Electronic Supplementary Information

Solvothermal Synthesis of Discrete Cages and Extended Networks Comprising {Cr(III)3O(O2CR)3(oxime)3}2- (R = H, CH3, C(CH3)3, C14H9) Building Blocks

Edel Houton,[b] Priyanka Comar,[c] Mateusz B. Pitak,[e] Simon J. Coles,[e] Alan. G. Ryder,[b] Stergios Piligkos,[d] Euan K. Brechin,[c] and Leigh F. Jones[a,b]*

[a] *School of Chemistry, Bangor University, Bangor, Wales. LL57 2DG. Tel: +44(0)1248-38-2391. Email: leigh.jones@bangor.ac.uk*

[b] *School of Chemistry, NUI Galway, University Road, Galway, Ireland.*

[c] *EaStCHEM School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, Scotland. EH9 3JJ. Email: ebrechin@staffmail.ed.ac.uk*

[d] *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Denmark.*

[e] *UK National Crystallographic Service, Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton, England, UK. SO17 1BJ.*

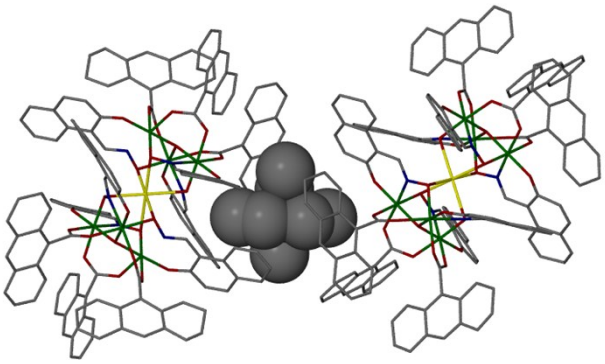

Figure S1 Two adjacent $\{NaCr(III)_6O_2(O_2C\text{-}C_{14}H_9)_6(Naphth\text{-}sao)_6\}^{3-}$ cages in **1** forming a hydrophobic pocket accommodating a space-fill represented $[NEt_4]^+$ counter anion (grey spheres).

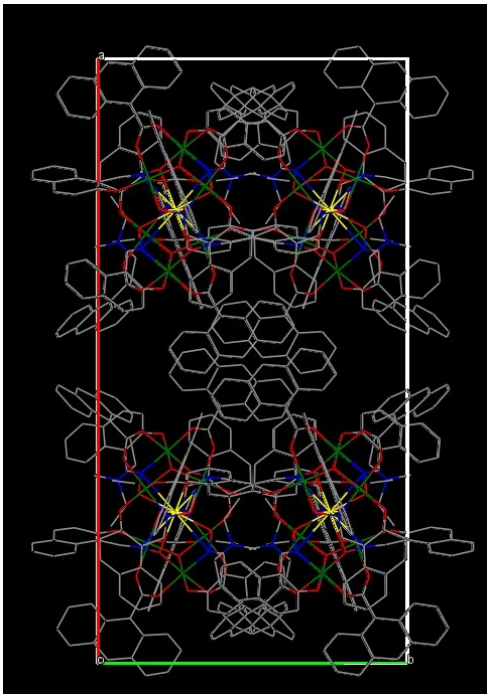

Figure S2 Crystal packing observed in **1** as viewed along the *c* unit cell direction. All hydrogen atoms and solvent molecules of crystallisation have been omitted for clarity. Colour code as main text.

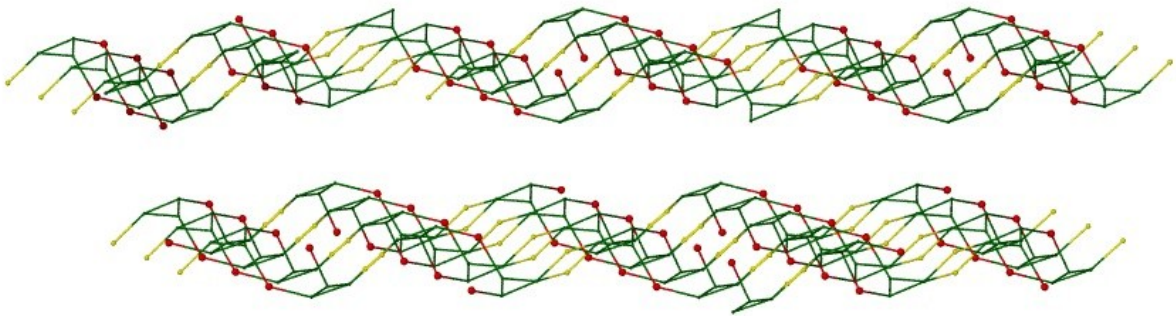

Figure S3 The 2-D sheets in **2** as viewed along the *b* direction of the unit cell. Colour code: Green (Cr), Yellow (Na), Red (O). All other atoms have been omitted for simplification and clarity.

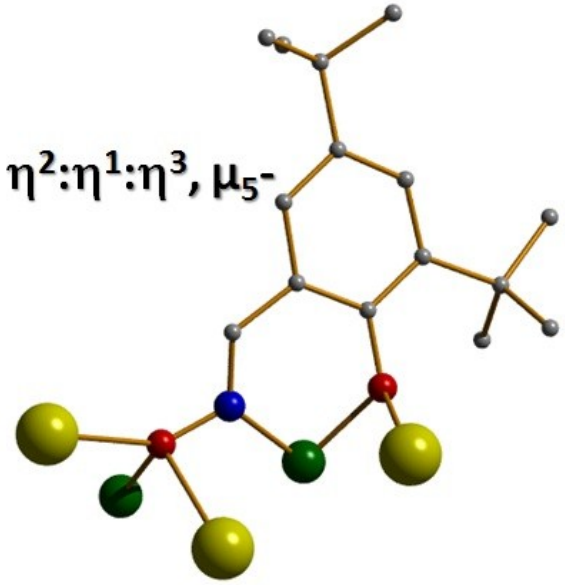

Figure S4 Bonding mode exhibited by the 3,5-di-*tert*-Bu-sao^{2-} ligands in **3**.

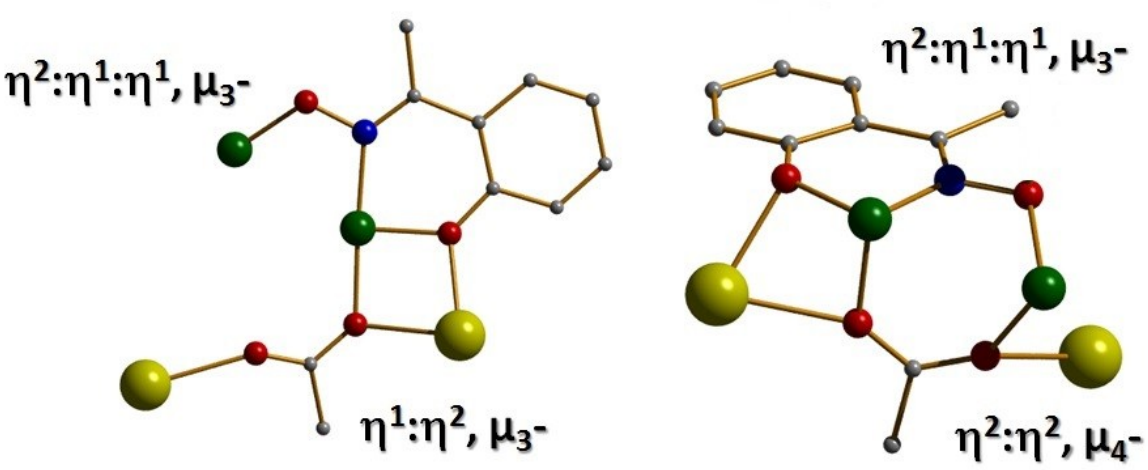

Figure S5: The bridging arrangements exhibited by the Me-sao^{2-} and acetate anions in the 2D network in **4**.

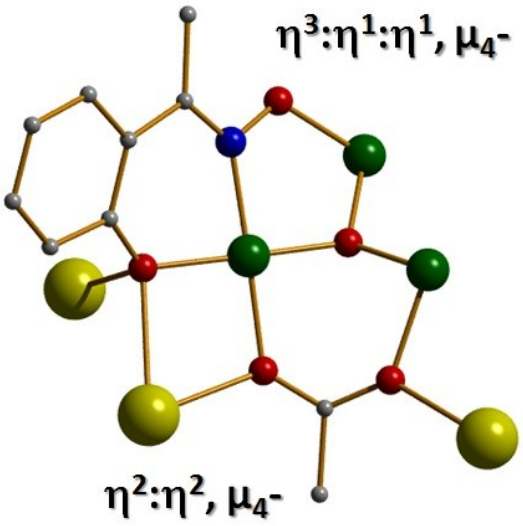

Figure S6 The bridging arrangements exhibited by the Me-sao^{2-} and acetate anions in the 2D network in **5**.

Table S1 Crystal data obtained from complexes **1**-**3**.

	1	**2**	**3**
Formula[a]	$C_{172}H_{136}N_8O_{26}Na_1Cr_6$	$C_{96}H_{88}N_{12}O_{30}Na_2Cr_6$	$C_{132}H_{198}N_{12}O_{26}Na_4Cr_6$
M_W	3065.87	2237.68	2772.98
Crystal System	Monoclinic	Monoclinic	Trigonal
Space group	C2/c	$P2_1/n$	R-3c
a/Å	39.800(2)	17.8061(18)	26.9779(12)
b/Å	17.2760(6)	12.4863(14)	26.9779(12)
c/Å	30.452(2)	22.4726(18)	71.622(4)
α/°	90	90	90
β/°	121.745(4)	91.553(9)	90
γ/°	90	90	120
V/Å^3	17805.9(19)	4994.5(9)	45143(5)
Z	4	2	12

T/K	150(2)	150(2)	150(2)
λ^b/Å	0.7107	0.7107	0.7107
D_c/g cm^{-3}	1.144	1.488	1.224
μ(Mo-Ka)/ mm^{-1}	0.419	0.724	0.496
Meas./indep.(R_{int}) refl.	72141/21163(0.2071)	9115/4123 (0.1742)	8855/4076(0.2348)
Restraints, Parameters	2210, 1945	0, 646	1286, 616
wR2 (all data)^c	0.4039	0.3020	0.2509
$R1^{d,e}$	0.1343	0.0967	0.0907
Goodness of fit on F^2	0.955	1.035	1.020

[a] Includes guest molecules (Note: Solvents of crystallisation in **1** and **3** respectively are not counted in formula as were calculated using SQUEEZE program.[b] Mo-Kα radiation, graphite monochromator. [c] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$. [d]For observed data. [e] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

Table S2 Crystal data obtained from extended networks **4** and **5**.

	4	**5**.3MeCN
Formula[a]	$C_{62}H_{66}N_7O_{27}Na_3Cr_6$	$C_{36}H_{39}N_6O_{19}Na_2Cr_3$
M_W	1719.16	1084.70
Crystal System	Monoclinic	Trigonal
Space group	I2/a	R-3
a/Å	26.3193(11)	15.5335(5)
b/Å	13.1295(5)	15.5335(5)
c/Å	22.7708(12)	36.608(2)
α/°	90	90
β/°	113.736(5)	90
γ/°	90	120
V/Å^3	7203.0(6)	7649.8(6)
Z	4	6
T/K	150(3)	150(3)
λ[b]/Å	0.7107	0.7107
D_c/g cm^{-3}	1.585	1.413
μ(Mo-Ka)/ mm^{-1}	0.977	0.726
Meas./indep.(R_{int}) refl.	6590/4621 (0.0387)	3118/2744 (0.00350)
Restraints, Parameters	0, 475	0, 205
wR2 (all data)[c]	0.1315	0.1304
$R1$[d,e]	0.0483	0.0473
Goodness of fit on F^2	1.019	1.146

[a] Includes guest molecules.[b] Mo-Kα radiation, graphite monochromator. [c] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$. [d]For observed data. [e] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

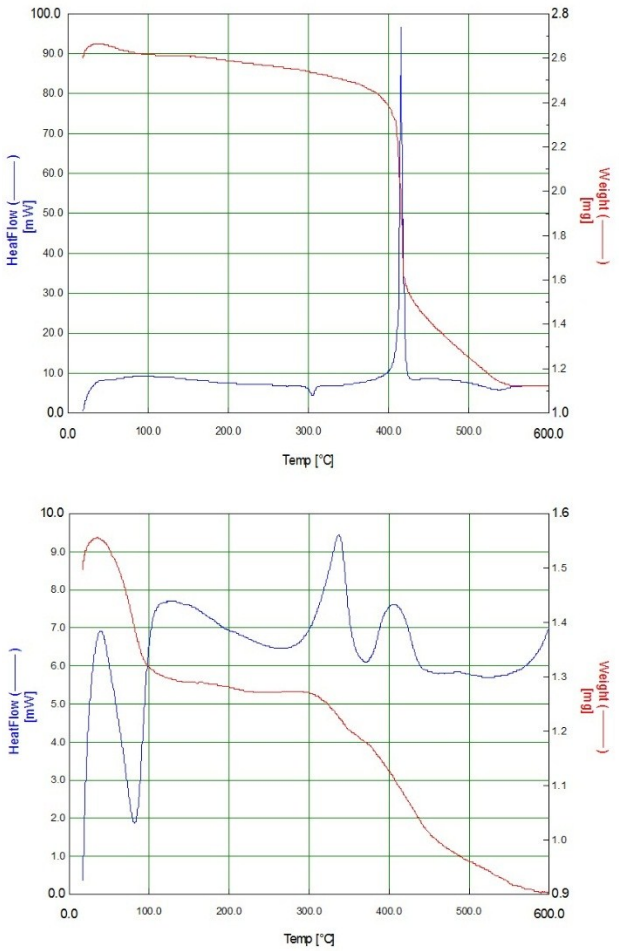

Figure S7 TGA trace obtained on crystalline samples of and **3** (top) and **5** (bottom) analyzed in the 25-600 °C temperature range in an N_2 atmosphere.