Supplementary Material (ESI) for Chemical Communications
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Bow-tie metallo-cryptophanes from a carboxylate derived cavitand.

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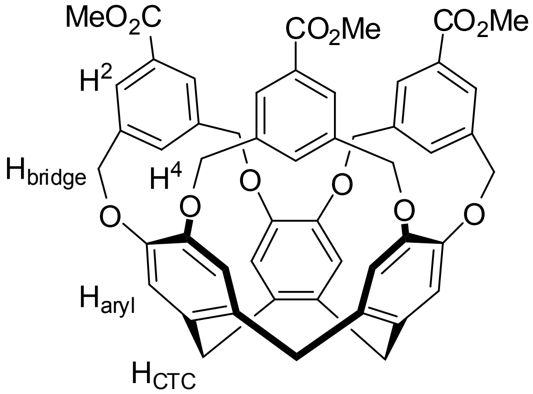
Supplementary Material

Synthesis

Cyclotricatechylene (CTC)[1] and methyl-3,5-bis(bromomethyl)benzoate[2] were prepared according to literature methods. All other chemicals were obtained from Sigma-Aldrich Chemical Company or Lancaster Synthesis Ltd and were used without further purification. Electrospray (ES) mass spectra were recorded using Micromass LCT or Bruker MicroTOF Focus mass spectrometers. ^{1}H Nuclear Magnetic Resonance spectra were recorded using a Bruker Avance 500 instrument. ^{13}C Nuclear Magnetic Resonance spectra were recorded using a Bruker DPX 300 instrument. ^{1}H spectra are referenced to tetramethylsilane and chemical shifts given in parts per million downfield from TMS. Microanalyses were obtained on a Carlo Erba Elemental Analyser MOD 1106 instrument, found composition is reported to the nearest 0.05 %. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer and samples analysed as solids.

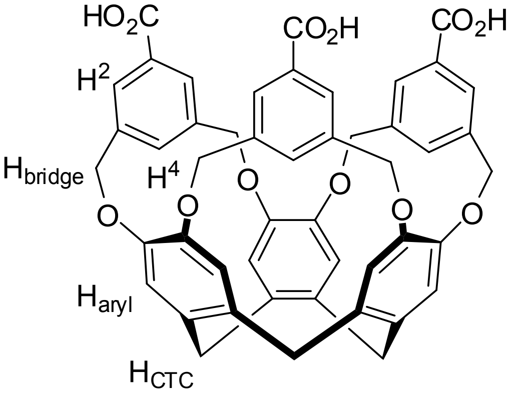
Preparation of tris[3,5-bis(methyl)methylbenzoate]cyclotricatechylene (Me_3L)



Prepared according to a method adapted from that of Wytko and Weiss for similar cavitands.[3]

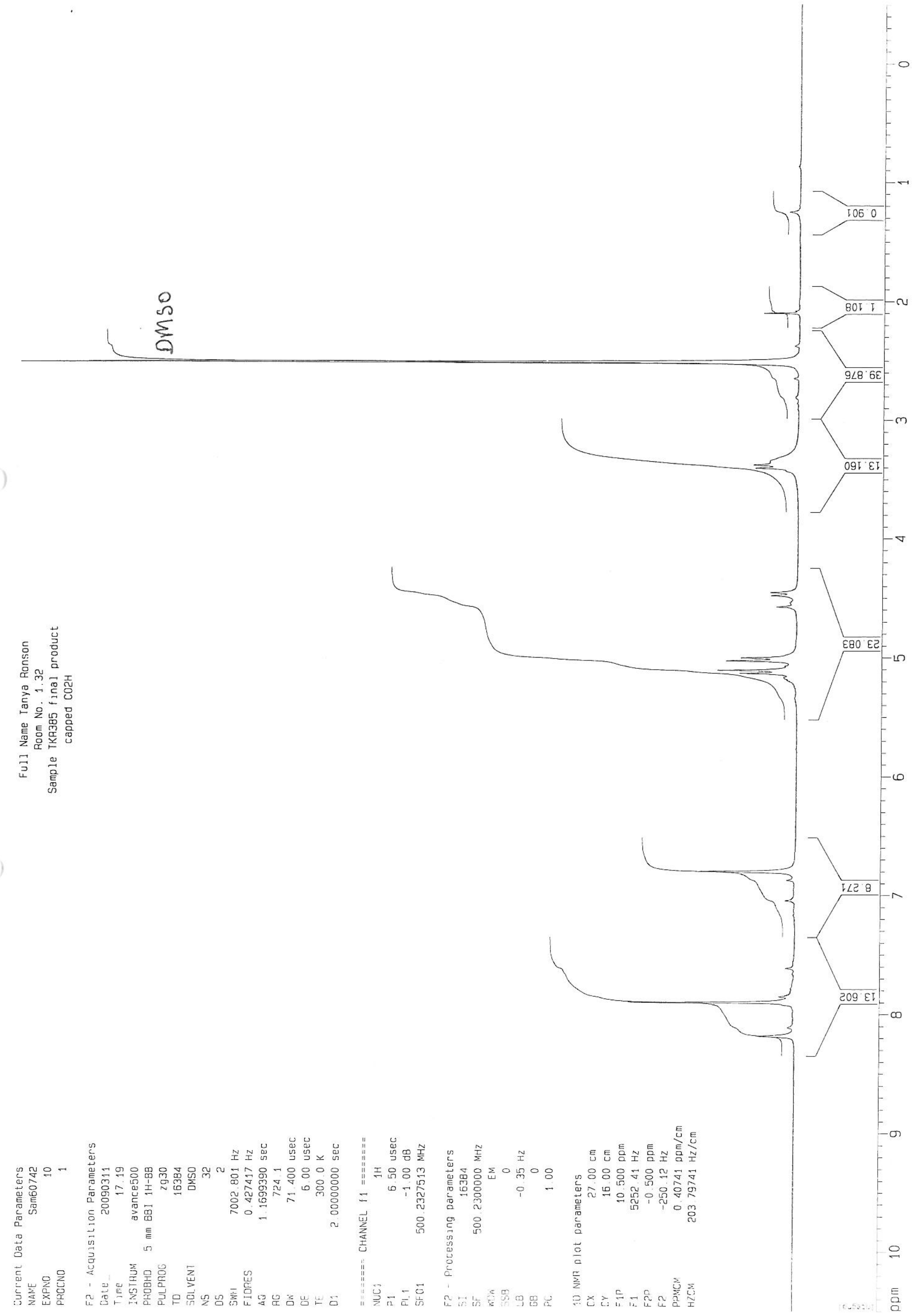
A solution of cyclotricatechylene (CTC) (300 mg, 0.819 mmol) and methyl-3,5-bis(bromomethyl)benzoate (870 mg, 2.702 mmol) in degassed DMF (100 mL, previously dried over 4 Å molecular sieves) was added under N_2 to a vigorously stirred suspension of Cs_2CO_3 (4.5 g) in degassed DMF (350 mL) at 70 °C. The suspension was stirred at 70 °C for 48 hours and the DMF removed *in vacuo*. The residue was taken up into water (200 mL) and CH_2Cl_2 (200 mL) and the aqueous layer washed with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with water (5 × 100 mL), dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by column chromatography (silica, 0-5 % MeOH in CH_2Cl_2) to afford tris[3,5-bis(methyl)methylbenzoate]cyclotricatechylene as a white powder (515 mg, 74 %). HR MS (ES^+): *m/z* 869.2576 (*MNa^+*); calc. for $C_{51}H_{42}O_{12}Na$ 869.2568. ^1H NMR (500 MHz, $CDCl_3$): δ(ppm) 8.08 (6H, s, H^2), 7.45 (3H, s, H^4), 6.50 (6H, s, aryl CH), 5.14 (12H, m, bridge CH_2), 4.42 (3H, d, CTG CH_2, J = 13.7 Hz), 3.83 (9H, s, CH_3), 3.22 (3H, d, CTC CH_2, J = 13.7 Hz). ^{13}C NMR (75 MHz, d_6-DMSO): δ(ppm) 166.0, 145.2, 139.5, 136.3, 131.7, 131.4, 130.9, 116.4, 68.6, 52.2, 34.7. Found C 69.10, H 5.50; $C_{51}H_{42}O_{12}(H_2O)_2$ requires C 69.37, H 5.25 %.

Preparation of tris[3,5-bis(methyl)benzoic acid]cyclotricatechylene (H_3L)



Tris[3,5-bis(methyl)methylbenzoate]cyclotricatechylene (515 mg, 0.608 mmol) was refluxed with K_2CO_3 (802 mg, 5.80 mmol) in MeOH/H_2O (7:1, 70 mL) for 24 hours. The MeOH was removed *in vacuo* and the mixture diluted with water (40 mL). The mixture was neutralised with 1M HCl and the off-white solid filtered off and dried *in vacuo*. Yield 365 mg, 75 %. HR MS (ES^-): *m/z* 803.2137 (*$M\text{-}H^-$*); calc. for $C_{48}H_{35}O_{12}$ 803.2134. ^1H NMR (500 MHz, D_6-DMSO): δ (ppm) 8.17 (3H, s, H^4), 7.87 (6H, s, H^2), 6.78 (6H, s, aryl CH), 5.04 (12H, m, bridge CH_2), 4.44 (3H, d, CTC CH_2, J = 13.2 Hz), 3.37 (3H, d, CTC CH_2, J = 13.2 Hz), 3.3 (broad, H_2O). RCO_2H peaks not observed due to broadening. ^{13}C NMR (75 MHz, D_6-DMSO): δ(ppm) 167.1, 145.6, 139.2, 136.3, 132.4, 132.1, 131.2, 117.2, 69.3, 34.7. Found C 68.40, H 4.85; $C_{48}H_{36}O_{12}(H_2O)_2$ requires C 68.57, H 4.80 %.

^{1}H NMR spectrum of H_3L in D_6-DMSO:



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Sample TKR385 final product
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F2P             -0.500 ppm
F2             -250.12 Hz
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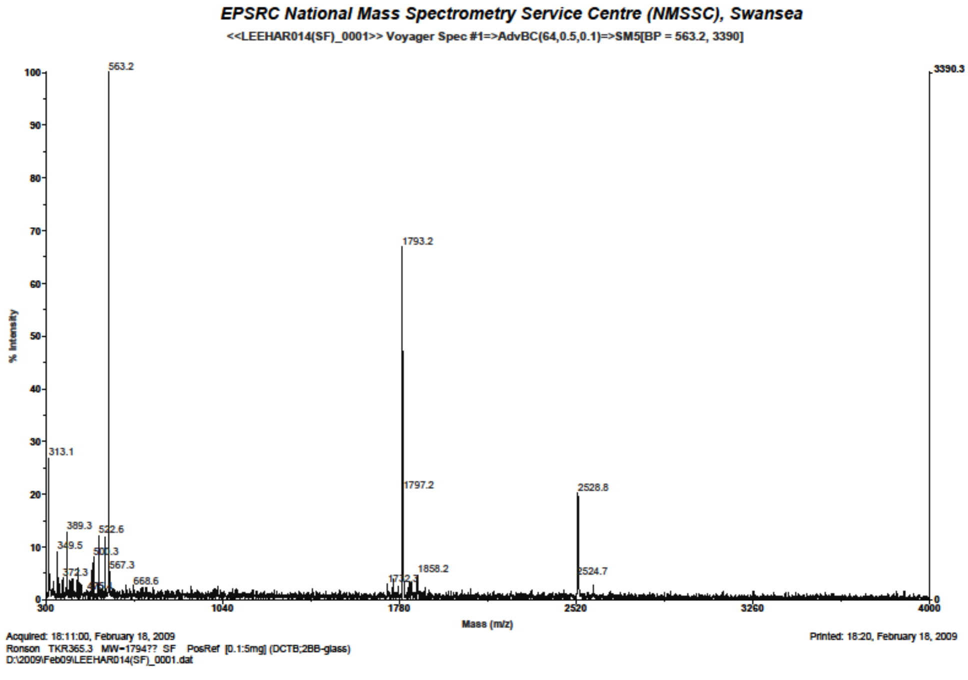
Preparation of $[Cu_3L_2(DMF)_3].2(DMF)$ 1. A DMF (1 mL) solution of H_3L (15 mg, 0.019 mmol) and $Cu(OAc)_2$ (11 mg, 0.055 mmol) in a sealed glass vial was heated to 90 °C at a rate of 1 °C per minute, held at 90 °C for 48 hours and then slowly cooled to room temperature at a rate of 0.1 °C per minute. The bright blue crystals of $[Cu_3L_2(DMF)_3].2(DMF)$ were collected by filtration and washed with diethyl ether. Yield 6 mg, 32 %. Crystals of $[Cu_3L_2(DMF)_3].2(DMF)$ can also be obtained in lower yield from the reaction of H_3L with 1.5 equivalents of $Cu(OAc)_2$. MS (solvent-free MALDI)[‡] 1793.2 $\{Cu_3(L)_2(H)\}^+$ (calcd. 1795.3), 2528.8 $\{Cu_2(L)_3(H)\}^+$ (calcd. 2533.5). IR (solid state): ν (cm^{-1}) 2885 (w), 1638 (s), 1599 (s), 1517 (m), 1505 (m), 1462 (m), 1417 (s), 1406 (s), 1375 (m), 1327 (m), 1275 (w), 1251 (s), 1205 (m), 1189 (m), 1162 (w), 1139 (m), 1076 (s), 1027 (m), 982 (m), 935 (w), 892 (m), 871 (w), 839 (m), 790 (m), 766 (m), 738 (w), 717 (w), 706 (m), 682 (w), 644 (w), 610 (m), 506 (w), 493 (w), 480 (w). Microanalysis indicated different levels of solvation in the dried crystals than was modelled in the crystal structure of $[Cu_3L_2(DMF)_3].2(DMF)$ **1**. Found C 59.35, H 3.95, N 1.00; $Cu_3(C_{48}H_{33}O_{12})_2(C_3H_7NO)_{1.5}(H_2O)_7$ requires C 59.46, H 4.49, N 1.04 %.

[‡] Initial attempted analysis of solid sample by EI failed, so solvent-free MALDI attempted. $M^{+\bullet}$ species observed with DCTB matrix in positive-reflectron mode.



EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea
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Printed: 18:20, February 18, 2009

Preparation of $[Cu_3L_2(DEF)_3].(DEF)$ 2 A DEF (1 mL) solution of H_3L (5 mg, 0.006 mmol) and $Cu(OAc)_2$ (2 mg, 0.010 mmol) in a sealed glass vial was heated to 90 °C at a rate of 1 °C per minute, held at 90 °C for 48 hours and then slowly cooled to room temperature at a rate of 0.1 °C per minute. The bright blue crystals of $[Cu_3L_2(DEF)_3].(DEF)$ were suitable for single crystal X-ray crystallography. $[Cu_3L_2(DEF)_3].(DEF)$ was not isolated in sufficient quantities for solid state analysis.

Preparation of [{Cu_3L_2(DMF)(H_2O)}$_2$(μ-BPE)].4(DMF) 3 (BPE = 1,2-bis(4-pyridyl)ethylene). A DMF (1.5 mL) solution of H_3L (10 mg, 0.012 mmol), $Cu(OAc)_2$ (3.8 mg, 0.019 mmol) and 1,2-bis(4-pyridyl)ethylene (3.4 mg, 0.019 mmol) in a sealed glass vial was heated to 90 °C at a rate of 1 °C per minute, held at 90 °C for 48 hours and then slowly cooled to room temperature at a rate of 0.1 °C per minute. The bright blue crystals of [{Cu_3L_2(DMF)(H_2O)}$_2$(μ-BPE)].4(DMF) were collected by centrifugation and washed with DMF and CH_2Cl_2. Yield 6.5 mg, 50 %. IR (solid state): ν (cm^{-1}) 2879 (w), 1639 (s), 1599 (s), 1516 (m), 1505 (m), 1461 (m), 1417 (s), 1406 (s), 1376 (m), 1327 (m), 1274 (m), 1249 (s), 1205 (m), 1189 (m), 1162 (w), 1138 (m), 1076 (s), 1027 (w), 1011 (w), 982 (w), 935 (w), 891 (w), 869 (w), 837 (w), 790 (w), 765 (m), 738 (w), 717 (w), 705 (m), 682 (w), 667 (w), 643 (w), 610 (m), 508 (w). Microanalysis indicated different levels of solvation in the dried crystals than was modelled in the crystal structure of complex **3** [{Cu_3L_2(DMF)(H_2O)}$_2$(μ-BPE)].4(DMF)**.** Example of analysis: found C 61.85, H 4.15, N 1.35; $Cu_6(C_{48}H_{33}O_{12})_4(C_{12}H_{10}N_2)(C_3H_7NO)_2(H_2O)_8$ requires C 62.09, H 4.27, N 1.38 %.

Preparation of [Co_7L_2(μ-OAc)$_4$(μ-O)$_2$(DMF)$_2$].(DMF).2(H_2O) complex 4. A DMF (1 mL) solution of H_3L (5 mg, 0.006 mmol) and $Co(OAc)_2$ (4.4 mg, 0.018 mmol) in a sealed glass vial was heated to 130 °C at a rate of 1 °C per minute, held at 130 °C for 48 hours and then slowly cooled to room temperature at a rate of 0.1 °C per minute. The dark purple crystals of complex **4** were suitable for single crystal X-ray crystallography. The sample was heterogeneous with [Co_7L_2(μ-OAc)$_4$(μ-O)$_2$(DMF)$_2$].(DMF).2(H_2O) isolated along with a brown solid and brown oil present.

X-Ray Crystallography

Crystals were mounted on a fibre under oil and flash frozen to 150(1) K using a stream of cold N_2. Data were collected on a Bruker-Nonius X8 diffractometer with an Mo-rotating anode (λ = 0.71073 Å), or, for complex **3**, on a Rigaku Saturn using synchrotron radiation (λ = 0.6889 Å) at station I19 at the Diamond Light Source. Data were corrected for Lorenztian and polarization effects and absorption corrections were applied using multi-scan methods. The structures were solved by direct methods using

SHELXS-97 [4] and refined by full-matrix on F^2 using SHELXL-97.[5] Unless otherwise specified, all non-hydrogen atoms were refined as anisotropic, and hydrogen positions were included at geometrically estimated positions. Additional details of the refinements are given below.

[$Cu_3L_2(DMF)_3$].2(DMF) 1: Both solvent DMF molecules were modeled as disordered.

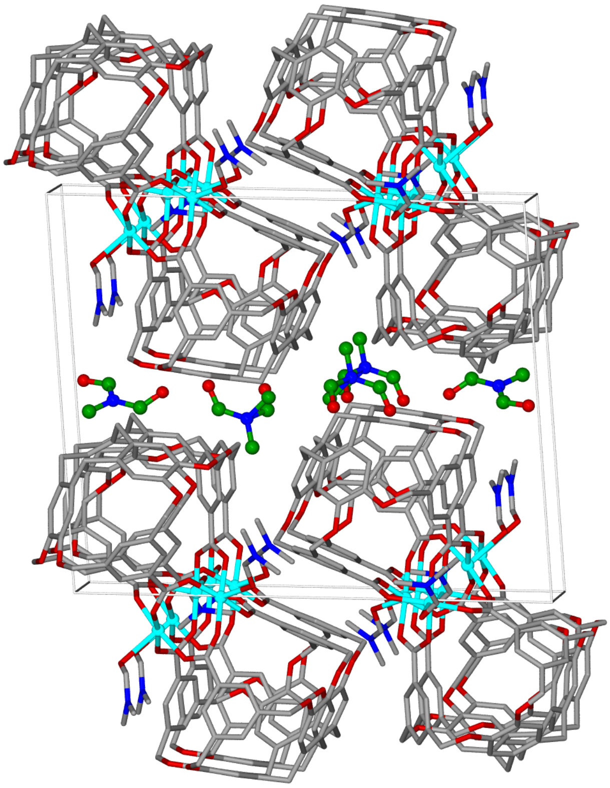
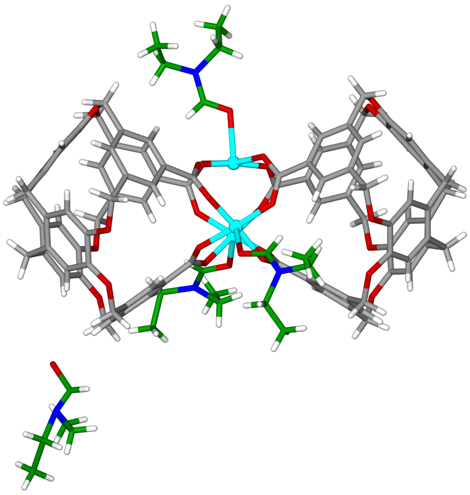


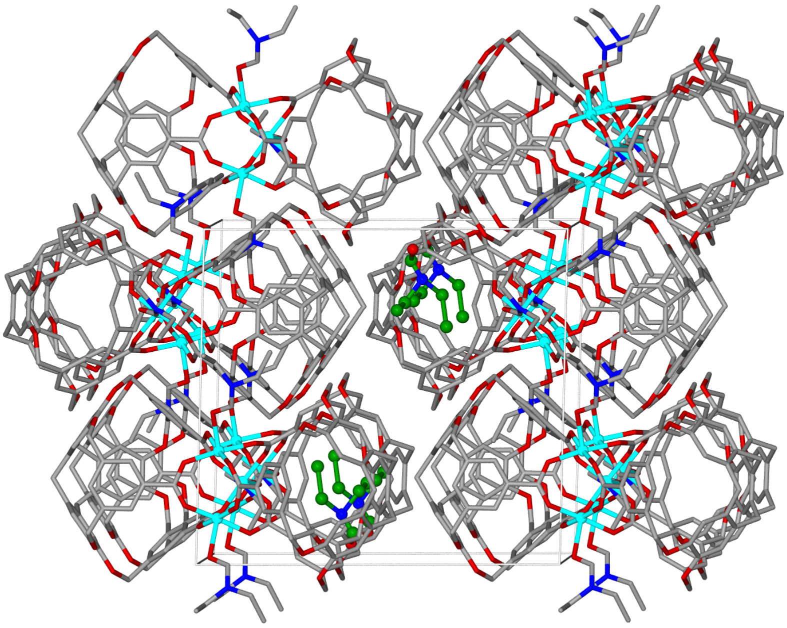
Figure S1: Packing diagram of the crystal structure of [$Cu_3L_2(DMF)_3$].2(DMF) **1** viewed down the *a* axis. Disordered solvent DMF shown in green.

[$Cu_3L_2(DEF)_3$].(DEF) 2: This is a poor quality structure that nevertheless establishes the structure of the complex. The crystals were of poor quality and showed significant twinning. CELL-NOW was used to determine the unit cells of three twin components and data integrated as a twin and scaled using TWINABS. The structure was refined using an HKLF 5 data file. While this lead to significant improvement in refinement residuals compared with data not treated as a twin, the data is still of such poor quality that only Cu centres were refined anisotropically. One C-C bond length on a DEF ligand was restrained to be chemically reasonable.

Crystal data: $C_{116}H_{110}Cu_3N_4O_{28}$, *Mr* = 2198.70, triclinic, *a* = 16.129(3), *b* = 17.520(3), *c* = 19.048(3) Å, α = 88.52(1), β = 83.42(1), γ = 88.02(1)°, *V* = 5342.5(15) Å^3, space group *P*-1, *T* = 150(1) K, *Mo-K*$_\alpha$ radiation (λ = 0.71073 Å), *Z* = 2, crystal size 0.19 x 0.17 x 0.14 mm, ρ_{calc} = 1.367 g.cm^{-3}, μ = 0.671 mm^{-1}, θ_{max} = 24.41 °, 86359 data collected, 42057 unique, R_{int} = 0.0723, 628 parameters, 1 restraint, R_1 = 0.1666 (for 32894 data $I > 2\sigma(I)$), wR_2 = 0.4079 (all data), *S* = 1.143. CCDC-776457.



(a)



(b)

Figure S2: Crystal structure of complex $[Cu_3L_2(DEF)_3].(DEF)$ **2** (a) asymmetric unit with DEF in green; (b) packing diagram viewed down *a* axis with solvent DEF in green.

[{Cu_3L_2(DMF)(H_2O)}$_2$(μ-BPE)].4(DMF) 3: Data was weak at high angles and cut at $2\theta = 45°$. The refinement left significant diffuse electron density that could not be adequately modeled as disordered solvent. There were void spaces within the crystal lattice of sufficient size to contain several solvent molecules. Hence the SQUEEZE routine of PLATON[6] was employed which lowered the R_1 value by ~ 6%. One solvent DMF molecule was refined with group anisotropic displacement parameters.

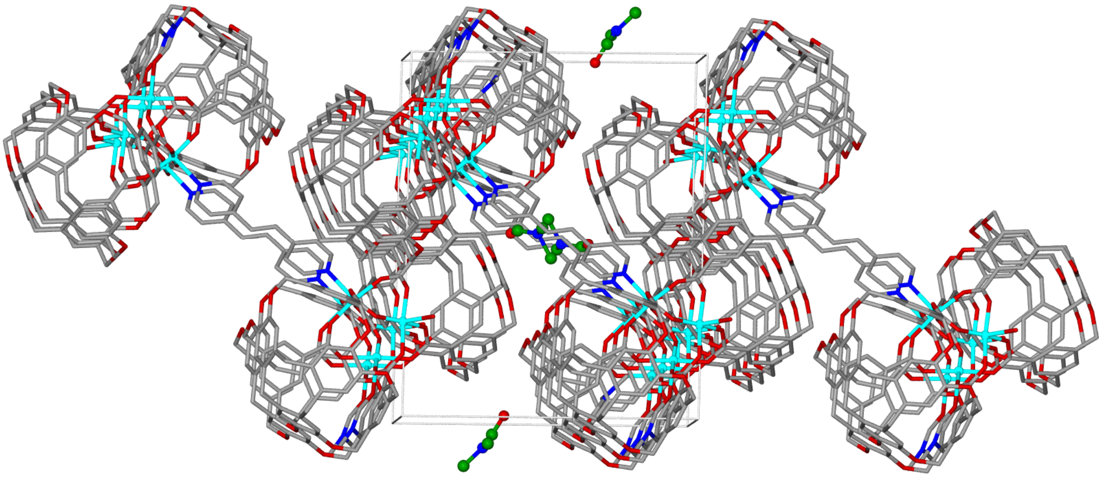


Figure S3: Packing diagram viewed down the *a* axis from the crystal structure of complex **3**. Solvent DMF shown in green.

[$Co_7(\mu_3\text{-L})_2(\mu_3\text{-OAc})_4(\mu_4\text{-O})_2(DMF)_2$].(DMF).2($H_2O$) 4 Crystals were twinned and CELL-NOW was used to determine the unit cells of two domains rotated 179.6° with respect to one another and twin law 1 0 0, 0 -1 0, 0 0 -1. Data was integrated as a twin and scaled using TWINABS. The structure was refined using an HKLF 5 data file. Voids in the crystal lattice are likely to be filled with disordered solvent that was too disordered to be adequately modelled.

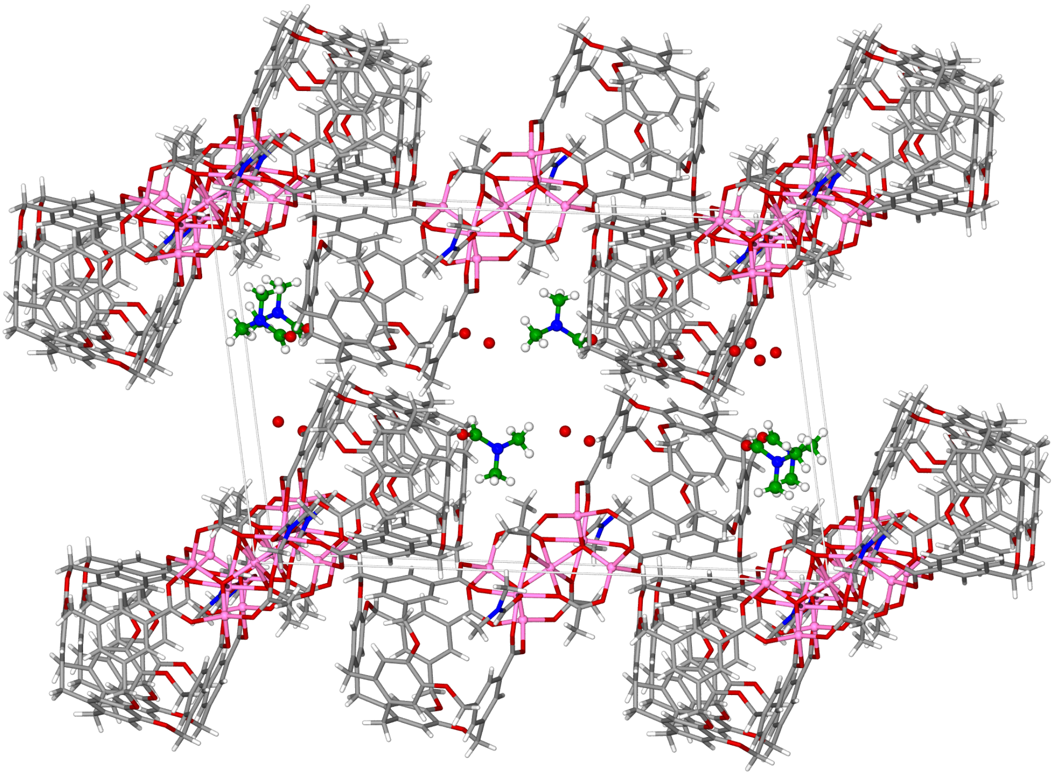


Figure S4: Packing diagram viewed down the *b* axis from the crystal structure of complex $[Co_7(\mu_3\text{-L})_2(\mu_3\text{-OAc})_4(\mu_4\text{-O})_2(DMF)_2].(DMF).(2H_2O)$ **4**. Solvent DMF shown in green.

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