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Supplementary Information

The effect of carboxylate position on the structure of a metal organic framework derived from cyclotriveratrylene

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Experimental

Synthesis of H_3L^1

Tribromocyclotriveratrylene (CTV-Br_3, 50 mg, 0.085 mmol), (4-(ethoxylcarbonyl)phenyl)boronic acid (4.5 equivalents, 75 mg., 0.38 mmol) and caesium fluoride (6 equivalents, 75 mg., 0.5 mmol) were dissolved in 1,4-dioxane (15 mL) and deaerated for 15 mins by bubbling N_2 through the solution. Tetrakis(triphenylphosphine)palladium (5 mol%, 5 mg) was added, and the reaction mixture stirred and then heated to 100 °C using microwave irradiation (200W) for 45 minutes, The reaction was checked for completion by TLC. The solvent was removed under reduced pressure and the product extracted with $CHCl_3$ (2 x 100 mL), and the organic solution was washed with 1 M HCl (100 mL), water (100 mL) and dried with $MgSO_4$. $CHCl_3$ was removed under reduced pressure and the residue washed with EtOH and filtered. The solid product was dissolved in the minimum amount of $CHCl_3$ and filtered through a plug of silica, eluting with EtOAc. The solvent was evaporated to yield **L^1**-ethyl ester (55 mg, 80%)

Hydroylsis of the ester was achieved by dissolving the ester in ethanol (15 mL) and THF (15 mL) and 2M NaOH (5 mL) added. This solution was stirred overnight at room temperature, and the solvent removed under reduced pressure and 2M HCl (10 mL) added to the residue. The product was then extracted with ethyl acetate (50 mL), washed with H_2O (3 × 50 mL) and the organic solution dried over $MgSO_4$. The solvent was then removed to give **H_3L^1** as a white powder (46 mg, 75% overall yield). Characterisation data is in agreement with that previously reported.[1]

Synthesis of H_3L^2

Synthesis of $\mathbf{H_3L^2}$ was performed in a manner identical to that described above, however with the use of (3-(ethoxycarbonyl)phenyl)boronic acid. From 50 mg starting material, 35.5 mg $\mathbf{H_3L^2}$ (58% yield) was obtained.

Crystal data for 1-Co

$C_{63}H_{72}Co_2N_4O_{15}$, M = 1243.10, orthorhombic *Pbca* (No. 61), a = 32.094(2), b = 9.8357(7), c = 37.7628(16), $\alpha = \beta = \gamma = 90$, V = 11920.5(13) Å^3, Z = 8, T = 120(2) K, D_{calcd} = 1.385 gcm^{-3}, μ = 4.950 mm^{-1}, N(unique) = 6634 (merged from 11890), R_{int} = 0.1346, R_1 = 0.0836, wR_2 (all data) = 0.2382, GOF = 1.029, max ΔF peak = 0.46 e Å^{-3}

Refinement special details for 1-Co

DMA residues B and C were found to be disordered over two orientations, the occupancies of which were constrained to sum to unity, with the major component having an occupancy of 0.60(1). The geometries of all three DMA molecules in the structure were restrained to have similar geometries (SAME), and the atoms of the minor disordered component C have been refined with isotropic displacement parameters which were restrained to have similar values (SIMU). A rigid bond restraint was applied to the anisotropic displacement parameters of all atoms in the structure (RIGU). Disordered DMA solvent molecules could not be sensibly modelled, so the structure was treated with PLATON SQUEEZE.[2] The number of molecules of DMA (the solvent used for crystallisation) per cell was calculated to be 16 resulting in 2 molecules of DMA per asymmetric unit, and these are included in the chemical formula and in all quantities calculated from it.

Crystal data for 1-Zn

$C_{59}H_{63}Zn_2N_3O_{14}$, M = 1168.86, orthorhombic *Pbca* (No. 61), a = 31.654(2), b = 9.7728(7), c = 37.310(2), $\alpha = \beta = \gamma = 90$, V = 11542.0(14) Å^3, Z = 8, T = 120(2) K, D_{calcd} = 1.345 gcm^{-3}, μ = 0.893 mm^{-1}, N(unique) = 7317 (merged from 17110), R_{int} = 0.2249, R_1 = 0.1460, wR_2 (all data) = 0.3889, GOF = 1.208, max ΔF peak = 0.71 e Å^{-3}

Refinement special details for 1-Zn

The structure was refined as a 2-component twin with a twin fraction of 0.290(3). The X-ray diffraction was weak with a low resolution diffraction limit, probably as a result of the large regions of diffuse solvent within the unit cell. Many attempts were made to grow more strongly diffracting crystals and synchrotron radiation was used to obtain the strongest possible diffraction data. Despite this, the diffraction limit was at 1.3 Å resolution so a cut off filter of 1.0 A was applied to the integration. As a result of this weak diffraction, the structure has a low data to parameter ratio and so where possible restraints have been applied to the geometric and atomic displacement parameters in the structure to aid refinement. DMA residues B and C were found to be disordered over two orientations, the occupancies of which were constrained to sum to unity, with the major component having an occupancy of 0.57(2). The occupancy of the acetate molecule was allowed to refine freely to a value of 0.68(2). However, the molecule has been included in the unit cell contents at full occupancy; the remainder of the molecule is likely to be in a disorder component which cannot be located in the electron density map. The geometries of the three DMA molecules and acetate molecule in the structure were restrained to have target values taken from suitable examples in the CSD. The DMA and acetate molecules were restrained to have planar geometries (FLAT). The isotropic atomic displacement parameters of disordered DMA molecules B and C were refined to a common value for each molecules [0.27(1) and 0.28(2), respectively]. The isotropic atomic displacement parameters of the acetate molecule were constrained to a value of 0.2. Chemically identical 1,2 and 1,3 atomic distances around the symmetrical ligand were restrained to have similar values (SADI). Similarity and rigid bond restraints have been applied to the anisotropic and isotropic displacement parameters of all atoms in the structure (RIGU and SIMU). All hydrogen atoms in the structure were geometrically placed and refined using a riding model. Disordered solvent molecules could not be sensibly modelled, so the structure was treated with PLATON SQUEEZE,[2] which identified a total of 374 electrons in the *P*-1 cell, equating to one dimethylacetamide (DMA) molecule per asymmetric unit. These molecules have been included in the unit cell contents and in the calculation of derived parameters.

Crystal data for 2-Zn

$C_{264}H_{331}Zn_6N_{21}O_{62}$, M = 5182.70, triclinic *P-1* (No. 2), a = 23.7409(14), b = 23.9301(14), c = 31.1933(16), α = 68.750(5), β = 88.214(4), γ = 60.764(6), V = 14179.1(16) Å^3, Z = 2, T = 120(2) K, D_{calcd} = 1.214 gcm^{-3}, μ = 0.533 mm^{-1}, N(unique) = 16964 (merged from 29553), R_{int} = 0.2211, R_1 = 0.1727, wR_2 (all data) = 0.4367, GOF = 1.484, max ΔF peak = 0.88 e Å^{-3}

Refinement special details for 2-Zn

The X-ray diffraction was weak and had a low angle cut-off despite the use of a synchrotron X-ray source. This is a result of the large regions of diffuse solvent molecules in between the macromolecules. A Shell command was used to truncate the data used in refinement to a maximum resolution of 1.0 Å. Large numbers of geometrical restraints reflecting the symmetry of the macrocyclic ligand were utilised to aid refinement of the structure. The anisotropic displacement parameters of all the atoms in the structure were restrained with a rigid bond restraint (RIGU). The elongated anisotropic displacement parameters of the methoxy carbon atoms were restrained to have more isotropic character as the implied disorder could not be sensibly refined (ISOR). Several carbon atoms within the ligand (C17, C40, C41, C89, C119) exhibiting outlying elongated anisotropic displacement parameters were restrained to have more isotropic character (ISOR). The six DMA molecules were refined with isotropic displacement parameters with all the atoms in each molecule refined as a common value (FVAR). Chemically identical 1,2 and 1,3 bond lengths within the four crystallographically independent ligands were restrained to have similar values (SADI). The carboxylate moieties were restrained to lie in a flat plane with the 1 and 4 positions of the attached phenyl rings (FLAT). All of the Zn to water distances were restrained to be similar (SADI). The geometries of the six DMA ligands were restrained to be similar (SAME), lie in a flat plane (FLAT) and the carbon-carbon and carbon-nitrogen bond lengths were restrained to have target values taken from examples in the CSD (DFIX). The hydrogen atoms of the ligands and DMA solvent molecules were geometrically placed and refined using a riding model. The hydrogen atoms of the water molecules which make strong hydrogen bonds to solvent molecules were observed in the difference maps; their positions were refined and restrained to have O-H distances of 0.84 Å and where appropriate intramolecular H...H distances of 1.37 Å (DFIX). The remaining hydrogen atoms on water were not observed in the difference map and not included in the model. However, they were included in the unit cell contents and moiety formula. Disordered solvent molecules could not be sensibly modelled, so the structure was treated with PLATON SQUEEZE,[2] which identified a total of 1423 electrons in the P-1 cell, equating to 15 dimethylformamide molecules per asymmetric unit. These molecules have been included in the unit cell contents and in the calculation of derived parameters.

References

1 J. T. Yu, J. Sun, Z. T. Huang, and Q. Y. Zheng, *CrystEngComm.*, **2012**, *14*, 112-115.
2 P. v.d. Sluis and A.L. Spek, *Acta Cryst*. **1990**, *A46*, 194-201