Electronic Supplementary Material (ESI) for Dalton Transactions

Ultrasound-driven preparation and pair distribution function-assisted structure solution of a copper-based coordination polymer

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Supplementary Information

Total Scattering Data Collection.

Total scattering data were collected at beamline 11-ID-B at the Advanced Photon Source, Argonne National Laboratory, IL, USA. A wavelength of 0.21280 Å was used for all experiments with a frame exposure time of 5 minutes. All data were recorded using a Perkin Elmer amorphous silicon area detector.[1] The sample-to-detector distance was determined as 151.338 mm by the use of a CeO_2 powder standard. The program FIT2D was used to integrate data.[2] An empty Kapton capillary was run for the same counting time in order to measure the air and Kapton contributions to the scattering intensity. These contributions were removed in data processing in PDFgetX2. Other standard corrections were applied to the total scattering data, and G(r) was obtained by the Fourier Transform of the corrected total scattering data using the program PDFGetX2.[3] Gaussian functions are fitted to peaks of interest in the PDF produced using the program Fityk[4].

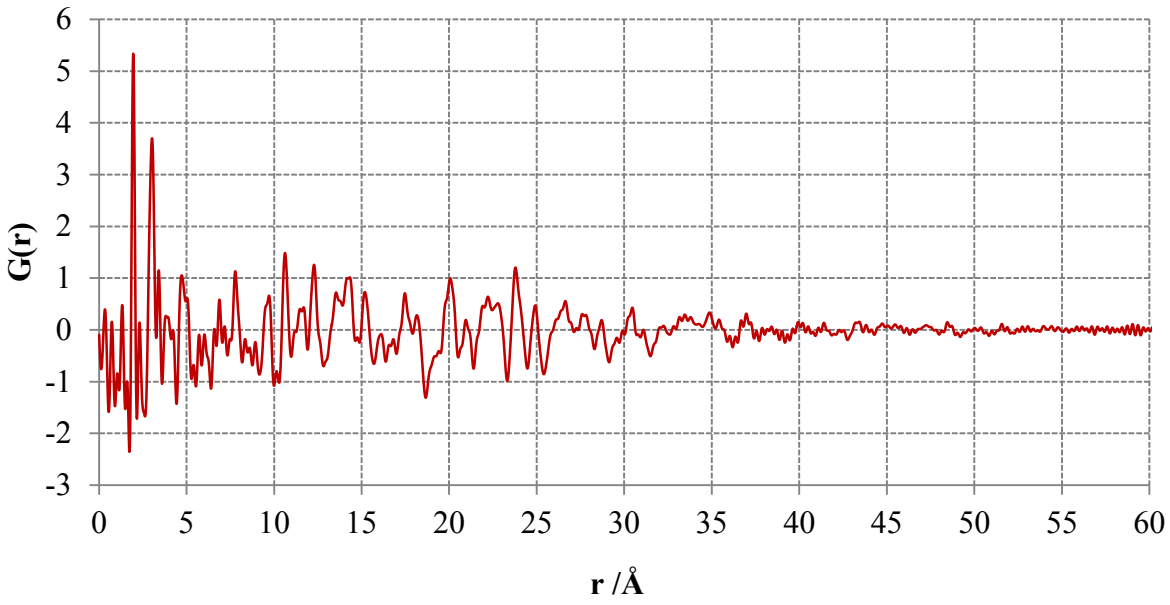

Figure S1. The PDF data for STAM-2 collected out to 60 Å. Data ends at about 50 Å.

Calculation of partial PDFs

Partial PDFs were calculated using PDFGui from the models from single crystal data. U_{11}, U_{22} and U_{33} were set to 0.005 Å^2 and cross diagonal terms were set to zero. A value for Q_{damp} was estimated using any data refinement which had been done, otherwise set to 0.08. The value for Q_{max} was taken from the data set being considered, otherwise set to 22 Å^{-1}.

Refinement against PDF data

Refinement of structural models against PDF data was performed in PDFFIT2 with PDFGui. A starting value for Q_{damp} of 0.08 was chosen for all refinements. S_{ratio} was set to a starting value of 0.5, with a cut-off distance, r_{cut}, of 3.6 Å. This value is the approximate M-M distance in the sample and allows the correlated movement of the secondary building blocks in the frameworks to be modelled. The inclusion of solvent molecules means that the atomic density, ρ_0, is not known, therefore the dataset scale parameter is refined. A starting value for the scale factor for the model was set by observational comparison of the two biggest peaks in the model and experimental PDFs.

The model from Rietveld refinement of PXRD data was refined against the PDF data set using the program PDFGui. Refinements were done in the r-range of 1.0 to 15.0 Å. The material was constrained to have P-1 symmetry as indicated by the PXRD data and the positions of all atoms were constrained by this symmetry. The thermal parameters were restrained by atom type; five distinct

thermal parameter environments were defined: (1) copper atoms, (2) carboxylate oxygen atoms used in framework bonding to the Cu-atoms, (3) the oxygens of the ester group, (4) the ester group thermal carbon, (5) all other carbon atoms. All atoms were refined isotropically, with $U_{11} = U_{22} = U_{33}$ and set to a starting value of 0.005 $Å^3$ and the cross diagonal terms U_{12}, U_{23} and U_{13} set to zero.

The best fit was achieved by refining the copper-positions and the oxygen positions early in the refinement until there was no appreciable change in the value of R_w with further refinement cycles. Unit cell parameters were added to the refinement and the parameters refined until stable. Thermal parameters were added to the refinement, although some of these values became unreasonably large and so were fixed to 0.06 $Å^3$. The scale factor and Q_{damp} were refined late on in the process and showed relatively little change or improvement to the refinement. The final R_w-value obtained was 31.2563%.

When the positions of the carbons atoms were allowed to refine in an unrestrained manner, the fit of the model to the data improved significantly. Unfortunately, because carbon contributed relatively little to the overall PDF, the model which was produced by this process did not keep the carbon positions in a sensible regime; the free refinement led to significant distortion of the benzene ring, and in some cases carbon atoms would move large distances into the channels of the material. In order to keep the benzene ring unit intact, it was possible to relate the position refinement parameters to each other. The refinement parameters for the C3 x, y and z positions were set as @154, @155 and @156. The refinement parameters for the other carbon atoms of the benzene ring were set relative to this position using known estimated bond distances.

Refinement using this rigid body improved the fit with comparison to having the carbon position unrefined (Table 1). The final R_w value obtained by refinement with restrained carbon atoms was 28.3122%. The R-factor obtained was not as good as allowing the carbon positions to refine freely, but the model produced was chemically sensible and so the refinement is considered superior to the previous model. The resulting structure made more chemical sense; the SBU and Cu-O framework held together well. The benzene ring was flat, though showed some slight distortion. The carboxylate group para- to the carboxylate group which bridged between Cu-atoms, which was not restrained as part of the rigid body, was twisted out of the plane. Bond lengths and angles are shown in Table 3.

Table 1: Refinement details for the refinement without carbon position refinement and restrained carbon position refinement. The esds on the numbers from the PDF analysis are undetermined as esds on the individual data points are unknown.

	Refinement with restrained carbon positions	Refinement with no carbon positions refined	Model from powder diffraction
a /Å	11.4332	11.425	11.2527 (3)
b /Å	10.5687	10.5839	10.6146 (3)
c /Å	5.6184	5.6293	5.74709 (2)
α /^{o}	85.18	85.3075	86.572 (2)
β /^{o}	96.248	96.1454	97.710 (2)
γ /^{o}	109.0506	109.164	106.834 (2)
r_w	28.3122	31.2563	

Table 2: Cu-O bond lengths and angles of the PDF refined structure of STAM-2. The esds on the numbers from the PDF analysis are undetermined as esds on the individual data points are unknown. Errors on PXRD values are not given due to the level of restraint required for the refinement to converge.

Atom 1	Atom 2	Distance from PXRD model /Å	Distance from PDF model /Å
Cu1	O2	1.8035	1.9493
	O1	1.8035	1.9493
	O13	1.9469	1.9836
	O14	1.9469	1.9836
Cu2	O6	2.2522	1.9375
	O3	1.8383	1.9592
	O13	1.8382	2.0701
	O15	2.3313	2.3498
Cu3	O5	2.2522	1.9375
	O4	1.8383	1.9592
	O14	1.8382	2.0701
	O16	2.3313	2.3498

Table3: Atomic positions for the PDF model of STAM-2.

	x	y	z	U_{iso}*/U_{eq}
Cu1	0	0	0	0.02495*
Cu2	0.028 (2)	0.153 (1)	0.512 (3)	0.02214*
Cu3	0.972 (2)	0.847 (1)	0.480 (3)	0.02214*
O1	0.888 (3)	0.103 (3)	0.900 (4)	0.00143*
O2	0.112 (3)	0.897 (3)	0.101 (4)	0.00143*
O3	0.982 (3)	0.297 (3)	0.331 (5)	0.00143*
O4	0.017 (3)	0.703 (3)	0.669 (5)	0.00143*
O5	0.911 (3)	0.685 (3)	0.303 (5)	0.00197*
O6	0.088 (3)	0.315 (3)	0.697 (5)	0.00197*
O7	0.658 (3)	0.608 (3)	0.068 (5)	0.00197*
O8	0.342 (3)	0.392 (3)	0.932 (5)	0.00197*
O9	0.546 (3)	0.149 (3)	0.277 (5)	0.00197*
O10	0.454 (3)	0.851 (3)	0.723 (5)	0.00197*
O11	0.517 (2)	0.311 (3)	0.352 (7)	0.00197*
O12	0.483 (2)	0.689 (3)	0.648 (7)	0.00025*
O13	0.125 (2)	0.058 (4)	0.761 (5)	0.00025*
O14	0.875 (2)	0.943 (3)	0.239 (5)	0.00871*
O15	0.201 (3)	0.179 (6)	0.307 (7)	0.00871*
O16	0.799 (3)	0.821 (6)	0.693 (7)	0.00871*
O17	0.319 (3)	0.188 (4)	0.688 (7)	0.00600*
O18	0.681 (3)	0.812 (4)	0.312 (7)	0.00600*
C1	0.893 (3)	0.208 (3)	0.039 (6)	0.06529*
C2	0.107 (3)	0.792 (3)	0.961 (6)	0.06529*
C3	0.817 (3)	0.280 (3)	0.923 (6)	0.02990*
C4	0.183 (3)	0.720 (3)	0.077 (6)	0.02990*
C5	0.830 (3)	0.403 (3)	0.055 (6)	0.02990*
C6	0.170 (3)	0.597 (3)	0.945 (6)	0.02990*
C7	0.757 (3)	0.471 (3)	0.956 (6)	0.02990*
C8	0.243 (3)	0.529 (3)	0.044 (6)	0.02990*
C9	0.672 (3)	0.416 (3)	0.722 (6)	0.02990*
C10	0.328 (3)	0.584 (3)	0.278 (6)	0.02990*
C11	0.663 (3)	0.293 (3)	0.594 (6)	0.02990*
C12	0.337 (3)	0.707 (3)	0.407 (6)	0.02990*

C13	0.734 (3)	0.225 (3)	0.690 (6)	0.02990*
C14	0.266 (3)	0.775 (3)	0.310 (6)	0.02990*
C15	0.772 (3)	0.606 (3)	0.099 (6)	0.01335*
C16	0.228 (3)	0.394 (3)	0.901 (6)	0.01335*
C17	0.570 (3)	0.233 (3)	0.350 (6)	0.03130*
C18	0.430 (3)	0.768 (3)	0.650 (6)	0.03130*
C19	0.506 (3)	0.287 (3)	0.132 (6)	0.06747*
C20	0.494 (3)	0.713 (3)	0.868 (6)	0.06747*

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