetone (15 mL) and diethyl ether (15 mL). To this 10 mL of 0.021 M solution of piperidine in acetone (0.212 mmol) and 10 mL of 0.010 M solution of copper perchlorate hexahydrate in acetone (0.100 mmol) were added and the mixture stirred for 8 hours. After the solvent was removed under reduced pressure and the residue was washed with acetone (3 x 30 mL), extracted in diethyl ether and recrystallized from slow evaporation of diethyl ether and acetonitrile, yielding small dark green crystals suitable for single crystal XRD. These were analysed and the remaining crystals collected by filtration. Yield 0.42 g (81.1 % based on **2**) Elemental anal. calculated (%) for $C_{359}H_{630}N_4O_{141}F_{32}Cr_{28}Ni_4Cu_4$: C 43.93, H 6.51, N 0.57, Cu 2.59; Found: C 43.72, H 6.77, N 0.53, Cu 2.77

2.5 Synthesis of {{[$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^{t}Bu)_{15}(O_2CC_6H_4CO_2)$]}$_6$[$Zn_4O$]} 6

Compound **2** (0.52 g, 0.211 mmol), was dissolved in acetone (15 mL) and diethyl ether (15 mL). To this 10 mL of 0.021 M solution of piperidine in acetone (0.212 mmol) and 10 mL of 0.010 M solution of zinc perchlorate hexahydrate in acetone (0.100 mmol) were added and the mixture stirred for 14 hours After the solvent was removed under reduced pressure and the residue was washed with acetone (3 x 30 mL), extracted in diethyl ether and recrystallized from slow evaporation of diethyl ether and acetonitrile, yielding small dark green crystals suitable for single crystal XRD. These were analysed and the remaining crystals collected by filtration. Yield 0.22 g (43.4 % based on **2**) Elemental anal. calculated (%) for $C_{534}H_{936}N_6O_{205}F_{48}Cr_{42}Ni_6Zn_4$: C 44.45, H 6.54, N 0.58, Zn 1.81; Found: C 44.09, H 6.49, N 0.55, Zn 1.80

3. X-Ray Crystallography

The crystal data contained within this report are generally very weak data. This is mainly due to the size of the crystals analysed, the inherent disorder and the sheer size of some of the molecules studied. This is reflected in the large number of restraints present in some of the models. However, although some R-factors may be higher than would be ideal, the locations of the metal sites and rigid bridging ligands i.e. fluorides and *iso*-phthalate groups are quite well defined and the components are easily identifiable. Based on the starting reagents we are highly confident of the models produced.

3.1 X-Ray Crystallographic Data {$Cr_7Ni(O_2CC_6H_4CO_2H)$} 2

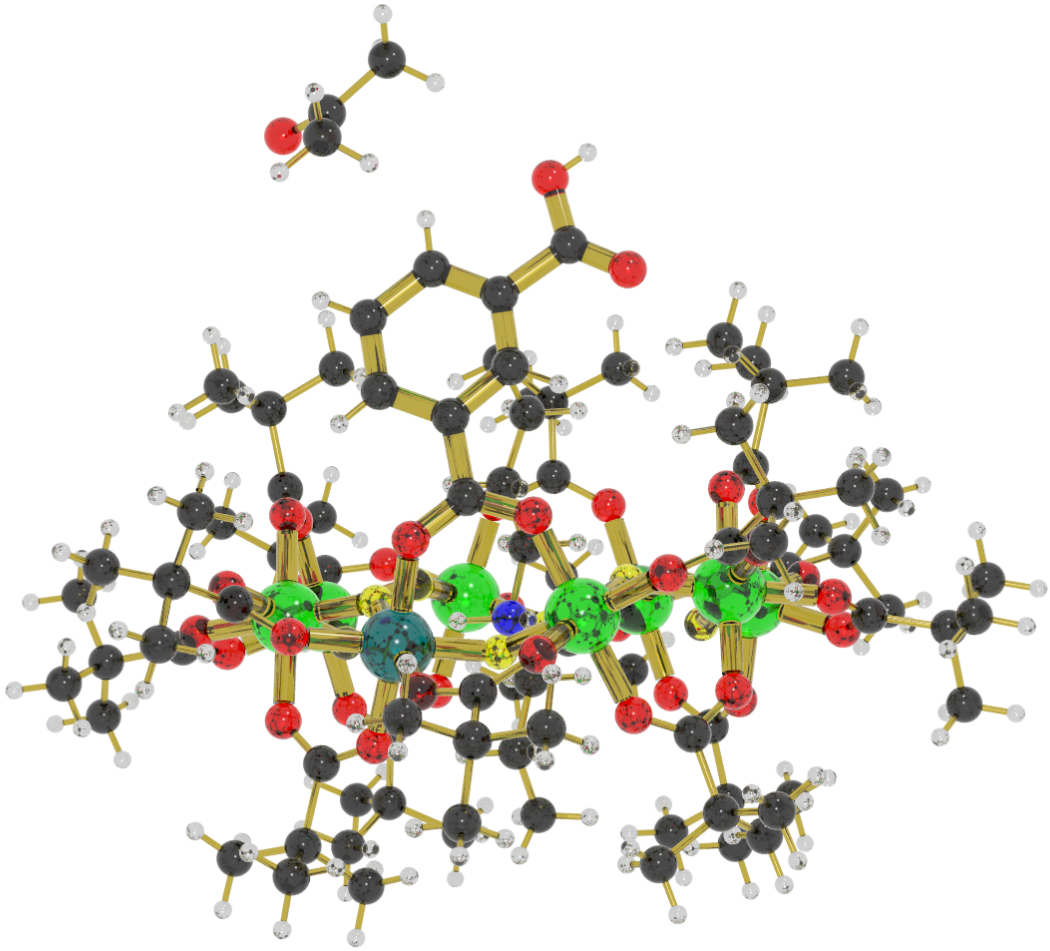

Fig. S1. The structure of **2** in the crystal. Colours: Cr = green, Ni = turquoise, F = yellow, O = red, C = black, N = blue, H = white.

3.1.1 Table S1: Crystal data and structure refinement for 2

Formula	$C_{92}H_{162}Cr_7F_8NNiO_{35}$
M	2416.92
Crystal system	Monoclinic
Space group	*C2/c*
a / Å	55.3514 (13)
b / Å	16.6288 (4)
c / Å	32.7345 (6)
β / °	115.557 (3)
U / Å^3	27181.7 (10)
T / K	100
Z	8
ρ / g cm^{-1}	1.181
Shape and colour	block, green
Size / mm	0.3 × 0.2 × 0.1
λ / Å	1.54178
μ / mm^{-1}	5.22
Unique data	22568
Absorption correction	multi-scan
Transmission max/min	0.358/0.247
Unique data [$F_o > 4\sigma F_o$]	17233
Parameters/Restraints	1277/2508
*R*1, *wR*2[a]	0.147, 0.385
Weighting scheme[b] [w^{-1}]	$1/[\sigma^2(F_o^2) + (0.1391P)^2 + 548.7802P]$
Goodness of fit	1.16
Largest residuals [e Å^{-3}]	1.45, -0.95

[a] *R*1 based on observed data, *wR*2 on all unique data.
[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

3.2 X-Ray Crystallographic Data $[C_5H_{10}NH_2]\{Cr_7Ni(O_2CC_6H_4CO_2)\}$ 3

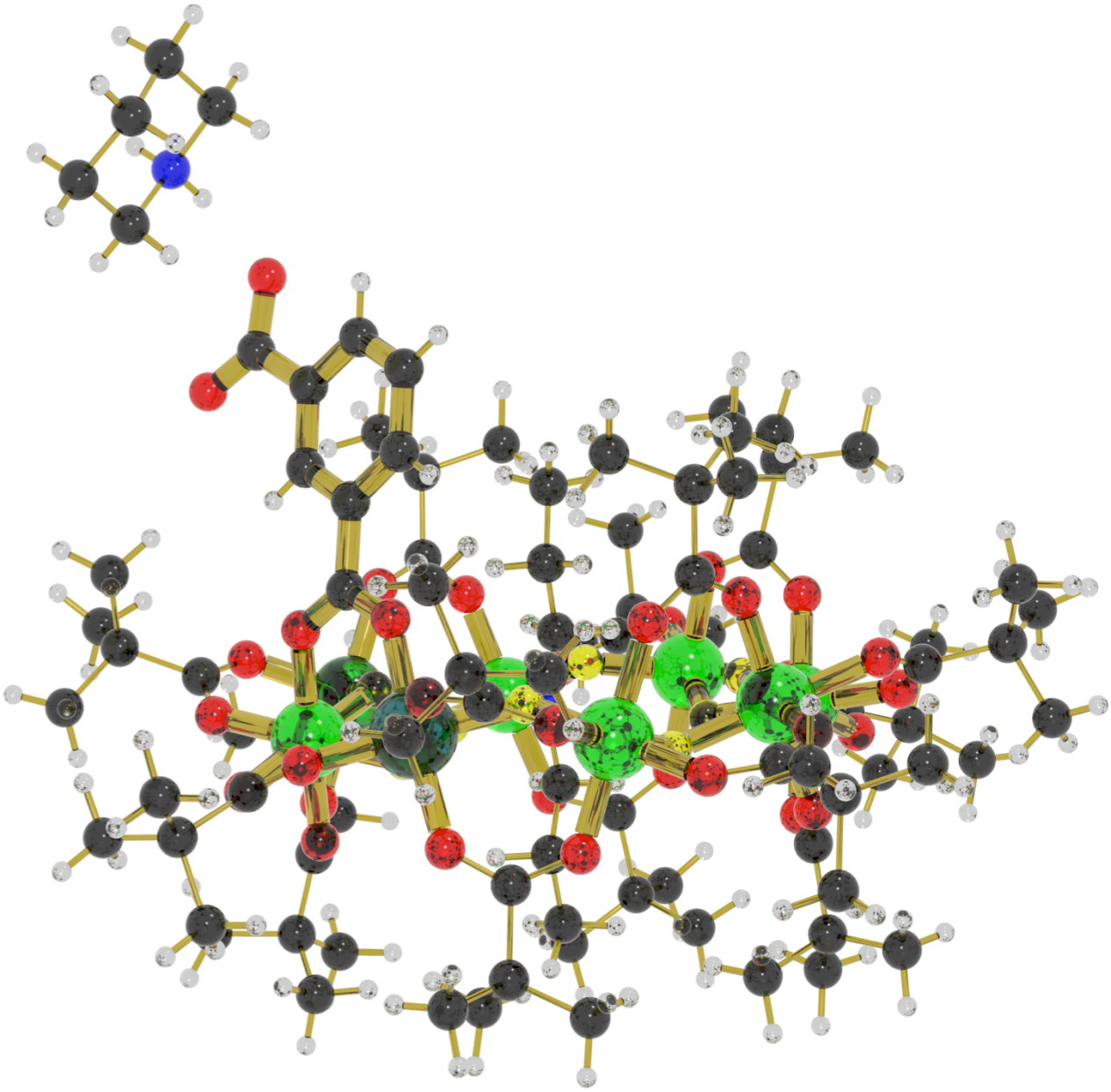

Fig. S2. The structure of **3** in the crystal. Colours as **S1**

3.2.1 Table S2: Crystal data and structure refinement for 3

Formula	$C_{94}H_{167}Cr_7F_8N_2NiO_{34}$
M	2443.99
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	25.0881 (11)
b / Å	16.4808 (7)
c / Å	33.9931 (15)
β / °	91.685 (15)
U / Å^3	14049.1 (11)
T / K	100
Z	4
ρ / g cm^{-1}	1.156
Shape and colour	Block, green
Size / mm	0.32 × 0.25 × 0.1
λ / Å	1.54178
μ / mm^{-1}	5.04
Unique data	11856
Absorption correction	multi-scan
Transmission max/min	1.00/0.170
Unique data [$F_o > 4\sigma F_o$]	6443
Parameters/Restraints	1315/1311
*R*1, *wR*2[a]	0.087, 0.245
Weighting scheme[b] [w^{-1}]	$1/[\sigma^2(F_o^2) + (0.1029P)^2 + 52.2056P]$
Goodness of fit	1.02
Largest residuals [e Å^{-3}]	0.73, -0.41

[a] *R*1 based on observed data, *wR*2 on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

3.3 X-Ray Crystallographic Data $[C_9H_{18}NH_2]\{Cr_7Ni(O_2CC_6H_4CO_2)\}$ 4

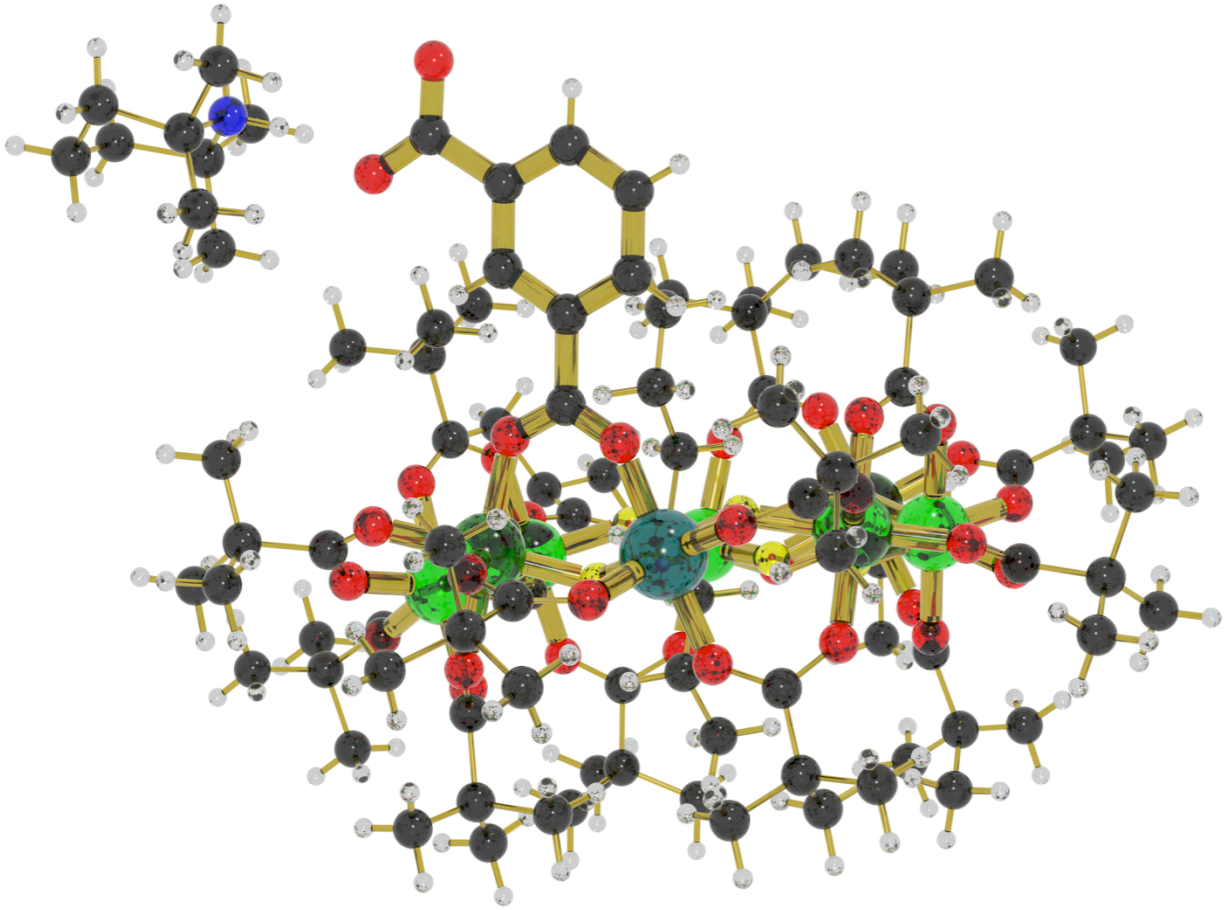

Fig. S3. The structure of **4** in the crystal. Colours as **S1**

3.3.1 Table S3: Crystal data and structure refinement for 4

Formula	$C_{98}H_{175}Cr_7F_8N_2NiO_{34}$
M	2500.10
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	16.2899 (8)
b / Å	30.037 (2)
c / Å	29.588 (2)
β / °	97.377 (6)
U / Å^3	14357.8 (17)
T / K	100
Z	4
ρ / g cm^{-1}	1.157
Shape and colour	Block, green
Size / mm	0.3 × 0.22 × 0.15
λ / Å	0.71073
μ / mm^{-1}	1.06
Unique data	14881
Absorption correction	multi-scan
Transmission max/min	1.00/0.970
Unique data [$F_o > 4\sigma F_o$]	8288
Parameters/Restraints	1351/6
*R*1, *wR*2[a]	0.098, 0.306
Weighting scheme[b] [w^{-1}]	$1/[\sigma^2(F_o^2) + (0.1538P)^2 + 41.2515P]$
Goodness of fit	1.02
Largest residuals [e Å^{-3}]	1.32, -0.43

[a] *R*1 based on observed data, *wR*2 on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

3.4 X-Ray Crystallographic Data $\{Cr_7Ni(O_2CC_6H_4CO_2)\}_4[Cu_4(OH)_4(OC_3H_6)]$ 5

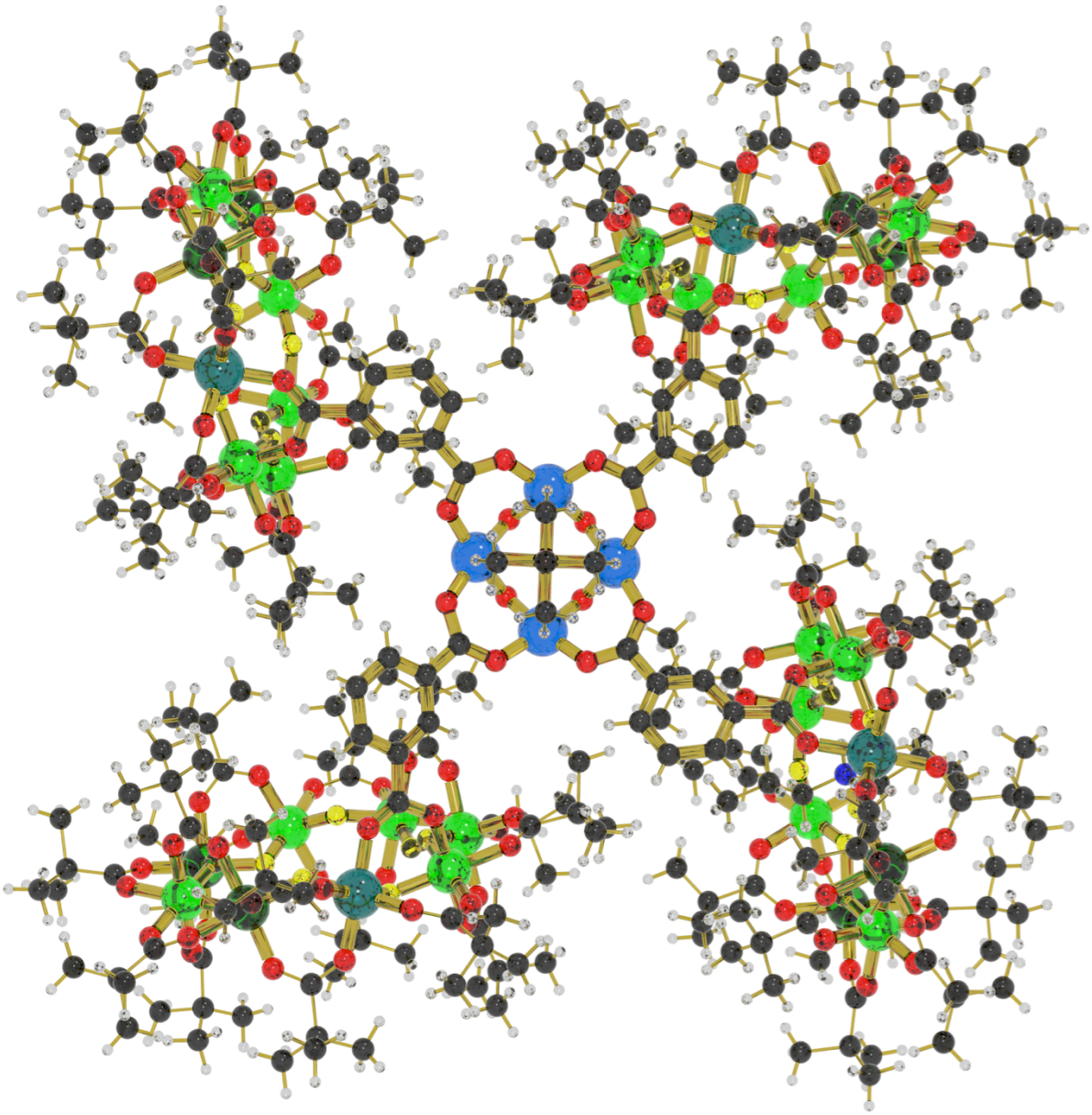

Fig. S4. The structure of **5** in the crystal. Colours as **S1**, Cu = light blue

3.4.1 Table S4: Crystal data and structure refinement for 5

Formula	$C_{359}H_{630}Cr_{28}Cu_4F_{32}N_4Ni_4O_{141}$
M	9811.67
Crystal system	Tetragonal
Space group	*P4/ncc*
a / Å	42.2890 (6)
c / Å	31.7707 (7)
U / Å^3	56817.4 (17)
T / K	150
Z	4
ρ / g cm^{-1}	1.147
Shape and colour	Block, green
Size / mm	0.05 × 0.04 × 0.04
λ / Å	0.6889
μ / mm^{-1}	1.18
Unique data	10565
Absorption correction	multi-scan
Transmission max/min	1.00/0.264
Unique data [$F_o > 4\sigma F_o$]	7041
Parameters/Restraints	1295/541
*R*1, *wR*2[a]	0.098, 0.306
Weighting scheme[b] [w^{-1}]	$1/[\sigma^2(F_o^2) + (0.1844P)^2 + 40.9481P]$
Goodness of fit	1.06
Largest residuals [e Å^{-3}]	1.54, -0.48

[a] *R*1 based on observed data, *wR*2 on all unique data.
[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

3.5 X-Ray Crystallographic Data $\{Cr_7Ni(O_2CC_6H_4CO_2)\}_6[Zn_4O]$ 6

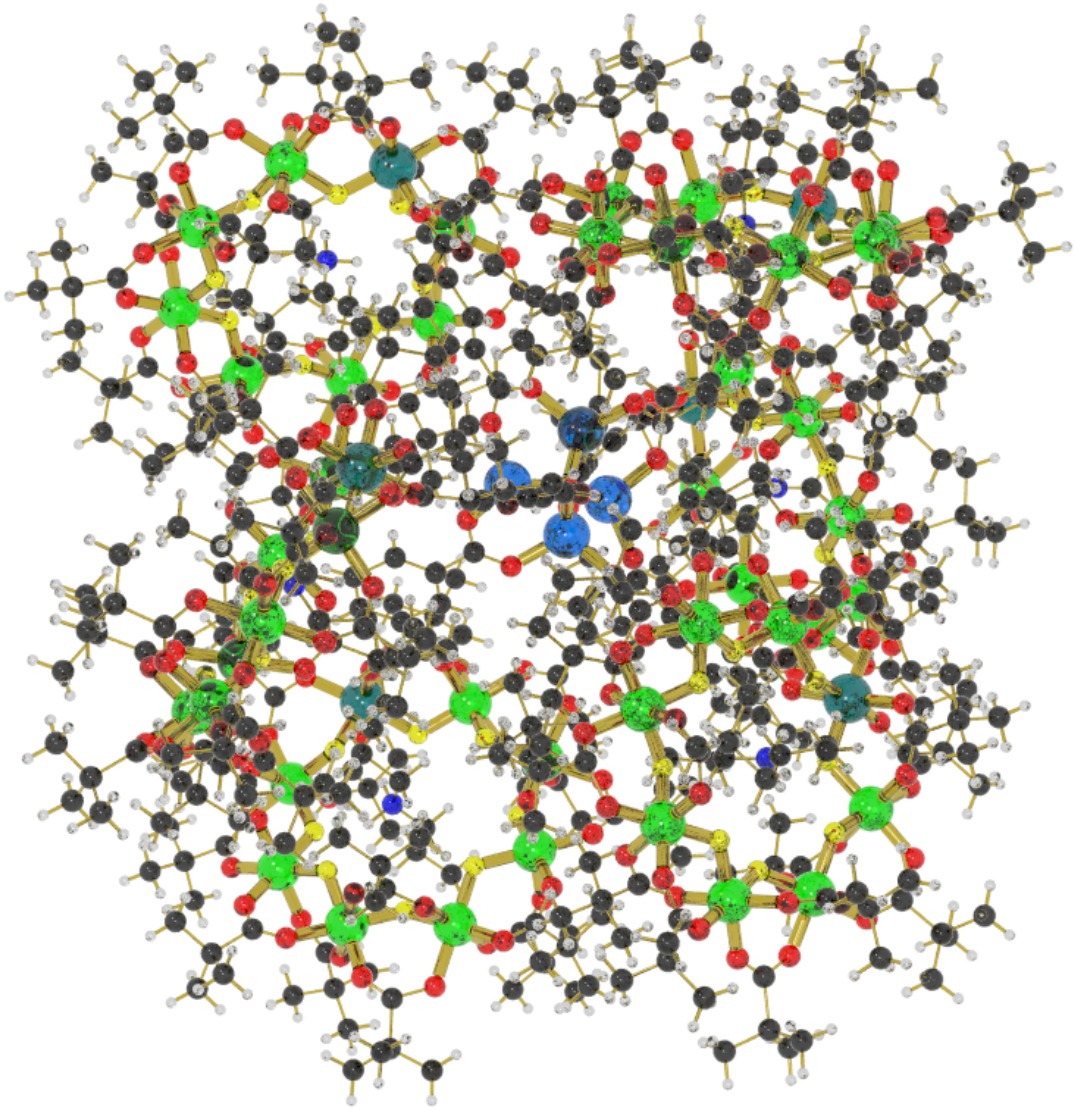

Fig. S5. The structure of **6** in the crystal. Colours as **S1**, Zn = light blue

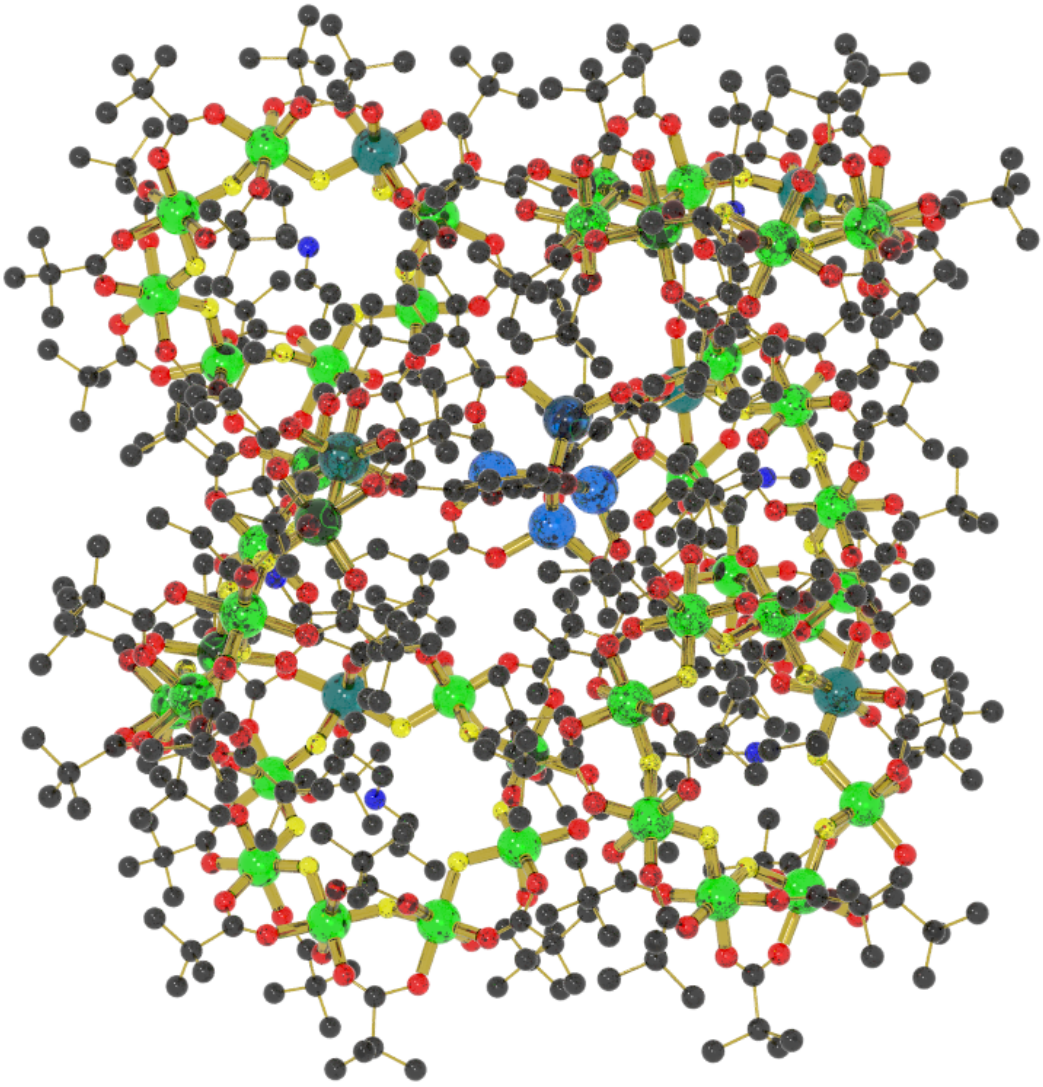

Fig. S6. The structure of **6** in the crystal. Colours as **S5**, H-omitted for clarity

3.5.1 Table S5: Crystal data and structure refinement for 6

Formula	$C_{549}H_{906}Cr_{42}F_{48}N_6Ni_6O_{207}Zn_4$
M	14636.67
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	39.9717 (15)
b / Å	48.6332 (16)
c / Å	43.5363 (15)
β / °	91.283 (3)
U / Å^3	84611 (5)
T / K	150
Z	4
ρ / g cm^{-1}	1.149
Shape and colour	Block, green
Size / mm	0.5 × 0.4 × 0.35
λ / Å	1.54178
μ / mm^{-1}	5.135
Unique data	51191
Absorption correction	multi-scan
Transmission max/min	1.0/0.167
Unique data [$F_o > 4\sigma F_o$]	32316
Parameters/Restraints	4994/40065
*R*1, *wR*2[a]	0.138, 0.418
Weighting scheme[b] [w^{-1}]	$1/[\sigma^2(F_o^2) + (0.2P)^2]$
Goodness of fit	1.577
Largest residuals [e Å^{-3}]	1.35, -0.62

[a] *R*1 based on observed data, *wR*2 on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

There is an unknown molecule incorporated in the crystal structure of **6**. It is quite well defined, and it has been refined as 1-phenoxy-3-ethoxybenzene, however the data is too weak to conclusively identify the nature of each atom in the molecule.

4. Magnetism

The magnetic properties of polycrystalline samples were investigated in the temperature range 1.8-300 K, by using a Quantum Design MPMS XL SQUID magnetometer equipped with a 7 T magnet. Data were corrected for the diamagnetism of the compounds by using Pascal's constants and for the diamagnetic contribution of the sample holder by measurement.

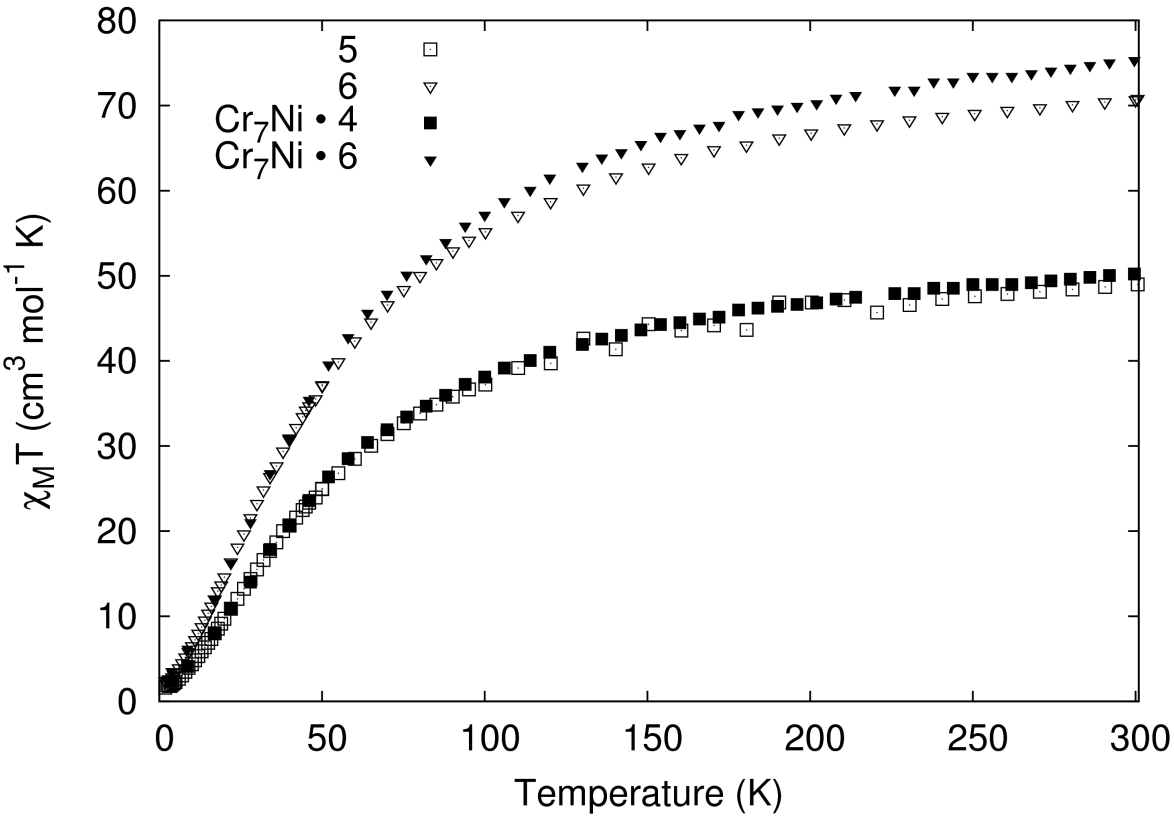

Figure S7. The product $\chi_m T$ against temperature for **5** (open squares) and **6** (open triangles) measured on powder samples in an external field of 0.1 T. The calculated values for $\chi_m T$ four {Cr_7Ni} rings (full squares) and six {Cr_7Ni} rings (full triangles) are also shown.

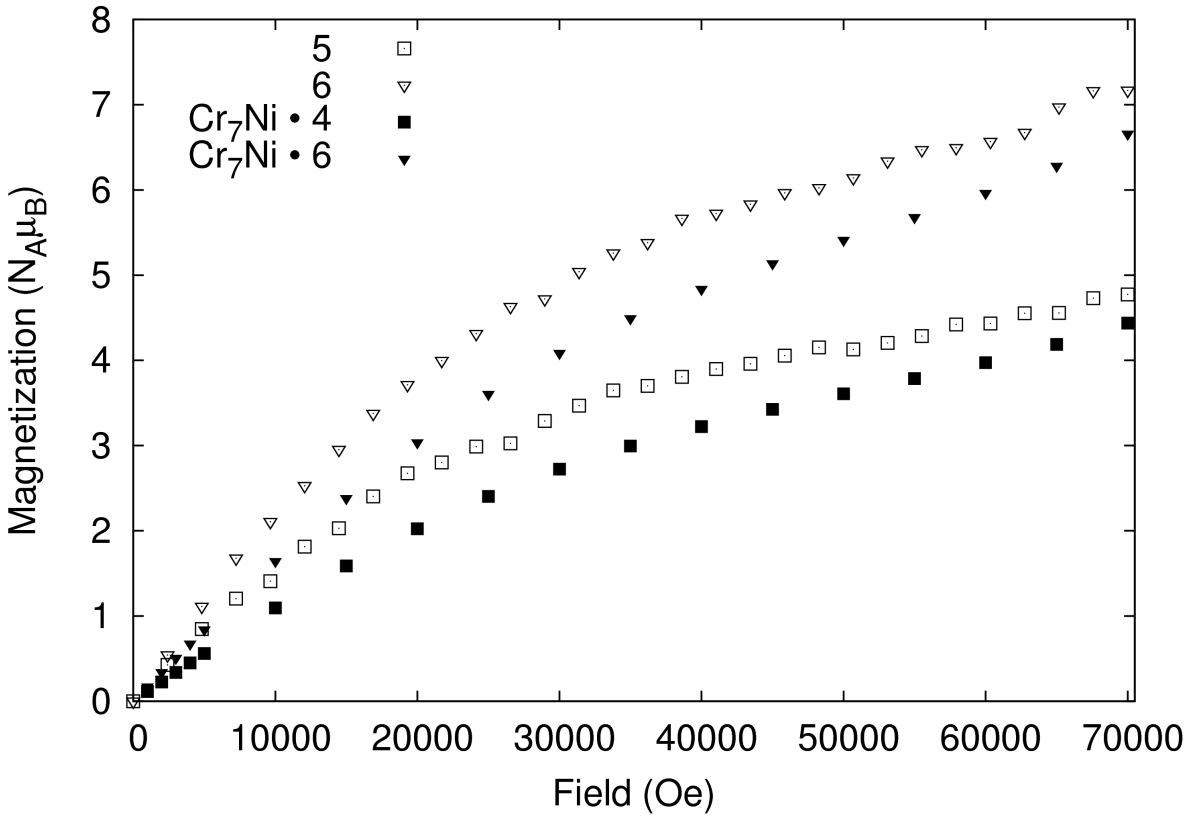

Figure S8. The magnetisation (*M*) against magnetic field (*H*) for **5** (open squares) and **6** (open triangles) measured on powder samples at 2 K. The calculated values for $\chi_m T$ four {Cr_7Ni} rings (full squares) and six {Cr_7Ni} rings (full triangles) are also shown, showing the clear divergence at low temperature.