Supplementary Information

Cages on a plane: a structural matrix for molecular 'sheets'

Hector W. L. Fraser,[a] Gary S. Nichol,[a] Amgalanbaatar Baldansuren,[b] Eric J. L. McInnes[b] and Euan K. Brechin[a*]

[a] *EaStCHEM School of Chemistry, The University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, UK. E-mail: E.Brechin@ed.ac.uk*

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

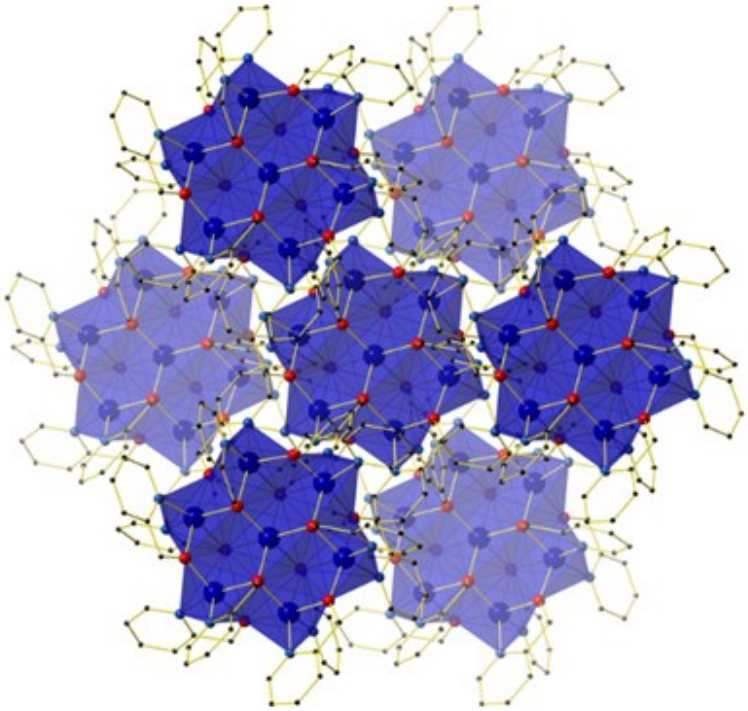

Figure S1. Crystal packing common to compounds **1**-**3** & **5** as viewed down the *c*-axis, highlighting the hexagonal packing arrangement formed by layers of molecules. H atoms, solvent molecules and counter anions omitted for clarity.

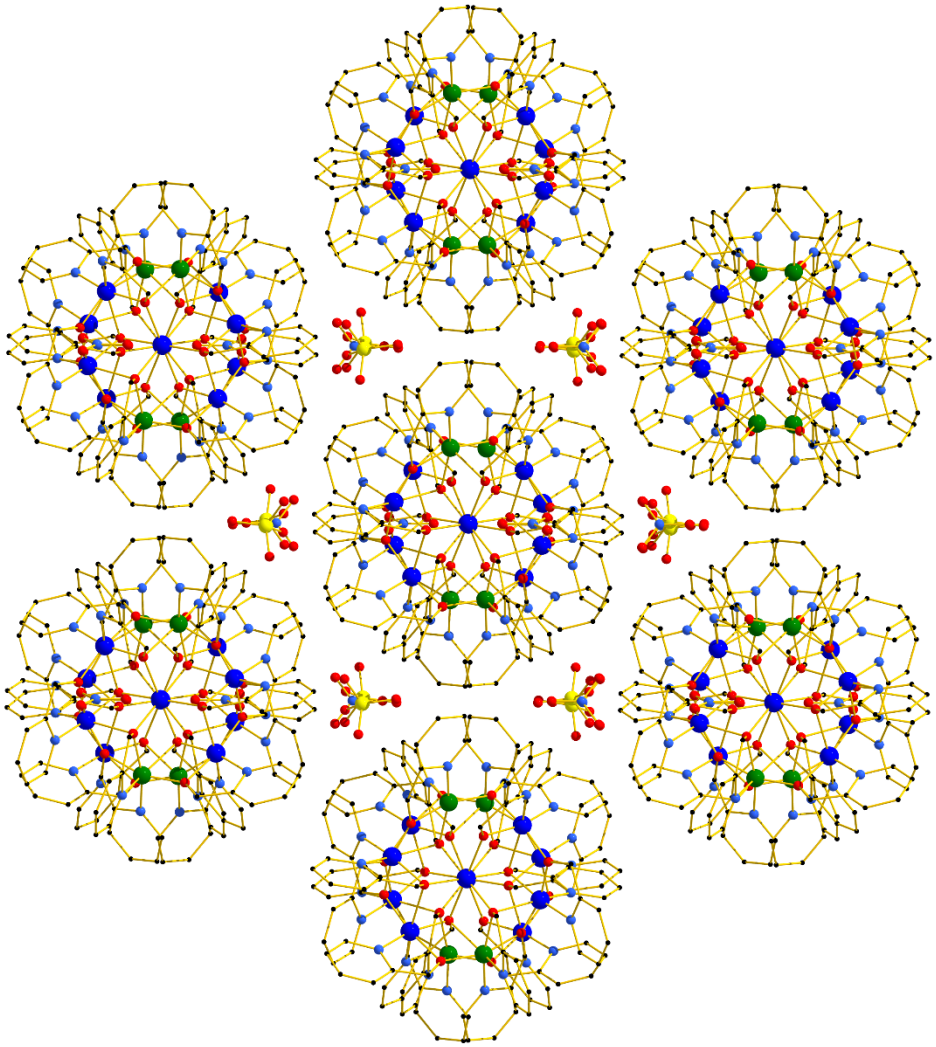

Figure S2. Packing diagram for compound **4** viewed down the *c*-axis. Colour code as Figure 4, Cl = yellow.

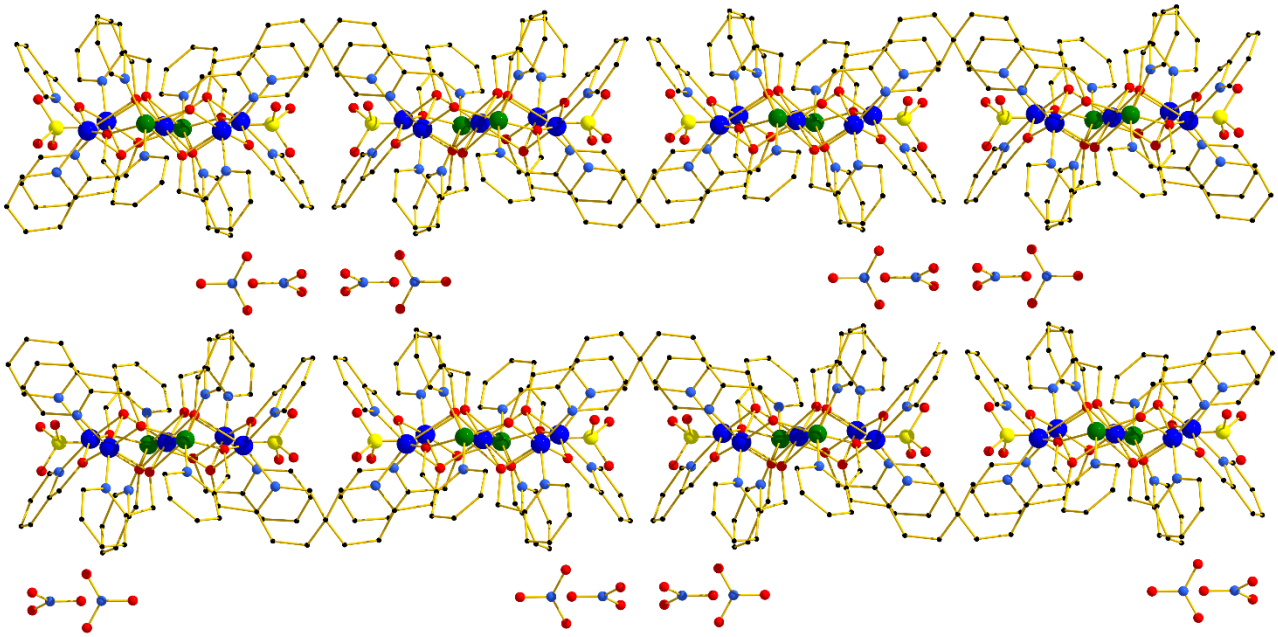

Figure S3. Packing diagram for compound **4** viewed down the *a*-axis. Colour code as Figure S2.

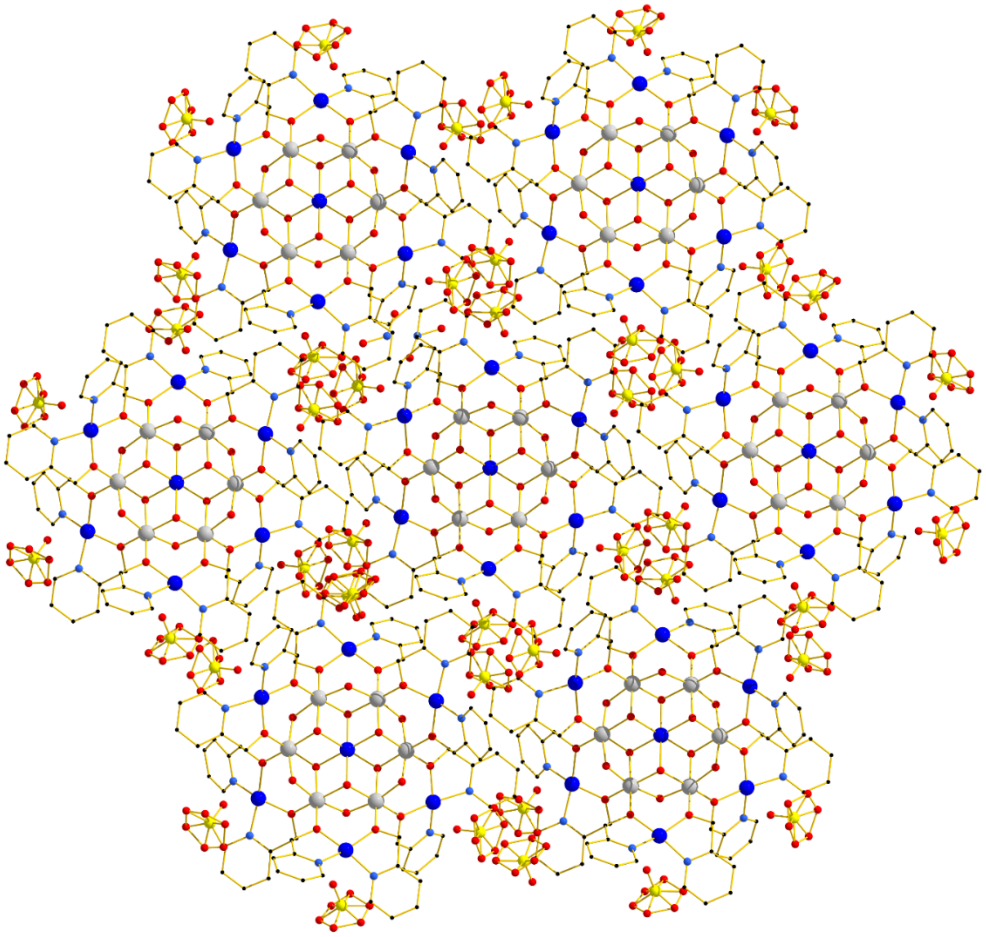

Figure S4. Packing diagram for compound **6** viewed down the *c*-axis. Colour code as Figure S3, Al = grey.

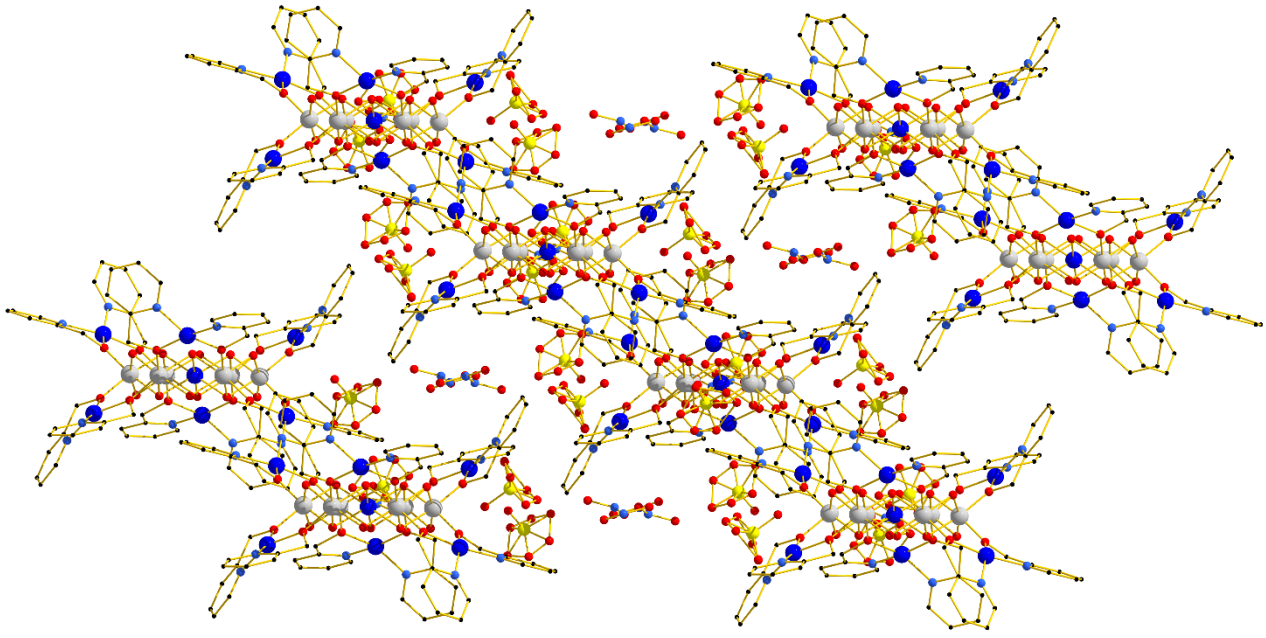

Figure S5. Packing diagram for compound **6** viewed down the *b*-axis. Colour code as Figure S3.

Table S1. Crystallographic information for compounds **1**-**6**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{81}H_{108}Cl_4Co_5Cr_2N_{12}O_{37}$	$C_{81}H_{108}Cl_4Cr_2Fe_5N_{12}O_{37}$	$C_{82}H_{112}Cl_4Cr_2Mn_5N_{12}O_{38}$	$C_{88}H_{136}Cl_2Cr_2Cu_5N_{14}O_{42}$	$C_{81}H_{108}Al_2Cl_4Co_5N_{12}O_{37}$	$C_{93}H_{168}Al_6Cl_6Cu_7N_{14}O_{75}$
$D_{calc.}$/ g cm^{-3}	1.657	1.682	1.672	1.859	1.637	1.468
μ/mm^{-1}	1.272	9.765	8.898	4.629	1.084	1.151
Formula Weight	2382.24	2366.84	2394.33	2554.70	2332.20	3501.76
Colour	dark pink	pale brown	pale purple	light purple	pale brown	dark blue
Shape	block	plate	plate	plate	plate	block
Size/mm^3	0.32×0.11×0.10	0.14×0.10×0.03	0.20×0.16×0.02	0.22×0.16×0.03	0.27×0.07×0.03	0.32×0.24×0.17
T/K	120.0	120.0	120.0	120	120.0	120.01(10)
Crystal System	trigonal	trigonal	trigonal	monoclinic	trigonal	trigonal
Space Group	R-3	R-3	R-3	*I*2/*a*	R-3	*R*-3
a/Å	14.7268(2)	14.6087(3)	14.7045(6)	14.5052(12)	14.6812(5)	27.8468(6)
b/Å	14.7268(2)	14.6087(3)	14.7045(6)	25.0735(19)	14.6812(5)	27.8468(6)
c/Å	38.1319(8)	37.9381(19)	38.106(5)	25.095(5)	38.0235(14)	17.6945(7)
α/°	90	90	90	90	90	90
β/°	90	90	90	90.268(13)	90	90
γ/°	120	120	120	90	120	120
V/Å^3	7162.0(2)	7011.8(5)	7135.4(11)	9127(2)	7097.5(5)	11882.8(7)
Z (Z')	3 (0.16667)	3 (0.16667)	3 (0.16667)	4 (0.5)	3 (0.16667)	3 (0.16667)
Wavelength/Å	0.71073	1.54184	1.54184	1.54184	0.71073	0.71073
Radiation type	MoK_α	Cu K_α	Cu K_α	Cu K_α	MoK_α	MoK_α
Θ_{min}/° - Θ_{max}/°	3.112 – 29.648	3.495 – 76.728	3.479 – 50.499	3.520 – 50.436	3.121 – 25.340	2.856 – 25.345
Measured Refl.	43856	32839	17837	10864	38106	49850
Independent Refl.	4234	3272	1673	10864	2893	4843
Reflections with I > 2(I)	3674	2673	1482	5280	2560	4209
R_{int}	0.0503	0.0968	0.0736	.	0.0900	0.0538
Parameters	196	199	260	205	196	274
Restraints	18	37	137	28	18	88
Largest Peak	0.428	1.455	0.633	3.431	0.728	1.219
Deepest Hole	-0.733	-1.027	-0.432	-1.655	-0.982	-0.604
GooF	1.069	1.052	1.074	1.558	1.136	1.055
wR_2 (all data) (wR_2)	0.0914 (0.0883)	0.2197 (0.2052)	0.2110 (0.2045)	0.4931 (0.4601)	0.1339 (0.1289)	0.1697 (0.1635)
R_1 (all data) (R_1)	0.0521 (0.0425)	0.0822 (0.0712)	0.0797 (0.0737)	0.2423 (0.1868)	0.0726 (0.0623)	0.0642 (0.0561)

Supplementary discussion: compound 4

This compound crystallized as apparently well-formed hexagonal plate-shaped crystals. Despite the optically attractive crystals the quality of the diffraction pattern was somewhat sub-par: weak (a 1 Å cut-off was applied during refinement) with some broad and diffuse streaking mixed with Bragg reflections. Plate stacking faults were assumed.

The original unit cell parameter determination suggested that the unit cell was hexagonal with $a = b = 28.97$ Å and $c = 25.10$ Å. With these unit cell parameters the structure solves to give two crystallographically inequivalent "wheels" and a model which refines to give classical R1 = 44.23%.

Further investigation of the diffraction pattern showed that a I-centred monoclinic cell (with parameters $a = 14.51$ Å, $b = 25.07$ Å, $c = 25.10$ Å, $\beta = 90.268°$) could be indexed. By iterative searching of the diffraction pattern two further orientations were found, each related by approximately 120°. The diffraction pattern was thus indexed and integrated as a three-component twin with each component rotated by approximately 120°, mimicking a hexagonal unit cell as shown in Figure S6.

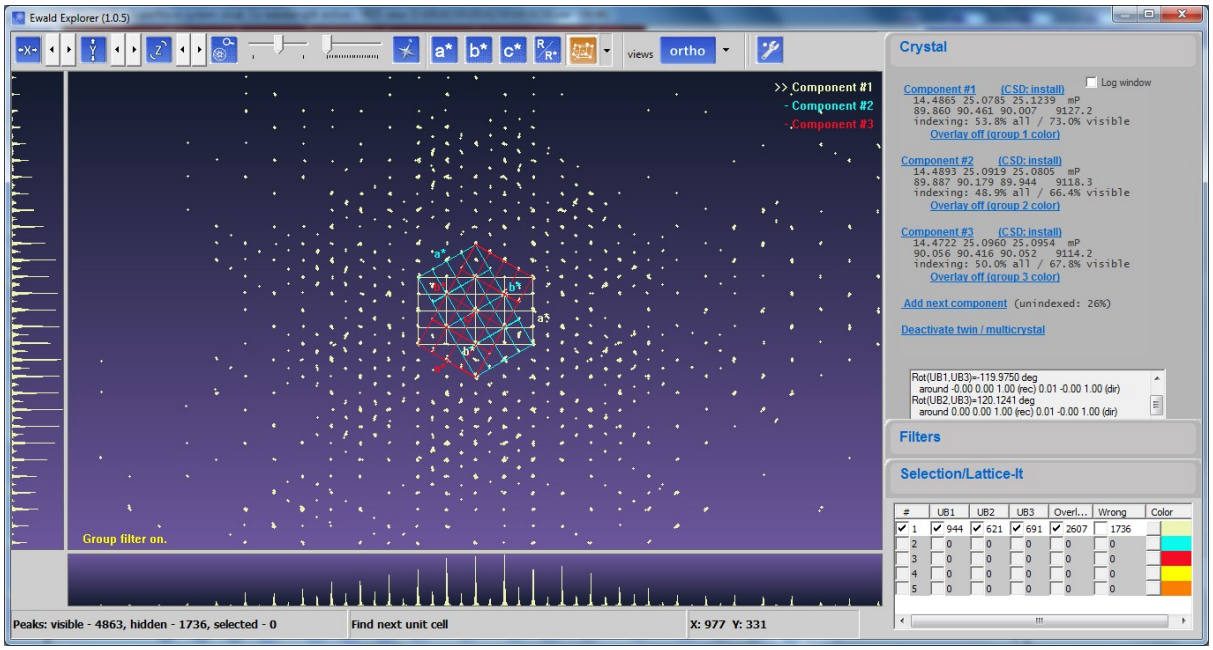

Figure S6. Reciprocal lattice plot (Ewald Explorer in CrysAlisPro) of the diffraction pattern of compound **4**. The three monoclinic unit cell orientations are indicated in the centre of the plot.

The structural model is not without problems. The metal centres were found easily by SHELXT and all non-H atoms of the wheel could be identified in a difference map without difficulty. The occupancies of the metals were allowed to refine and the location of the chromium centre was quite clear. Similarly, the atoms of the perchlorate counter ion were all easily identified. The nitrate anions were more

difficult to locate and were identified by looking for the shape of the species, over symmetry elements or not.

Refinement of the model proved more troublesome. All 6-membered rings have been fixed in place using the SHELXL AFIX 66 idealized hexagonal constraint. Similarly, the geometry in the Ph-C(H2)-O 'arm' was restrained using average bond distances determined by a search of the Cambridge Structural Database. The perchlorate anion was restrained using 1,2- and 1,3- distance restraints on all bonds and angles The nitrate anions were also restrained using 1,2- and 1,3- distance restraints. All of the metal sites, the chlorine, some oxygen and some nitrogen sites were refined using an isotropic model. All other sites were refined using an isotropic model for reasons of stability in the model. Some of the atoms were modelled with U(iso) allowed to refine, initially, and then fixed. This includes some atoms of the 6-membered rings.

No attempt to identify any solvent molecules was made. The SQUEEZE routine of PLATON, when fed a LIST 8-style structure factor file, was able to account for 524 electrons per unit cell. This approximates to 8 methanol per asymmetric unit or 16 per complete wheel. This missing additional solvent was included in the total chemical formula and derived values, triggering checkCIF alerts which should be ignored.

The model is presented refined as far as practical given the quality of the data and the twinning. The refinement restraints and constraints were needed to keep the model into the shape of something which was chemically reasonable. The structure is presented as part of a family of similar compounds, all with similar charge balance and other similar properties.

Twinning information (deconvoluted with CrysAlisPro):

Component 2 rotated by 120.0851° around [-0.00 0.00 1.00] (reciprocal) or [0.00 0.00 1.00] (direct).

Component 3 rotated by -119.9041° around [-0.00 0.00 1.00] (reciprocal) or [0.01 -0.00 1.00] (direct).

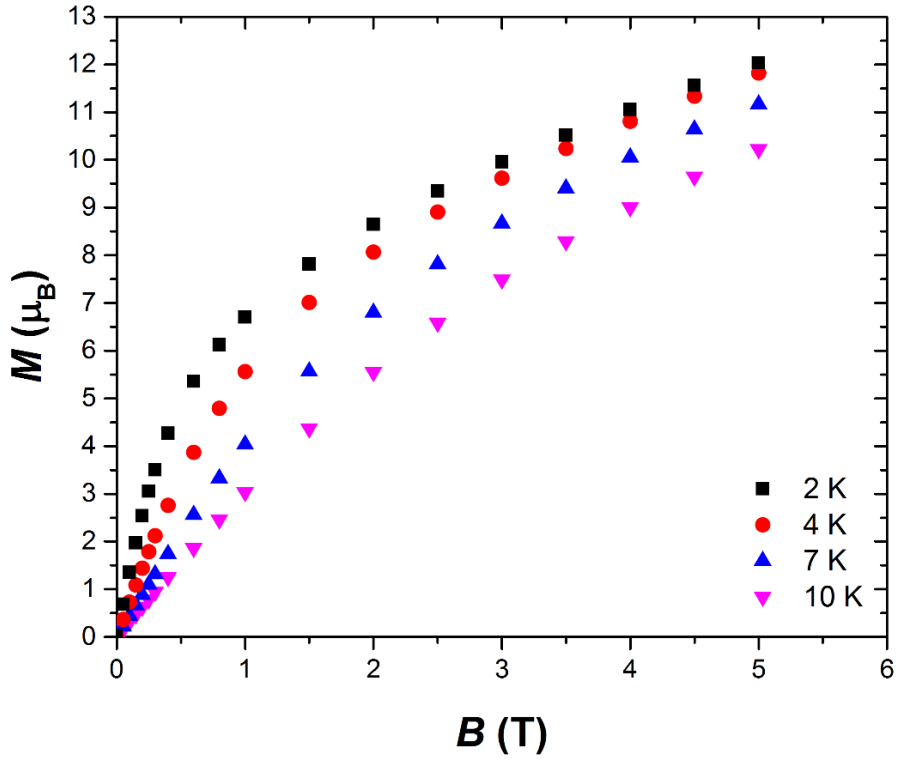

Figure S6. Plot of magnetisation (***M***) versus field (***B***) for compound **1** in the indicated field and temperature ranges.

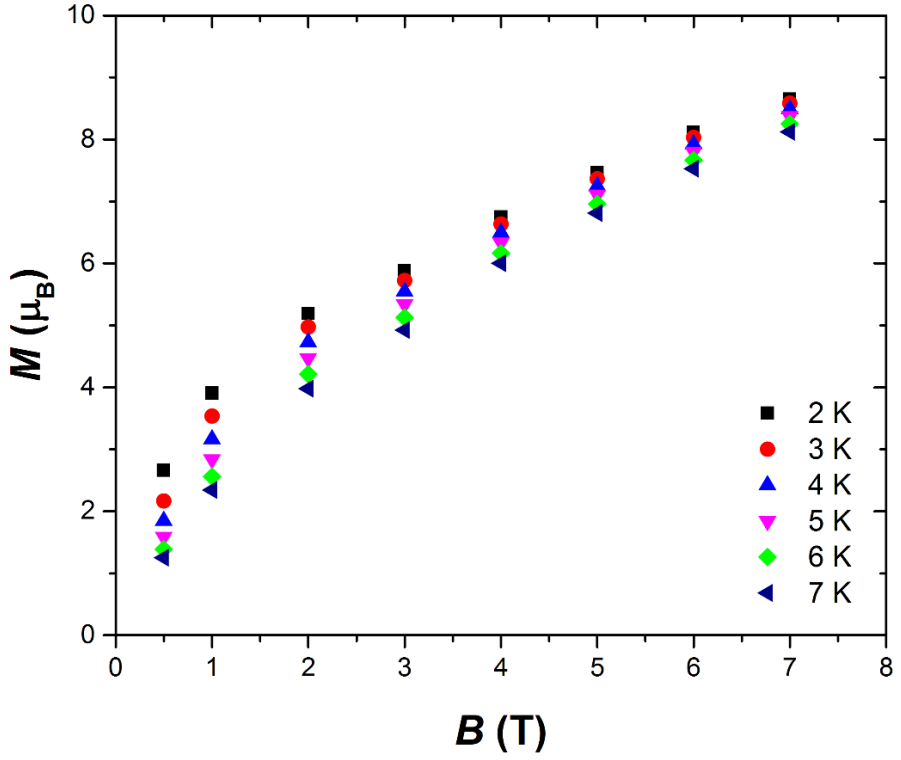

Figure S7. Plot of magnetisation (***M***) versus field (***B***) for compound **2** in the indicated field and temperature ranges.

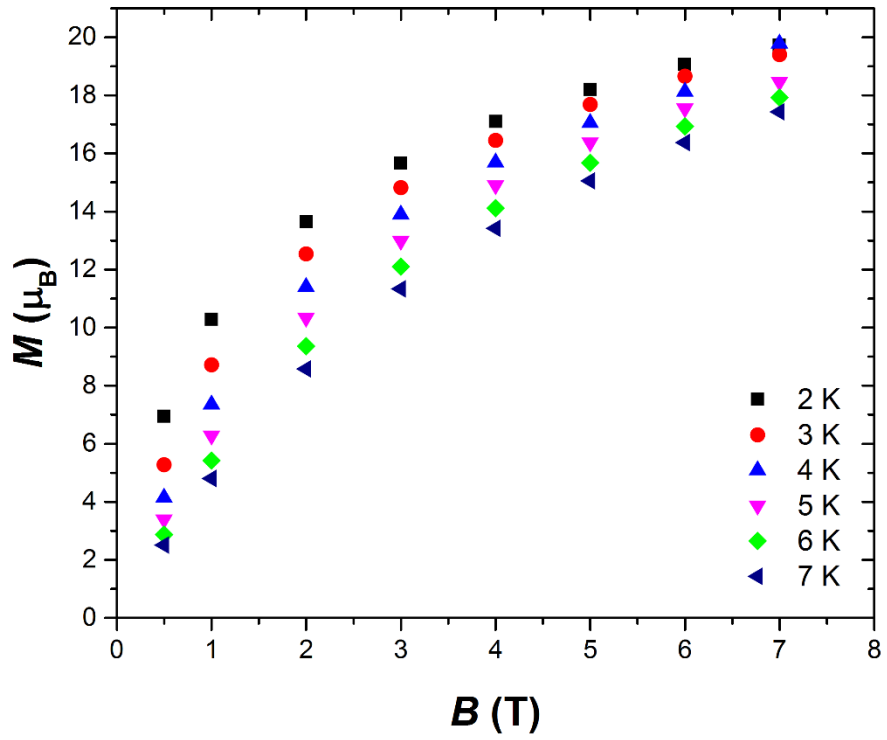

Figure S8. Plot of magnetization (***M***) versus field (***B***) for compound **3** in the indicated field and temperature ranges.

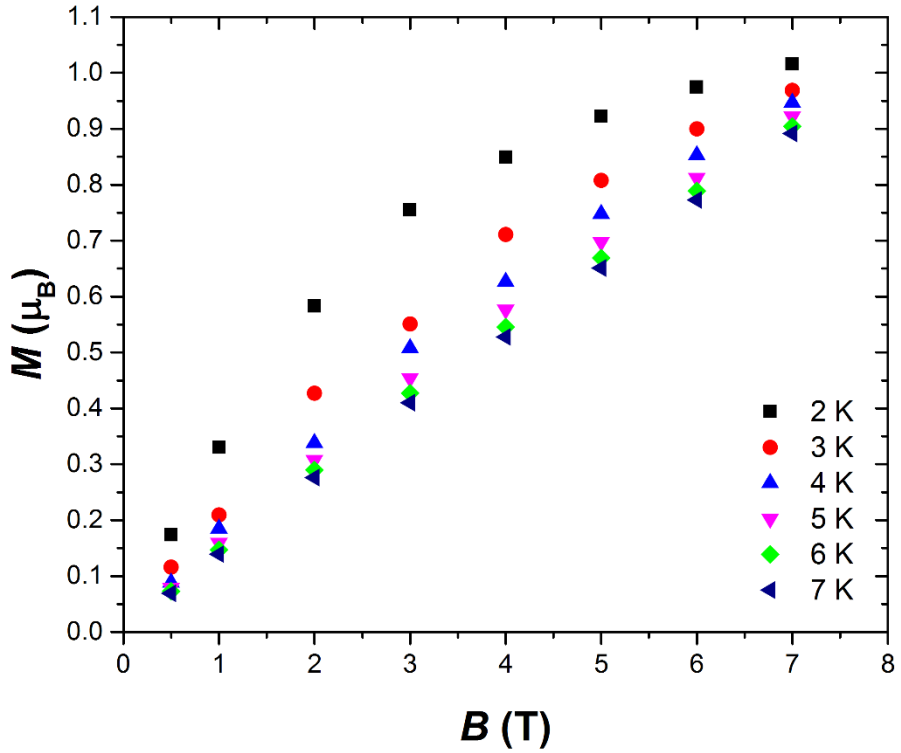

Figure S9. Plot of magnetisation (***M***) versus field (***B***) for compound **4** in the indicated field and temperature ranges.

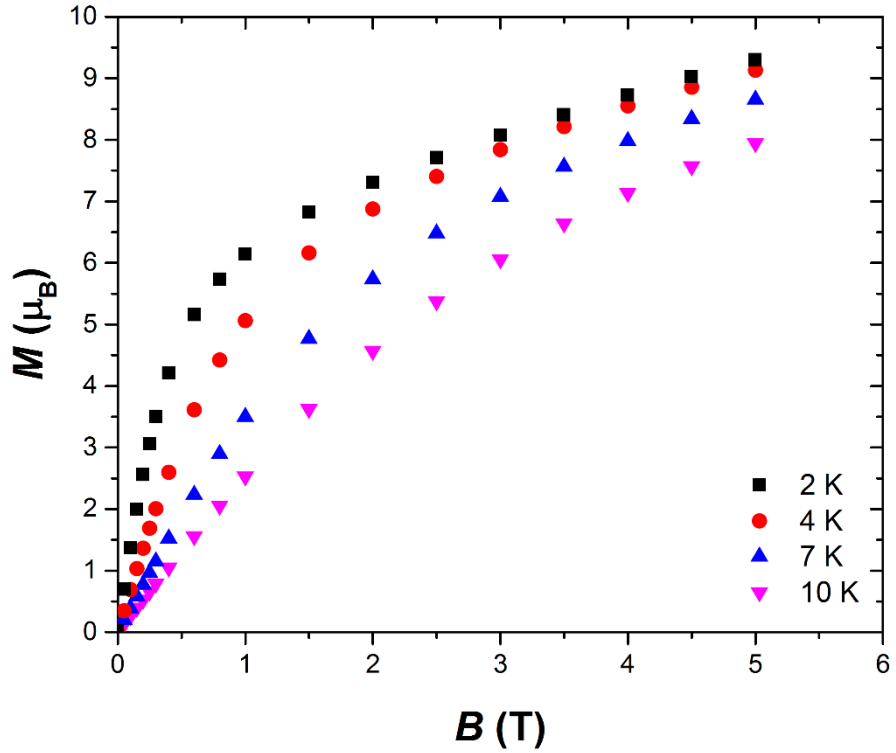

Figure S10. Plot of magnetization (***M***) versus field (***B***) for compound **5** in the indicated field and temperature ranges.

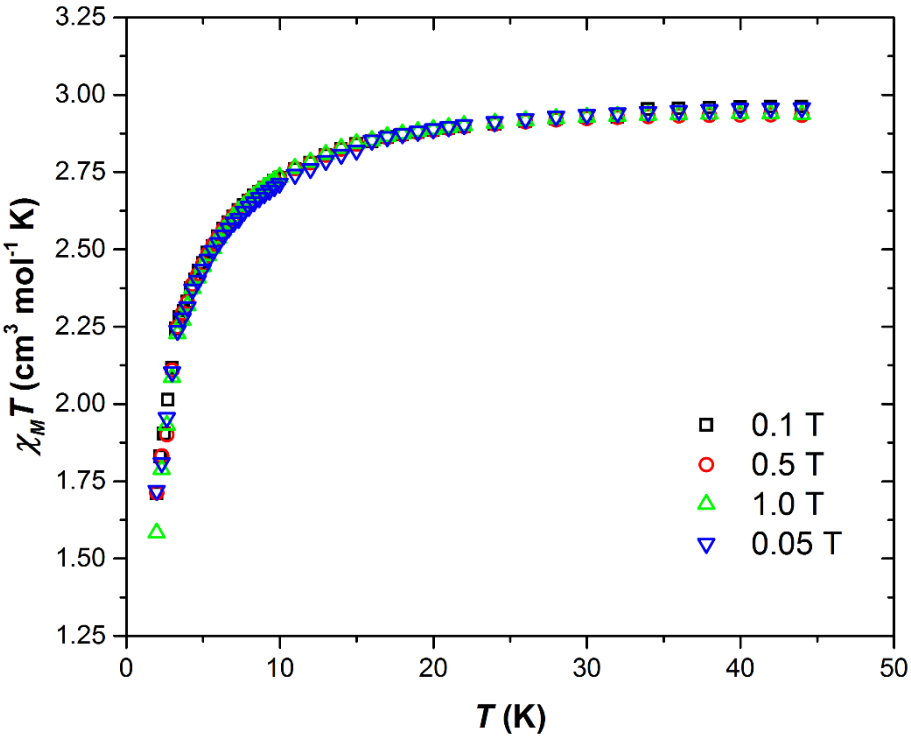

Figure S11. Plot of the $\chi_M T$ product versus T for complex **6** from 44-2 K under fields of 0.05, 0.1, 0.5 and 1.0 T. See text for details.