Electronic Supplementary Information


Seán T. Meally,$^a$ Georgios Karotsis,$^b$ Euan K. Brechin,$^b$ Giannis S. Papaefstathiou,$^c$ Peter W. Dunne,$^a$ Patrick McArdle,$^a$ and Leigh F. Jones.$^{a*}$

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 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$_9$H$_{11}$N$_1$O$_2$: C 65.43, H 6.71, N 8.47; Found: C 64.95, H 6.27, N 8.33. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 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 L$^2$ in 60 % yield (1.58 g). Elemental analysis calcd (%) for C$_9$H$_{10}$N$_1$O$_2$Br: C 44.28, H 4.10, N 5.74; Found: C 44.75, H 4.98, N 5.47. $^1$H (400 MHz, CDCl$_3$): $\delta$ = 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$_7$(µ$_3$-OH)$_6$(L$^1$)$_6$(NO$_3$)$_2$] (1)

Ni(NO$_3$)$_2$.6H$_2$O (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$_8$O$_{24}$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 \([\text{Ni}_7(\mu_3\text{-OH})_6(\text{L}^2)_6](\text{NO}_3)_2\cdot3\text{NO}_2\text{Me} \ (2)\)

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\(_2\)Me whereby green hexagonal crystals of 2 were obtained in 15 % yield upon slow Et\(_2\)O diffusion. Elemental analysis calculated (%) for C\(_{57}\)H\(_{75}\)N\(_{11}\)O\(_{30}\)Ni\(_7\) (2.3NO\(_2\)Me): 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 \([\text{Ni}_7(\mu_3\text{-OH})_6(\text{L}^2)_6](\text{NO}_3)_2\cdot2\text{MeCN} \ (3)\)

Ni(NO\(_3\))\(_2\)-6H\(_2\)O (0.25 g, 0.85 mmol), \(\text{L}^2\) (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 evaporated to dryness. The green solid was then redissolved in MeCN and from which crystals of 3 were obtained upon Et\(_2\)O diffusion in 23 % yield. Elemental analysis calculated (%) for C\(_{58}\)H\(_{66}\)N\(_{10}\)O\(_{24}\)Br\(_6\)Ni\(_7\) (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. S12 The (6,12)-connected net with a (4^{15})(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. S14** The 10-connected $(3^{12}.4^{28}.5^{5})$-bct in 3 blue spheres represent the 10-connected [Ni$_2$] units.

**Fig. S15** TGA trace obtained on crystalline samples of 2 analysed in the 25 – 600 °C temperature range in a N$_2$ atmosphere.
Fig. S16 Plots of $1/\chi$ vs. T obtained from complexes 1(top) and 3(bottom) giving Curie-Weiss constants ($\theta$) of +18.7 and +29.0 K respectively.

Fig. S17 Plots of magnetisation ($M / N\mu_B$) 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.