

Supporting Information

Synthetic and Crystallographic Investigation of the Layered Coordination Framework Copper-1,3-bis(4-carboxyphenyl)-5- ethoxybenzene

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Experimental Synthesis

Preparation of 1,3-bis(4-carboxyphenyl)-5-ethoxybenzene

1,3-bis(4-carboxyphenyl)-5-hydroxybenzene¹

A mixture of acetonitrile (60 mL) and distilled water (60 mL) were degassed in a Schlenk flask at room temperature for 1 hour under argon, before 3,5-dibromophenol (1.89 g, 7.50 mmol), 4-carboxyphenylboronic acid (2.74 g, 16.5 mmol) and dried potassium carbonate (8.23 g, 59.55 mmol) were added. The flask was evacuated and back filled with argon 3 times before bis(triphenylphosphine) palladium (II) dichloride (0.50 g, 0.71 mmol) was added and the flask was evacuated and back filled with argon a further 3 times. The flask was heated at 100 °C under argon for 72 hours. Upon cooling to room temperature, the resulting suspension was filtered and then diluted to 200 mL volume with distilled water. The solution was washed once with hexane: ethyl acetate (1:1) (50 mL) and acidified with 2M hydrochloric acid to produce an off-white precipitate, which was dried in air (3.44 g, 10.29 mmol, 69% yield). ¹H (400 MHz, *d*₆-DMSO) δ_H 8.03 (4H, m), 7.84 (4H, m), 7.46 (1H, t, *J* = 3.6 Hz), 7.16 (2H, d, *J* = 1.2 Hz).

1,3-bis(4-methoxycarbonylphenyl)-5-hydroxybenzene¹

1,3-bis(4-carboxyphenyl)-5-hydroxybenzene (3.44 g, 10.32 mmol) was suspended in methanol (225 mL), before concentrated sulfuric acid (5.69 mL, 106.75 mmol) was added at room temperature. The suspension was heated at 80 °C for 48 hours, before being cooled to room temperature. The solution was diluted to 900 mL volume with distilled water, to produce an off-white precipitate that was filtered and washed copiously with distilled water, before being dried in air (2.37 g, 6.54 mmol, 63% yield). ¹H (400 MHz, *d*₆-DMSO) δ_H 9.96 (1H, s), 8.05 (4H, m), 7.88 (4H, m), 7.49 (1H, t, *J* = 3.2 Hz), 7.16 (2H, d, *J* = 1.6 Hz), 3.89 (s, 6H).

1,3-bis(4-methoxycarbonylphenyl)-5-ethoxybenzene

1,3-bis(4-methoxycarbonylphenyl)-5-hydroxybenzene (2.37 g, 6.54 mmol) and dried potassium carbonate (1.72 g, 12.43 mmol) were suspended in acetone (100 mL) and heated under reflux for

2 hours, before iodoethane (0.60 mL, 7.50 mmol) was added and the suspension was stirred under reflux for a further 3 days. Upon cooling to room temperature, the acetone was removed under reduced pressure, before the resulting solid was suspended in dichloromethane (60 mL) and distilled water (60 mL). The solution was extracted with dichloromethane (3 x 60 mL) and the combined organic fractions were washed with brine (60 mL), before being dried over anhydrous magnesium sulfate. The dichloromethane was removed under reduced pressure and the beige solid was dried in air (2.38 g, 6.10 mmol, 93% yield). ^1H (400 MHz, d_6 -DMSO) δ_{H} 8.05 (4H, m), 7.95 (4H, m), 7.62 (1H, t, $J=3.2$ Hz), 7.31 (2H, d, $J=1.6$ Hz), (4.22, 2H, q, $J=20.8$ Hz), 3.89 (6H, s), 1.39 (3H, t, $J=14.0$ Hz).

1,3-bis(4-carboxyphenyl)-5-ethoxybenzene

Potassium hydroxide (1.71 g, 30.50 mmol) was dissolved in methanol (120 mL) and 1,3-bis(4-methoxycarbonylphenyl)-5-ethoxybenzene (2.38 g, 6.10 mmol) was suspended in the solution. The suspension was heated at 80 °C for 18 hours. The resulting solution was cooled to room temperature and 2M hydrochloric acid (120 mL) was added to produce a white precipitate. The precipitate was washed copiously with water until the washings reached pH 5-6, before being dried in air (1.94 g, 5.35 mmol, 88% yield). ^1H (400 MHz, d_6 -DMSO) δ_{H} 8.03 (4H, m), 7.93 (4H, m), 7.62 (1H, t, $J=3.2$ Hz), 7.31 (2H, d, $J=1.6$ Hz), 4.23 (2H, q, $J=20.8$ Hz), 1.40 (3H, t, $J=14.0$ Hz).

Preparation of Copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene

Copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene was synthesized by stirring 1,3-bis(carboxyphenyl)-5-ethoxybenzene (0.27 g, 0.75 mmol) in ethanol (3.51 mL, 60.00 mmol) and DMF (0.75 mL, 9.69 mmol) for 10 minutes at ambient temperature. A separate solution of copper acetate monohydrate (0.15 g, 0.75 mmol) in distilled water (2.37 mL, 131.25 mmol) was then added and the solution was stirred for a further 10 minutes at ambient temperature. The solution was sealed in a Teflon-lined stainless-steel autoclave and was heated at 110 °C for 5 days. The solution was filtered upon cooling and the resulting blue crystalline solid was washed with distilled water and ethanol, before being dried in air (0.22 g, 0.25 mmol, 33% yield).

Soxhlet extraction was performed on the solid to remove residual DMF in the sample, where the sample was placed inside a Soxhlet extraction apparatus for 5 days, using ethanol as the exchange solvent. After recovery, the solid was dried in an oven overnight.

Characterization Methods

Single Crystal X-ray Diffraction

Single crystals of copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene(DMF) were initially collected at 173 K on a Rigaku MM-007HF diffractometer with Cu K α radiation source ($\lambda=1.54184$ Å) and a RigakuXtaLAB P100K detector. Absorption corrections were applied using multi-scan methods in CrysAlisPro 1.171.38.46.² The structure solution was obtained using SHELXT³ and refined by full matrix on F^2 using SHELXL⁴ within the Olex2⁵ suite. Ethyl chains were disordered over two crystallographic sites, each of which was 50% occupied. All full occupancy non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Aromatic and aliphatic hydrogen atoms were included at their geometrically calculated positions and hydrogen atoms belonging to coordinated water molecules were not modelled. A half-occupancy DMF molecule bound to the copper paddlewheel unit was modelled, and other residual disordered solvent molecules were masked during the refinement. After Soxhlet extraction, single crystals of copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene were collected at 125 K on a Rigaku MM-007HF diffractometer with Cu K α radiation source ($\lambda=1.54184$ Å) and a RigakuXtaLAB P200K detector. The molecule was refined as before, including masking of residual disordered solvent molecules.

Powder X-ray Diffraction

Powder X-ray diffraction was collected on a STOE STADIP primary beam monochromator diffractometer using $\text{CuK}\alpha_1$ radiation in glass capillaries at 298 K. Structure refinement was performed using the GSAS analysis software⁶ and the EXPGUI graphical user interface.⁷

Thermal Gravimetric Analysis

Thermal gravimetric analysis was performed in air, using a Stanton Redcroft STA-780 thermal analyzer from ambient temperature to 750 °C, with a 10 °C per minute heating rate.

Infrared Spectroscopy

Infrared spectra were collected on a Shimadzu IRAffinity-1S spectrometer.

Powder X-ray Diffraction Refinement Data

Figure S1. Comparison of bulk material with the single crystal phase by a whole-pattern (Le Bail type) refinement of the unit cell against the X-ray diffraction data to confirm sample purity. The blue tick marks represent peaks from the copper oxide (Cu_2O) impurity.

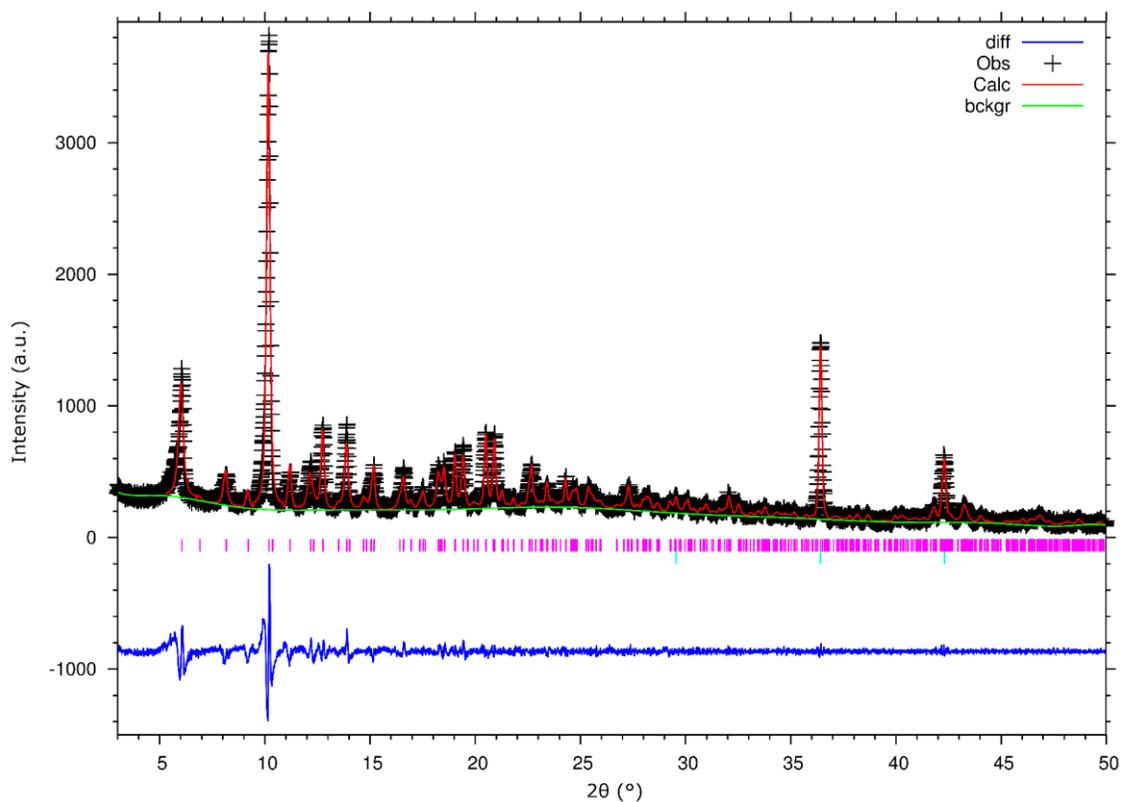


Table S1. Crystallographic parameters from the Le Bail powder diffraction refinement of copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene and comparison with single crystal data.

	Powder	Single Crystal
Temperature	298 K	125 K
Unit cell dimensions	a = 15.7078(13) Å	a = 15.5652(7) Å
	b = 21.5154(26) Å	b = 21.2718(15) Å
	c = 28.925(4) Å	c = 29.0545(9) Å
Unit cell angles	$\alpha = 90^\circ$	$\alpha = 90^\circ$
	$\beta = 90^\circ$	$\beta = 90^\circ$
	$\gamma = 90^\circ$	$\gamma = 90^\circ$
Space Group	<i>Ibam</i>	<i>Ibam</i>
wRp	0.0963	-
Rp	0.0704	-

Full Crystallographic Data

Table S2. Full crystallographic details from the structure determination of copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene(DMF) and copper-3,5-bis(4-carboxyphenyl)-5-ethoxybenzene.

Identification code	Copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene(DMF)	Copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene
Empirical formula	C _{45.5} H _{35.5} Cu ₂ N _{0.5} O ₁₂	C ₄₄ H ₃₂ Cu ₂ O ₁₂
Formula weight	908.32 g mol ⁻¹	879.77 g mol ⁻¹
Temperature	173 K	125 K
Wavelength	1.54184 Å	1.54184 Å
Crystal system, space group	Orthorhombic, <i>Ibam</i>	Orthorhombic, <i>Ibam</i>
Unit cell dimensions	a = 15.7246(5) Å b = 20.1588(8) Å c = 28.9989(9) Å	a = 15.5652(7) Å b = 21.2718(15) Å c = 29.0545(9) Å
Volume	9192.3(5) Å ³	9619.9(9) Å ³
Z	8	8
Calculated density	1.313 g cm ⁻³	1.215 g cm ⁻³
Absorption coefficient	1.635 mm ⁻¹	1.544 mm ⁻¹
F(000)	3728.0	3600.0
GooF on F²	1.049	1.000
Crystal size	0.03 x 0.03 x 0.02 mm ³	0.04 x 0.04 x 0.02 mm ³
Theta range for data collection	6.096 to 136.684°	6.084 to 151.536°
Reflections collected/unique	47728/4302 [R(int) = 0.1094]	54930/5051 [R(int) = 0.2107]
Final R indices (I>2σ(I))	R ₁ = 0.0510 wR ₂ = 0.1477	R ₁ = 0.0953 wR ₂ = 0.2672
Final R indices (all data)	R ₁ = 0.0717 wR ₂ = 0.1609	R ₁ = 0.1428 wR ₂ = 0.3092

Crystallographic Tables for Copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene(DMF)

Table S3. Selected bond lengths for copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene(DMF)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu01	Cu01 ¹	2.6188(13)	Cu02	Cu02 ⁴	2.6384(14)
Cu01	O2 ²	1.969(2)	Cu02	O3	1.953(3)
Cu01	O2 ¹	1.969(2)	Cu02	O3 ⁵	1.953(3)
Cu01	O1 ³	1.962(2)	Cu02	O4 ⁴	1.956(3)
Cu01	O1	1.962(2)	Cu02	O4 ⁶	1.956(3)
Cu01	O1W	2.191(4)	Cu02	O5	2.165(5)

Symmetry transformations used to generate equivalent atoms:



Table S4. Selected bond angles for copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene(DMF)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2 ¹	Cu01	Cu01 ²	81.72(8)	O3 ⁴	Cu02	Cu02 ⁵	82.81(9)
O2 ²	Cu01	Cu01 ²	81.72(8)	O3	Cu02	Cu02 ⁵	82.81(9)
O2 ²	Cu01	O2 ¹	91.65(16)	O3	Cu02	O3 ⁴	88.23(19)
O2 ²	Cu01	O1W	91.90(12)	O3	Cu02	O4 ⁵	168.20(13)
O2 ¹	Cu01	O1W	91.90(12)	O3 ⁴	Cu02	O4 ⁵	91.29(14)
O1 ³	Cu01	Cu01 ²	87.16(7)	O3	Cu02	O4 ⁶	91.29(14)
O1	Cu01	Cu01 ²	87.16(7)	O3 ⁴	Cu02	O4 ⁶	168.20(13)
O1	Cu01	O2 ¹	87.27(11)	O3 ⁴	Cu02	O5	94.85(13)
O1	Cu01	O2 ²	168.87(11)	O3	Cu02	O5	94.85(13)
O1 ³	Cu01	O2 ²	87.27(11)	O4 ⁶	Cu02	Cu02 ⁵	85.43(9)
O1 ³	Cu01	O2 ¹	168.87(11)	O4 ⁵	Cu02	Cu02 ⁵	85.43(9)
O1	Cu01	O1 ³	91.66(16)	O4 ⁶	Cu02	O4 ⁵	86.8(2)
O1	Cu01	O1W	99.20(11)	O4 ⁵	Cu02	O5	96.94(14)
O1 ³	Cu01	O1W	99.20(11)	O4 ⁶	Cu02	O5	96.94(14)
O1W	Cu01	Cu01 ²	170.81(13)	O5	Cu02	Cu02 ⁵	176.72(15)

Symmetry transformations used to generate equivalent atoms:

¹1-X,1-Y,+Z ²1-X,1-Y,2-Z ³+X,+Y,2-Z ⁴+X,+Y,1-Z ⁵2-X,1-Y,1-Z ⁶2-X,1-Y,+Z

Crystallographic Tables for Copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene

Table S5. Selected bond lengths for copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu01	Cu01 ¹	2.635(2)	Cu02	Cu02 ⁴	2.626(3)
Cu01	O3	1.963(4)	Cu02	O1 ⁵	1.949(5)
Cu01	O3 ²	1.963(4)	Cu02	O1 ⁴	1.949(5)
Cu01	O4 ³	1.972(5)	Cu02	O2 ⁶	1.952(6)
Cu01	O4 ¹	1.972(5)	Cu02	O2	1.952(6)
Cu01	O2W	2.176(6)	Cu02	O1W	2.147(10)

Symmetry transformations used to generate equivalent atoms:

¹1-X,1-Y,1-Z ²+X,+Y,1-Z ³1-X,1-Y,+Z ⁴2-X,1-Y,-Z ⁵2-X,1-Y,+Z ⁶+X,+Y,-Z

Table S6. Selected bond angles for copper-1,3-bis(4-carboxyphenyl)-5-ethoxybenzene

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Cu01	Cu01 ¹	86.44(14)	O1 ⁴	Cu02	Cu02 ⁵	83.85(17)
O3 ²	Cu01	Cu01 ¹	86.44(14)	O1 ⁵	Cu02	Cu02 ⁵	83.85(17)
O3 ²	Cu01	O3	91.0(3)	O1 ⁴	Cu02	O1 ⁵	89.0(4)
O3 ²	Cu01	O4 ³	168.62(19)	O1 ⁴	Cu02	O2 ⁶	167.6(3)
O3	Cu01	O4 ¹	168.62(19)	O1 ⁴	Cu02	O2	90.6(3)
O3 ²	Cu01	O4 ¹	87.5(2)	O1 ⁵	Cu02	O2 ⁶	90.6(3)
O3	Cu01	O4 ³	87.5(2)	O1 ⁵	Cu02	O2	167.6(3)
O3	Cu01	O2W	97.1(2)	O1 ⁵	Cu02	O1W	94.9(3)
O3 ²	Cu01	O2W	97.1(2)	O1 ⁴	Cu02	O1W	94.9(3)
O4 ³	Cu01	Cu01 ¹	82.21(14)	O2	Cu02	Cu02 ⁵	83.82(19)
O4 ¹	Cu01	Cu01 ¹	82.21(14)	O2 ⁶	Cu02	Cu02 ⁵	83.82(19)
O4 ¹	Cu01	O4 ³	91.7(3)	O2	Cu02	O2 ⁶	87.2(4)
O4 ³	Cu01	O2W	94.3(2)	O2 ⁶	Cu02	O1W	97.5(3)
O4 ¹	Cu01	O2W	94.3(2)	O2	Cu02	O1W	97.5(3)
O2W	Cu01	Cu01 ¹	175.0(2)	O1W	Cu02	Cu02 ⁵	178.2(3)

Symmetry transformations used to generate equivalent atoms:

$^11-X,1-Y,1-Z$ $^2+X,+Y,1-Z$ $^31-X,1-Y,+Z$ $^42-X,1-Y,+Z$ $^52-X,1-Y,-Z$ $^6+X,+Y,-Z$

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