Supplementary Material for CrystEngComm

Electronic Supplementary Information

Planar [Ni_7] Discs as Double-Bowl, Pseudo Metallacalix[6]arene Host Cavities

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Synthesis of (L^1)

To a solution of o-vanillin (4.00 g, 26.3 mmol) in MeOH (40 cm^3) was added a 1:10 excess of $MeNH_2$ (20 cm^3 of a 40 % aqueous solution). The solution rapidly adopted an intense-yellow colour on addition of $MeNH_2$ and was then agitated for 10 h. A bright yellow crystalline solid of $\mathbf{L^1}$ was obtained solution via slow evaporation of the reaction mixture in a 62 % yield (2.69 g). The crystalline solid was then washed with n-hexane and dried under vacuum. Elemental analysis calcd (%) for $C_9H_{11}N_1O_2$: C 65.43, H 6.71, N 8.47; Found: C 64.95, H 6.27, N 8.33. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.47(s) (3H, N-CH_3), 3.89(s) (3H, O-CH_3), 6.75-6.90 (m, Ar-H), 8.30(s), (1H, N=CH).

Synthesis of (L^2)

To a solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.50 g, 10.82 mmol) in MeOH (40 cm^3) was added a 1:12 excess of $MeNH_2$ (10 cm^3 of a 40 % aqueous solution). The solution adopted an intense-yellow colour on addition of $MeNH_2$ and was left to stir for 10 h. The bright yellow needle-like crystalline product was obtained via slow evaporation of the reaction mixture and washed in n-Hexane to give $\mathbf{L^2}$ in 60 % yield (1.58 g). Elemental analysis calcd (%) for $C_9H_{10}N_1O_2Br$: C 44.28, H 4.10, N 5.74; Found: C 44.75, H 4.98, N 5.47. ^1H (400 MHz, $CDCl_3$): δ = 3.47(s) (3H, N-CH_3), 3.86(s) (3H, O-CH_3), 6.93-6.95 (m, Ar-H), 8.19(s), (1H, N=CH).

Synthesis of [$Ni_7(\mu_3\text{-}OH)_6(L^1)_6](NO_3)_2$ (1)

$Ni(NO_3)_2.6H_2O$ (0.25 g, 0.85 mmol), L^1 (0.14 g, 0.85 mmol) and NaOH (0.034 g, 0.85 mmol) were dissolved in 30 cm^3 EtOH and stirred for 4 h. The resultant green solution was then filtered and from which X-ray quality crystals of **1** were obtained in 30 % yield upon slow evaporation. Elemental analysis calculated (%) for $C_{54}H_{66}N_8O_{24}Ni_7$ (**1**): C, 39.98; H, 4.10; N, 6.91; Found: C, 40.44; H, 4.91; N, 7.02. FT-IR (cm^{-1}): 3415 (w), 2968 (w), 2932 (w), 1627 (s), 1602 (w), 1559 (w), 1459 (m), 1406 (w), 1315 (s), 1221 (s), 1171 (w), 1148 (w), 1072 (m), 1044 (w), 1018 (w), 963 (m), 864 (m), 828 (w), 793 (m), 743 (s).

Synthesis of $[Ni_7(\mu_3\text{-}OH)_6(L^2)_6](NO_3)_2.3NO_2Me$ (2)

The reaction mixture obtained from **1** (above) and filtered and the filtrate left to evaporate to dryness. The green solid was then redissolved in 10 cm^3 NO_2Me wherby green hexagonal crystals of **2** were obtained in 15 % yield upon slow Et_2O diffusion. Elemental analysis calculated (%) for $C_{57}H_{75}N_{11}O_{30}Ni_7$ (**2**.$3NO_2Me$): C, 37.93; H, 4.19; N, 8.54; Found: C, 38.31; H, 4.59; N, 8.29. FT-IR (cm^{-1}): 3625(w), 2931(w), 1628(s), 1601(m), 1555(s), 1476(s), 1460(s), 1433(m), 1407(m), 1337(m), 1316(m), 1221(m), 1171(w), 1147(w), 1086(w), 1072(w), 1018(w), 865(w), 795(w), 743(w).

Synthesis of $[Ni_7(\mu_3\text{-}OH)_6(L^2)_6](NO_3)_2.2MeCN$ (3)

$Ni(NO_3)_2.6H_2O$ (0.25 g, 0.85 mmol), L^2 (0.21 g, 0.85 mmol) and NaOH (0.034 g, 0.85 mmol) were dissolved in 30 cm^3 EtOH and stirred for 4 h. The resultant green precipitous solution was then filtered and evaportaed to dryness. The green solid was then redissolved in MeCN and from which crystals of **3** were obtained upon Et_2O diffusion in 23 % yield. Elemental analysis calculated (%) for $C_{58}H_{66}N_{10}O_{24}Br_6Ni_7$ (**3**.2MeCN): C, 31.99; H, 3.06; N, 6.43; Found: C, 31.38; H, 3.34; N, 6.64. FT-IR (cm^{-1}): 3620(w), 3261(wb), 2916(w), 2258(w), 1630(s), 1590(w), 1542(w), 1456(m), 1436(m), 1393(m), 1352(m), 1307(s), 1236(m), 1212(m), 1150(w), 1093(w), 1039(w), 1018(w), 966(w), 956(w), 841(w), 789(w), 754(w), 690(w).

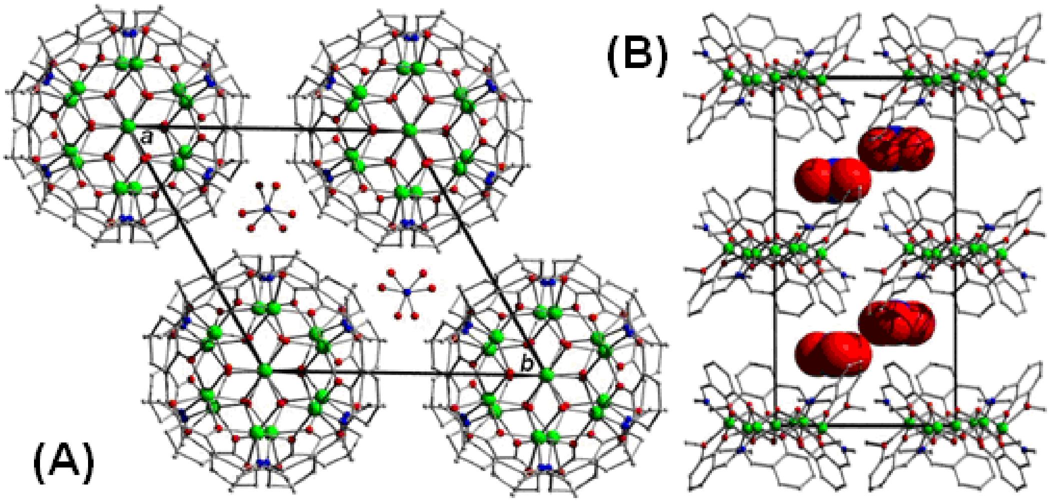

Figure SI1 (A) Crystal packing observed in **1** as viewed down the *c* axis of the unit cell respectively. Note that packing of **2** is identical to that of **1** minus disordered $MeNO_2$ guests. (B) View along a axis of the cell in **1**. H-atoms omitted for clarity. Large spheres represent NO_3^- counter anions.

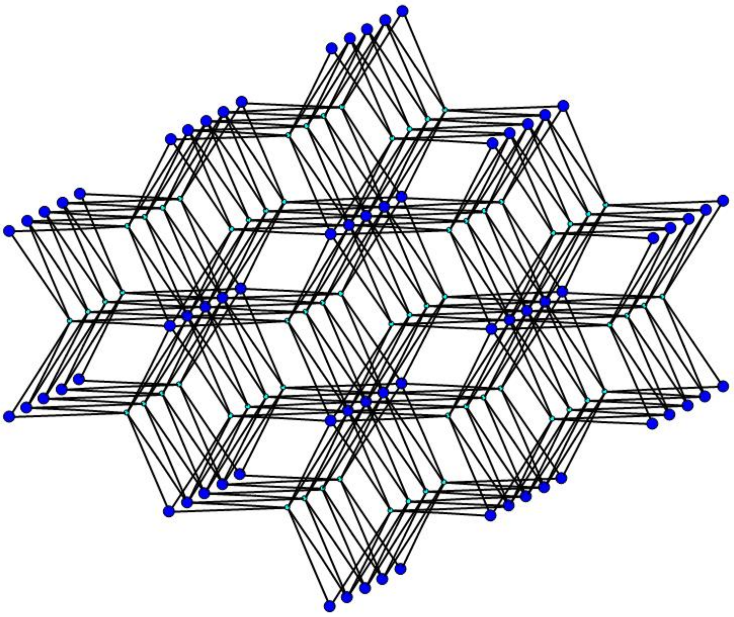

Fig. SI2 The (6,12)-connected net with a $(4^{15})_2(4^{48}.6^{18})$-**alb** topology in **1** and **2**
Big blue spheres represent the 12-connected $[Ni_7]$ units while smaller cyan spheres represent the 6-connected NO_3^-.

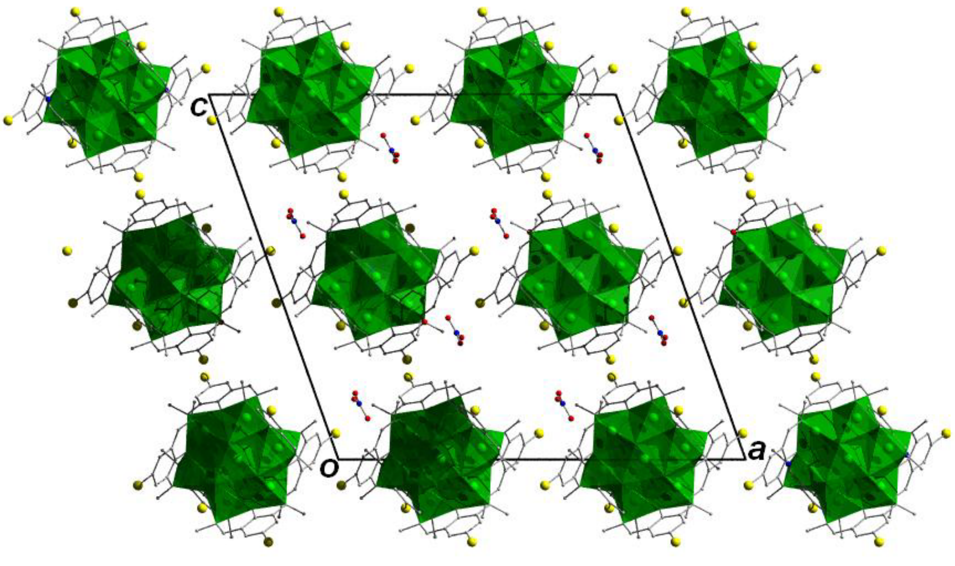

Figure S13 (top) Polyhedral representation of crystal packing in **3** as viewed down the *b* axis. H atoms omitted for clarity.

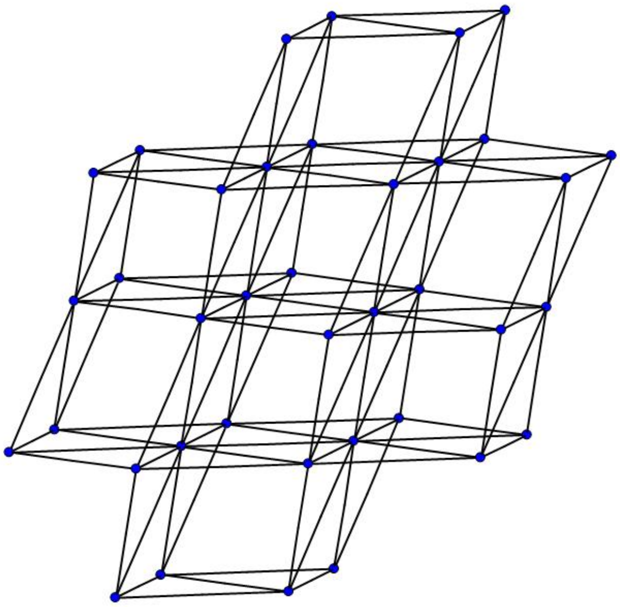

Fig. SI4 The 10-connected ($3^{12}.4^{28}.5^{5}$)-**bct** in **3** blue spheres represent the 10-connected [Ni_7] units.

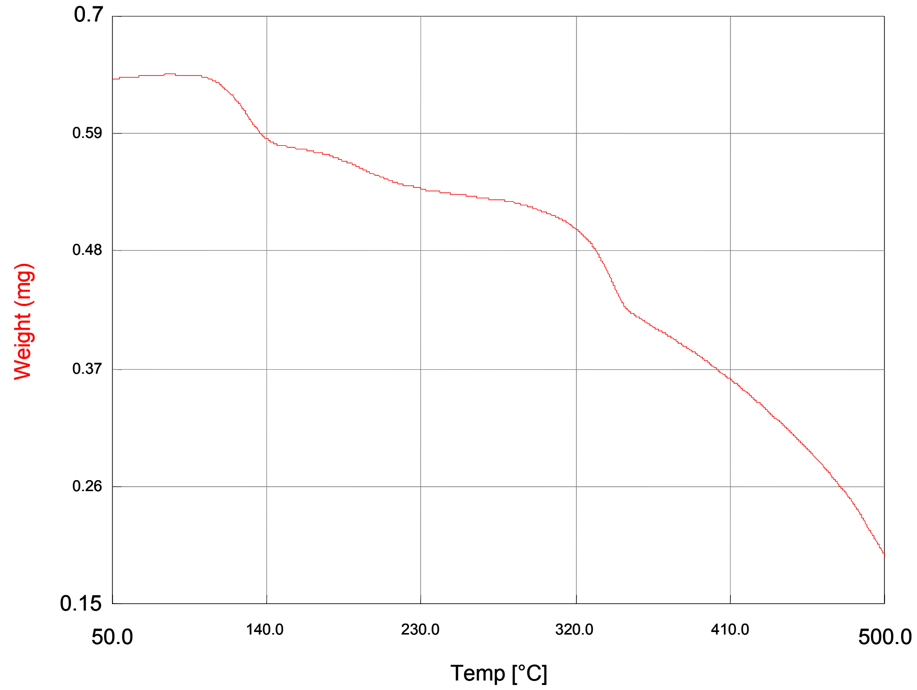

Fig. SI5 TGA trace obtained on crystalline samples of **2** analysed in the 25 – 600 ºC temperature range in a N_2 atmosphere.

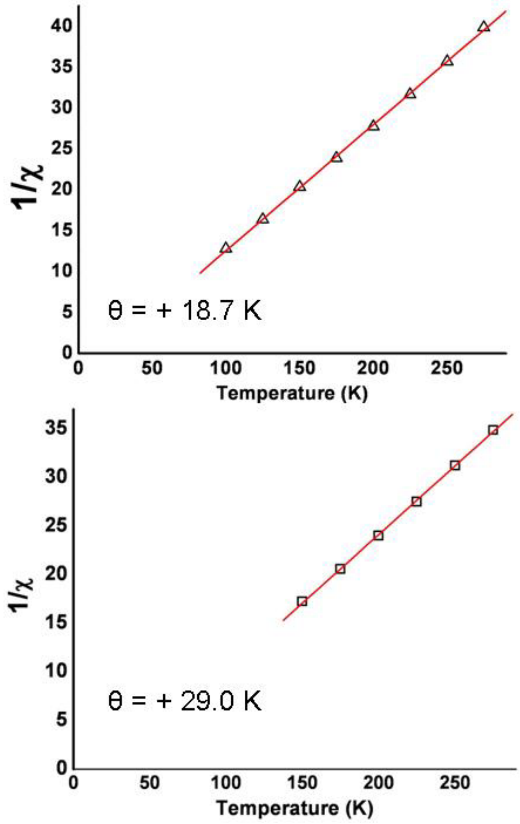

Fig. SI6 Plots of 1/χ vs. T obtained from complexes 1(top) and 3(bottom) giving Curie-Weiss constants (θ) of +18.7 and +29.0 K respectively.

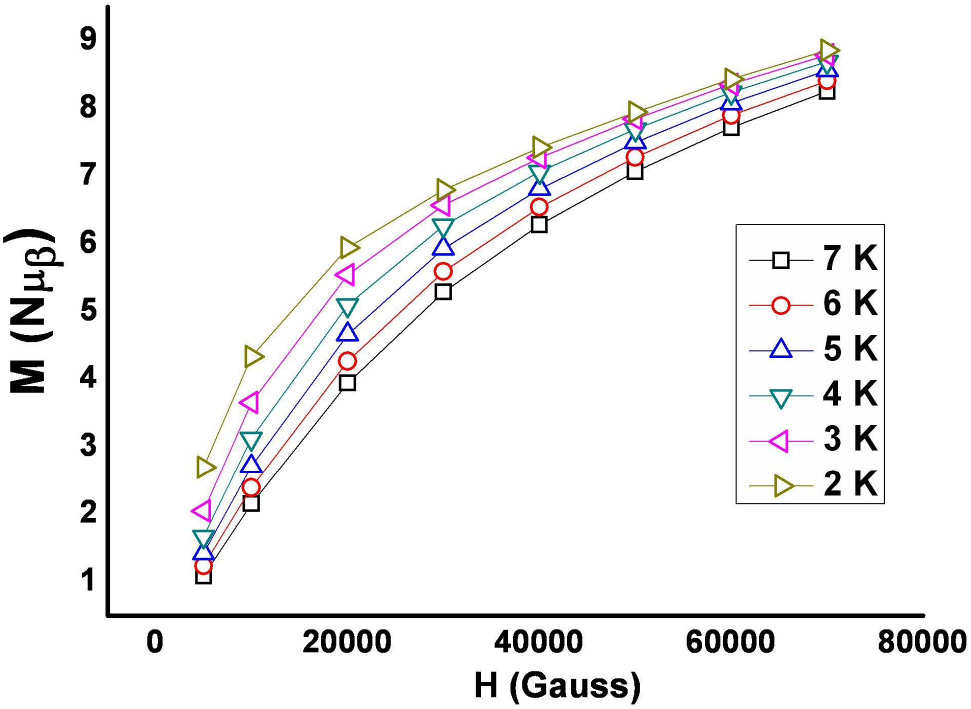

Fig. SI7 Plots of magnetisation (M/ $N\mu_\beta$) vs. H (G) obtained from complex **3** in the 2-7 K temperature range and fields of 0.5- 7 T.

X-ray diffraction details on the collection of 1-3

The structures of **1-3** were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source**.** Each data reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)[1] and refined by full matrix least squares using SHELXL-97.[2] SHELX operations were automated using the OSCAIL software package.[3] All hydrogen atoms were placed in calculated positions. The non hydrogen atoms were refined anisotropic except for the disordered guest $MeNO_2$ and MeCN molecules which were left isotropic. DFIX and FLAT restraints were required on the disordered $MeNO_2$ guest molecules as a result of high isotropic thermal parameters upon refinement.

1. G. M. Sheldrick, *Acta. Crystallogr., Sect. A: Found. Crystallogr.,* 1990, **A46**, 467.
2. G. M. Sheldrick, SHELXL-97, A computer programme for crystal structure determination, University of Gottingen, 1997.
3. P. McArdle, P. Daly and D. Cunningham, *J. Appl. Crystallogr.*, 2002, **35**, 378.