Supporting Information

An extended framework of cages formed of pre-synthesised and functionalised heterometallic cages

George F. S. Whitehead[a], Simon J. Teat[b], Kevin J. Gagnon[b], Grigore A. Timco[a], Richard E. P. Winpenny[a]

[a] *The School of Chemistry and Photon Science Institute, The University of Manchester, Oxford Road, Manchester M13 9PL*

[b] *Advanced Light Source, Lawrence Berkeley Laboratory, 1 Cyclotron Road, MS2-400, Berkeley, California 94720, USA.*

Email: richard.winpenny@manchester.ac.uk

Table of Contents

1. General Experimental Section

All reagents and solvents were commercially available and used as received. Green [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^{t}Bu)_{14}(O_2CC_5H_4N)_2$] (**3**) was prepared by the published method.[1] [$Fe_2CoO(O_2C^{t}Bu)_6(HO_2C^{t}Bu)_3$] (**4**) was prepared by the published method.[2] 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.

[1] G. F. S. Whitehead, *et al*, *Chem. Commun.*, 2013, **49**, 7195.

[2] K.O.Abdulwahab, *et al*, *Chem. Mater*. 2014, **26**, 999.

2. Synthesis and Experimental Section

2.1 Synthesis of ({[$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^{t}Bu)_{14}(O_2CC_5H_4N)_2$]}$_3${[$Fe_2CoO(O_2C^{t}Bu)_6$]}$_2$)$_n$ 5

4 (31.6 mg, 0.029 mmol) was dissolved in acetone (5 mL) and added to a warm solution of **3** (0.100 g, 0.043 mmol) in acetone (15 mL) with stirring. A precipitate immediately formed and the solution was refluxed for a further 10 min. The reaction was allowed to cool to room temperature, after which the precipitate was collected by filtration, washed with warm acetone (3 x 25 mL) and extracted in minimal THF (15 mL). This was left to recrystallize by slow evaporation (180 days), resulting in

small green-brown elongated thin plates. Some of these suitable for X-ray structure study were separated and the remainder were collected by filtration, washed with acetone and dried. Yield 0.118 g, 95% based on **4**. Anal. Calcd. for $C_{324}H_{558}Co_2Cr_{21}F_{24}Fe_4N_9Ni_3O_{122}$ **5**: C, 45.27; H, 6.54; N, 1.47, Co, 1.37; Cr, 12.70; Fe, 2.60; Ni, 2.05. Found: C, 45.45; H, 6.82; N, 1.38, Co, 1.08; Cr, 12.62; Fe, 2.61; Ni, 2.01

3. X-Ray Crystallography

3.1 X-Ray Crystallographic Data for 5

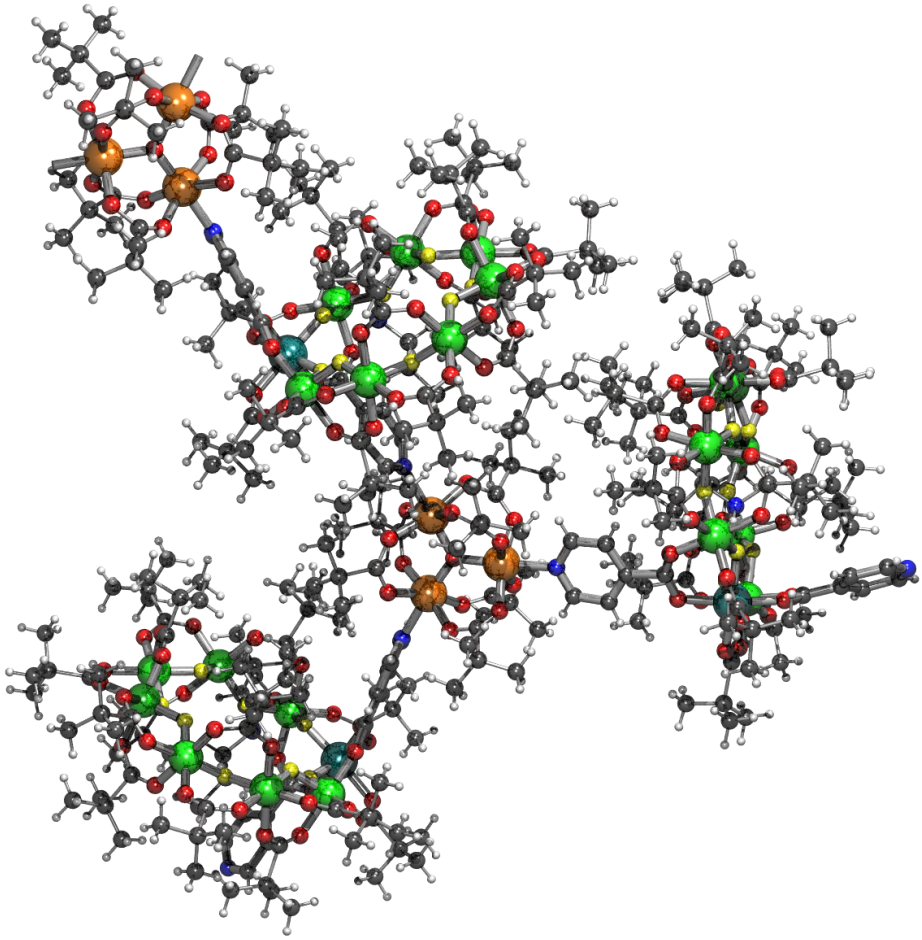


Figure S1: Graphical representation of the asymmetric unit of the X-ray crystal structure **5**
Colours: Cr = green, Ni = turquoise, O = red, F = yellow, N = blue, C = grey, H = white, Fe/Co = orange

3.1.1 Table S1: Crystal data and structure refinement for 5

Compound	**5**
Formula	$C_{324}H_{558}Co_2Cr_{21}F_{24}Fe_4N_9Ni_3O_{122}$
M_r	8596.95
Crystal System	*Monoclinic*
Space Group	*C2/c*
a [Å]	63.4959 (10)
b [Å]	38.2021 (7)
c [Å]	71.4099 (11)
β [°]	114.799 (2)
V [Å^3]	157244 (5)
Z	8
T / K	100(2)
Crystal Size [mm]	0.01x0.05x0.3
ρ calc. / g cm^{-3}	0.726
Crystal Shape	Elongated plate
Colour	Green-brown
Radiation	Synchrotron
Unique data	31071
Unique data [$F_o > 4\sigma F_o$]	20393
R_{int}	0.076
Parameters	2946
Restraints	14177
R_1, wR_2[a]	0.1083, 0.3323
weighting scheme[w^{-1}][b]	[$s^2(Fo^2)+(0.02P)^2$]
goodness of fit	1.267
largest residuals[eÅ^{-3}]	0.54,-0.329

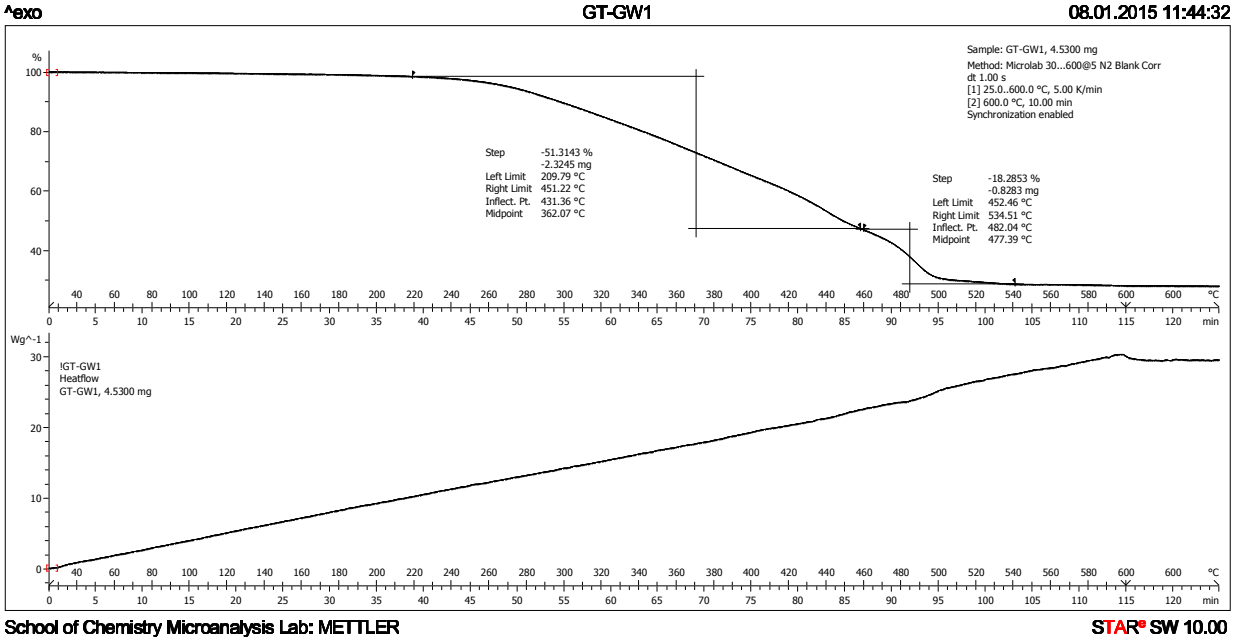
[a] *R*1 based on observed data, *wR*2 on all unique data.

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

The crystal contains very large solvent accessible voids (82684.3 Å^3). However, the location of discrete solvent molecules within this void could not be determined and residual electron density within the void was modelled using SQUEEZE. The formula given is for the lattice without including solvent molecules. The low sine(theta_max)/wavelength ratio is due to the very weakly diffracting nature of the crystal. The large number of isotropic non-H atoms is due to the requirement to keep a reasonable data to parameter ratio. The large number of restraints applied is required to model the *t*-butyl groups of the pivalate moieties.

4. Thermogravimetric Analysis

Thermogravimetric analysis was performed by the Analytical Service of the School of Chemistry, The University of Manchester, using a METTLER TOLEDO TGA/DSC1 STAR^{e} System instrument with METTLER TOLEDO ultra-micro balance, on 4.53 mg of compound **5.** The measurement was taken by heating the sample under nitrogen gas flow (100 ml/min) to 600ºC with a rate of 5.0 K/min.



5. TOPOS analysis.

For the purposes of analysis with TOPOS the framework structure was deconstructed, replacing each cluster with an individual points with arbitrary labels; **3** was deconstructed to Ti sites and **4** to O sites.

```
######
5:test
######

Topology for O1
-------------------
Atom O1 links by bridge ligands and has
Common vertex with                                R(A-A)        f
O  2    0.1764    0.6039    0.7695   (-1 0 0)    21.555A       1
O  2    0.6764    1.1039    0.7695   ( 0 1 0)    21.570A       1
O  2    0.6764    0.8961    1.2695   ( 0 1 0)    21.599A       1
Topology for O2
-------------------
Atom O2 links by bridge ligands and has
Common vertex with                                R(A-A)        f
O  1    1.0154    0.3284    0.9389   ( 0-1 0)    21.555A       1
O  1    0.5154   -0.1716    0.9389   ( 0-1 0)    21.570A       1
O  1    0.5154    0.1716    0.4389   ( 0 1-1)    21.599A       1
-------------------------
Structural group analysis
-------------------------

-------------------------
Structural group No 1
-------------------------
Structure consists of 3D framework with Ti3O2
There are 2 interpenetrating nets
FISE: Full interpenetration symmetry elements
---------------------------------------------
1: -1
---------------------------------------------
PIC: [1/2,1/2,0][1/2,-1/2,0][0,0,1] (PICVR=1)

Zt=1; Zn=2

Class IIa  Z=2

Coordination sequences
----------------------
O1:  1  2  3  4  5   6   7   8   9  10
Num  3  6 12 24 38  56  77 102 129 160
Cum  4 10 22 46 84 140 217 319 448 608
----------------------
O2:  1  2  3  4  5   6   7   8   9  10
Num  3  6 12 24 38  56  77 102 129 160
Cum  4 10 22 46 84 140 217 319 448 608
----------------------
TD10=608

Vertex symbols for selected sublattice
--------------------------------------
O1 Point symbol:{10^3}
Extended point symbol:[10(2).10(4).10(4)]
--------------------------------------
O2 Point symbol:{10^3}
Extended point symbol:[10(2).10(4).10(4)]
--------------------------------------
Point symbol for net: {10^3}
3-c net; uninodal net

Topological type: ths ThSi2; 3/10/t4 (topos&RCSR.ttd) {10^3} - VS [10(2).10(4).10(4)] (5452 types in
2 databases)
Elapsed time: 7.58 sec.
```