

catena-Poly[[bis(3-carboxy-5-nitrobenzoato- κO^1)copper(II)]- μ -1,3-di-4-pyridylpropane- $\kappa^2 N:N'$]

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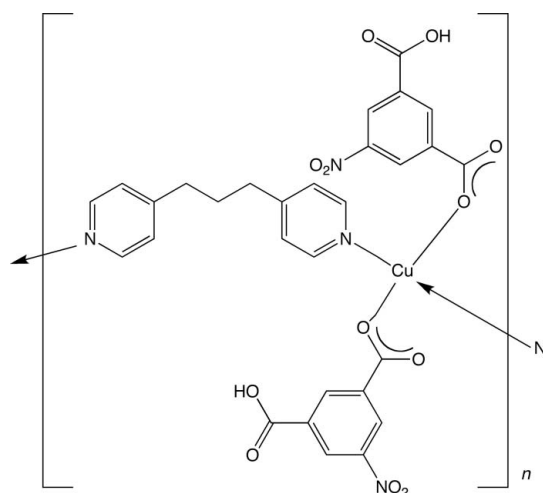
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.041; wR factor = 0.112; data-to-parameter ratio = 11.3.

In the title compound, $[Cu(C_8H_4NO_6)_2(C_{13}H_{14}N_2)]_n$, the square-planar coordinated Cu^{II} ion lies on an inversion centre and is coordinated by two protonated 5-nitroisophthalate ligands. The Cu^{II} ions are linked into a one-dimensional coordination polymer by tethering 1,3-di-4-pyridylpropane ligands, whose central methylene C atoms are situated on twofold rotation axes. The chains are oriented parallel to the c axis, and stack into a supramolecular three-dimensional structure through $O-H \cdots O$ hydrogen-bonding interactions.

Related literature

For some recent divalent copper dicarboxylate coordination polymers containing 1,3-di-4-pyridylpropane, see: Wang *et al.* (2009).



Experimental

Crystal data

$[Cu(C_8H_4NO_6)_2(C_{13}H_{14}N_2)]$
 $M_r = 682.05$
 Monoclinic, $C2/c$
 $a = 25.2976$ (8) Å
 $b = 5.3702$ (2) Å
 $c = 21.3122$ (7) Å
 $\beta = 115.865$ (2)°

$V = 2605.29$ (15) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.92$ mm⁻¹
 $T = 173$ K
 $0.22 \times 0.22 \times 0.11$ mm

Data collection

Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{min} = 0.821$, $T_{max} = 0.905$

10349 measured reflections
 2401 independent reflections
 2087 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.112$
 $S = 1.08$
 2401 reflections
 213 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 1.10$ e Å⁻³
 $\Delta\rho_{min} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H3A \cdots O2^i$	0.85 (4)	1.86 (2)	2.668 (3)	158 (4)

Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CrystalMaker (Palmer, 2007); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2526).

References

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 Wang, G. R., Li, Z. G., Jia, H. Q., Hu, N. H. & Xu, J. W. (2009). CrystEngComm, 11, 292–297.

supplementary materials

Acta Cryst. (2009). E65, m1082 [doi:10.1107/S1600536809031821]

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Comment

The title compound, (I), was prepared by the hydrothermal reaction of copper nitrate, 5-nitroisophthalic acid (nip) and 1,3-di-4-pyridylpropane (dpp). Its asymmetric unit contains a copper atom on an inversion centre, one singly protonated nip (Hnip) ligand, and one-half of a dpp ligand, whose central methylene carbon atom is situated on a 2-fold axis. Operation of the inversion centre at Cu reveals a square planar coordination environment with *trans* O atom donors from protonated nip ligands and *trans* N donors from two dpp ligands (Fig. 1). The Hnip ligands are bound to Cu in a simple monodentate fashion *via* an O atom belonging to the non-protonated carboxylate terminus.

Operation of the 2-fold rotation axes indicates that dpp ligands connect neighboring Cu atoms into a one-dimensional [Cu(Hnip)₂(dpp)]_n coordination polymer chain (Fig. 2), which is oriented parallel to the *c*-axis. The methylene groups within the dpp ligands adopt a *gauche-gauche* conformation, providing a Cu...Cu separation of 10.656 (4) Å. Neighboring chains aggregate by hydrogen-bonding mechanisms (Table 1) involving the hydroxyl groups of the protonated Hnip ligands and unligated O atoms of the monodentate Hnip carboxylate groups, thus forming the three-dimensional supramolecular structure (Fig. 3).

Experimental

All starting materials were obtained commercially. A mixture of copper nitrate trihydrate (90 mg, 0.37 mmol), 5-nitroisophthalic acid (79 mg, 0.37 mmol), 1,3-di-4-pyridylpropane (73 mg, 0.37 mmol) and 10.0 g water (550 mmol) was placed into a 23 ml Teflon-lined Parr Acid Digestion bomb, which was then heated under autogenous pressure at 363 K for 24 h. Blue blocks of (I) were obtained along with a light-blue amorphous powder.

Refinement

All H atoms bound to C atoms were placed in calculated positions, with C—H = 0.95 - 0.99 Å, and refined in riding mode with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. The H atom bound to the protonated carboxylate O atom was found in a difference Fourier map, restrained with O—H = 0.89 Å, and refined with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{O})$.

The maximum and minimum residual electron density peaks of 1.10 and -0.31 e Å⁻³, respectively, were located 1.08 Å and 0.68 Å from the C14 and C17 atoms, respectively.

Figures

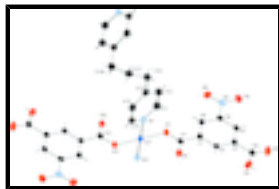


Fig. 1. The coordination environment of (I), showing 50% probability ellipsoids and atom numbering scheme. Hydrogen atom positions are shown as grey sticks. Color codes: dark blue Cu, light blue N, orange O, black C. Symmetry codes: (i) $-x, -y, -z$ (ii) $-x, y, -z + 1/2$.

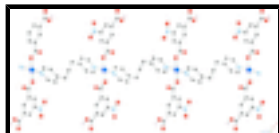


Fig. 2. A view of the coordination polymer chain motif in (I).

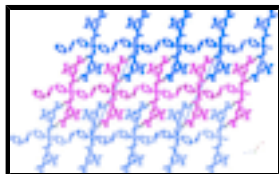


Fig. 3. Stacking diagram for (I), viewed down the b axis. Hydrogen bonding contacts are indicated as dashed bars.

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Crystal data

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$M_r = 682.05$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 25.2976\ (8)\ \text{\AA}$

$b = 5.3702\ (2)\ \text{\AA}$

$c = 21.3122\ (7)\ \text{\AA}$

$\beta = 115.865\ (2)^\circ$

$V = 2605.29\ (15)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1396$

$D_x = 1.739\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 10349 reflections

$\theta = 1.8\text{--}25.4^\circ$

$\mu = 0.92\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Block, blue

$0.22 \times 0.22 \times 0.11\ \text{mm}$

Data collection

Bruker APEXII
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173\ \text{K}$

ω and φ scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.821$, $T_{\max} = 0.905$

10349 measured reflections

2401 independent reflections

2087 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 25.4^\circ$

$\theta_{\min} = 1.8^\circ$

$h = -30 \rightarrow 28$

$k = -6 \rightarrow 6$

$l = -24 \rightarrow 25$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.112$	$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 8.8582P]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
2401 reflections	$(\Delta/\sigma)_{\max} < 0.001$
213 parameters	$\Delta\rho_{\max} = 1.10 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.0000	0.0000	0.0000	0.01865 (18)	
O1	0.07835 (8)	-0.1413 (4)	0.04676 (10)	0.0209 (5)	
O2	0.11395 (9)	0.1584 (4)	0.00388 (11)	0.0273 (5)	
O3	0.31946 (10)	0.1103 (5)	0.04659 (13)	0.0332 (6)	
H3A	0.3473 (12)	0.154 (7)	0.0365 (19)	0.040*	
O4	0.37815 (10)	-0.2063 (5)	0.10363 (13)	0.0374 (6)	
O5	0.30010 (10)	-0.7828 (4)	0.22279 (12)	0.0325 (6)	
O6	0.20769 (10)	-0.7829 (4)	0.19827 (11)	0.0279 (5)	
N1	0.01902 (10)	0.2420 (5)	0.07966 (12)	0.0207 (5)	
N2	0.25020 (11)	-0.6974 (5)	0.19249 (12)	0.0222 (6)	
C1	0.17873 (12)	-0.1639 (6)	0.07286 (14)	0.0180 (6)	
C2	0.22615 (12)	-0.0740 (6)	0.06286 (14)	0.0178 (6)	
H2	0.2213	0.0694	0.0348	0.021*	
C3	0.28055 (12)	-0.1922 (6)	0.09360 (14)	0.0189 (6)	
C4	0.28838 (12)	-0.3992 (6)	0.13549 (14)	0.0187 (6)	
H4	0.3252	-0.4823	0.1562	0.022*	

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C5	0.24125 (13)	-0.4817 (5)	0.14633 (14)	0.0187 (6)	
C6	0.18627 (12)	-0.3712 (6)	0.11546 (14)	0.0178 (6)	
H6	0.1545	-0.4349	0.1231	0.021*	
C7	0.11985 (12)	-0.0359 (6)	0.03800 (14)	0.0190 (6)	
C8	0.33175 (12)	-0.0985 (6)	0.08267 (15)	0.0230 (7)	
C11	0.06442 (14)	0.2091 (7)	0.14297 (17)	0.0299 (7)	
H11	0.0897	0.0709	0.1492	0.036*	
C12	0.07641 (14)	0.3641 (7)	0.19921 (16)	0.0300 (8)	
H12	0.1088	0.3305	0.2428	0.036*	
C13	0.04037 (13)	0.5719 (6)	0.19170 (16)	0.0255 (7)	
C14	-0.00464 (13)	0.6150 (6)	0.12500 (16)	0.0270 (7)	
H14	-0.0290	0.7579	0.1164	0.032*	
C15	-0.01359 (13)	0.4504 (6)	0.07206 (16)	0.0265 (7)	
H15	-0.0445	0.4844	0.0274	0.032*	
C16	0.05196 (14)	0.7391 (7)	0.25328 (16)	0.0297 (7)	
H16A	0.0841	0.8549	0.2586	0.036*	
H16B	0.0662	0.6344	0.2957	0.036*	
C17	0.0000	0.8934 (9)	0.2500	0.0293 (10)	
H17A	-0.0137	1.0023	0.2084	0.035*	0.50
H17B	0.0137	1.0023	0.2916	0.035*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0127 (3)	0.0208 (3)	0.0223 (3)	0.0016 (2)	0.0075 (2)	-0.0009 (2)
O1	0.0152 (9)	0.0220 (12)	0.0241 (10)	0.0019 (9)	0.0072 (8)	0.0005 (9)
O2	0.0225 (10)	0.0269 (13)	0.0338 (12)	0.0092 (10)	0.0135 (9)	0.0115 (10)
O3	0.0267 (12)	0.0337 (14)	0.0471 (14)	0.0025 (11)	0.0235 (11)	0.0139 (12)
O4	0.0198 (11)	0.0438 (15)	0.0491 (14)	0.0036 (11)	0.0153 (10)	0.0089 (12)
O5	0.0296 (12)	0.0306 (14)	0.0346 (12)	0.0131 (10)	0.0116 (10)	0.0145 (11)
O6	0.0330 (12)	0.0236 (12)	0.0294 (11)	-0.0015 (10)	0.0158 (10)	0.0040 (10)
N1	0.0171 (12)	0.0233 (14)	0.0213 (12)	0.0037 (11)	0.0079 (10)	0.0006 (11)
N2	0.0278 (14)	0.0191 (14)	0.0196 (12)	0.0036 (11)	0.0103 (11)	0.0000 (10)
C1	0.0160 (13)	0.0193 (15)	0.0174 (13)	0.0025 (12)	0.0061 (11)	-0.0026 (12)
C2	0.0197 (14)	0.0177 (15)	0.0157 (13)	0.0016 (12)	0.0075 (11)	0.0016 (11)
C3	0.0177 (14)	0.0212 (16)	0.0172 (13)	0.0008 (12)	0.0071 (11)	-0.0022 (12)
C4	0.0152 (13)	0.0203 (15)	0.0173 (13)	0.0032 (12)	0.0039 (11)	-0.0017 (12)
C5	0.0223 (14)	0.0176 (15)	0.0139 (13)	0.0015 (12)	0.0059 (11)	0.0002 (12)
C6	0.0161 (13)	0.0194 (16)	0.0173 (13)	-0.0022 (12)	0.0066 (11)	-0.0038 (12)
C7	0.0169 (14)	0.0216 (17)	0.0158 (13)	0.0018 (12)	0.0046 (11)	-0.0030 (12)
C8	0.0175 (14)	0.0279 (17)	0.0222 (15)	-0.0001 (13)	0.0072 (12)	-0.0001 (13)
C11	0.0274 (16)	0.0300 (19)	0.0332 (17)	0.0041 (14)	0.0142 (14)	0.0028 (15)
C12	0.0304 (17)	0.032 (2)	0.0257 (16)	-0.0019 (15)	0.0105 (13)	0.0022 (14)
C13	0.0227 (15)	0.0277 (18)	0.0283 (16)	-0.0034 (13)	0.0129 (13)	0.0012 (14)
C14	0.0239 (15)	0.0255 (18)	0.0327 (17)	-0.0002 (14)	0.0133 (13)	0.0007 (14)
C15	0.0217 (15)	0.0339 (19)	0.0236 (15)	0.0000 (14)	0.0098 (13)	0.0031 (14)
C16	0.0268 (17)	0.034 (2)	0.0261 (16)	-0.0030 (15)	0.0092 (13)	-0.0004 (14)
C17	0.033 (2)	0.030 (3)	0.025 (2)	0.000	0.0131 (19)	0.000

Geometric parameters (Å, °)

Cu1—O1	1.9427 (19)	C3—C8	1.500 (4)
Cu1—O1 ⁱ	1.9427 (19)	C4—C5	1.383 (4)
Cu1—N1 ⁱ	2.022 (2)	C4—H4	0.9500
Cu1—N1	2.022 (2)	C5—C6	1.386 (4)
O1—C7	1.276 (3)	C6—H6	0.9500
O2—C7	1.243 (4)	C11—C12	1.380 (5)
O3—C8	1.318 (4)	C11—H11	0.9500
O3—H3A	0.85 (4)	C12—C13	1.405 (5)
O4—C8	1.206 (4)	C12—H12	0.9500
O5—N2	1.229 (3)	C13—C14	1.399 (4)
O6—N2	1.224 (3)	C13—C16	1.510 (5)
N1—C11	1.349 (4)	C14—C15	1.372 (5)
N1—C15	1.358 (4)	C14—H14	0.9500
N2—C5	1.472 (4)	C15—H15	0.9500
C1—C2	1.393 (4)	C16—C17	1.529 (4)
C1—C6	1.396 (4)	C16—H16A	0.9900
C1—C7	1.509 (4)	C16—H16B	0.9900
C2—C3	1.392 (4)	C17—C16 ⁱⁱ	1.530 (4)
C2—H2	0.9500	C17—H17A	0.9900
C3—C4	1.385 (4)	C17—H17B	0.9900
O1—Cu1—O1 ⁱ	180.00 (11)	O2—C7—C1	120.7 (3)
O1—Cu1—N1 ⁱ	89.75 (9)	O1—C7—C1	115.1 (3)
O1 ⁱ —Cu1—N1 ⁱ	90.25 (9)	O4—C8—O3	124.6 (3)
O1—Cu1—N1	90.25 (9)	O4—C8—C3	123.3 (3)
O1 ⁱ —Cu1—N1	89.75 (9)	O3—C8—C3	112.1 (2)
N1 ⁱ —Cu1—N1	180.0	N1—C11—C12	124.0 (3)
C7—O1—Cu1	118.18 (18)	N1—C11—H11	118.0
C8—O3—H3A	112 (3)	C12—C11—H11	118.0
C11—N1—C15	115.8 (3)	C11—C12—C13	119.6 (3)
C11—N1—Cu1	122.9 (2)	C11—C12—H12	120.2
C15—N1—Cu1	121.3 (2)	C13—C12—H12	120.2
O6—N2—O5	123.6 (3)	C14—C13—C12	116.5 (3)
O6—N2—C5	118.5 (2)	C14—C13—C16	123.2 (3)
O5—N2—C5	117.9 (2)	C12—C13—C16	120.2 (3)
C2—C1—C6	119.6 (3)	C15—C14—C13	119.9 (3)
C2—C1—C7	119.9 (3)	C15—C14—H14	120.1
C6—C1—C7	120.6 (2)	C13—C14—H14	120.1
C3—C2—C1	120.7 (3)	N1—C15—C14	124.0 (3)
C3—C2—H2	119.7	N1—C15—H15	118.0
C1—C2—H2	119.7	C14—C15—H15	118.0
C4—C3—C2	120.2 (3)	C13—C16—C17	116.5 (2)
C4—C3—C8	118.6 (3)	C13—C16—H16A	108.2
C2—C3—C8	121.2 (3)	C17—C16—H16A	108.2
C5—C4—C3	118.3 (3)	C13—C16—H16B	108.2

supplementary materials

C5—C4—H4	120.9	C17—C16—H16B	108.2
C3—C4—H4	120.9	H16A—C16—H16B	107.3
C4—C5—C6	122.9 (3)	C16—C17—C16 ⁱⁱ	114.4 (4)
C4—C5—N2	118.1 (3)	C16—C17—H17A	108.7
C6—C5—N2	118.9 (3)	C16 ⁱⁱ —C17—H17A	108.7
C5—C6—C1	118.3 (3)	C16—C17—H17B	108.7
C5—C6—H6	120.9	C16 ⁱⁱ —C17—H17B	108.7
C1—C6—H6	120.9	H17A—C17—H17B	107.6
O2—C7—O1	124.2 (3)		
N1 ⁱ —Cu1—O1—C7	94.8 (2)	Cu1—O1—C7—C1	-176.93 (17)
N1—Cu1—O1—C7	-85.2 (2)	C2—C1—C7—O2	-4.5 (4)
O1—Cu1—N1—C11	-17.8 (2)	C6—C1—C7—O2	175.1 (3)
O1 ⁱ —Cu1—N1—C11	162.2 (2)	C2—C1—C7—O1	175.8 (2)
O1—Cu1—N1—C15	161.9 (2)	C6—C1—C7—O1	-4.6 (4)
O1 ⁱ —Cu1—N1—C15	-18.1 (2)	C4—C3—C8—O4	6.5 (5)
C6—C1—C2—C3	1.5 (4)	C2—C3—C8—O4	-173.9 (3)
C7—C1—C2—C3	-178.9 (3)	C4—C3—C8—O3	-174.8 (3)
C1—C2—C3—C4	-1.0 (4)	C2—C3—C8—O3	4.8 (4)
C1—C2—C3—C8	179.4 (3)	C15—N1—C11—C12	4.0 (5)
C2—C3—C4—C5	-0.8 (4)	Cu1—N1—C11—C12	-176.3 (2)
C8—C3—C4—C5	178.9 (3)	N1—C11—C12—C13	-0.7 (5)
C3—C4—C5—C6	2.1 (4)	C11—C12—C13—C14	-3.1 (5)
C3—C4—C5—N2	-178.3 (2)	C11—C12—C13—C16	178.3 (3)
O6—N2—C5—C4	-174.7 (3)	C12—C13—C14—C15	3.4 (5)
O5—N2—C5—C4	4.8 (4)	C16—C13—C14—C15	-178.0 (3)
O6—N2—C5—C6	5.0 (4)	C11—N1—C15—C14	-3.6 (4)
O5—N2—C5—C6	-175.5 (3)	Cu1—N1—C15—C14	176.7 (2)
C4—C5—C6—C1	-1.5 (4)	C13—C14—C15—N1	-0.1 (5)
N2—C5—C6—C1	178.8 (2)	C14—C13—C16—C17	24.3 (5)
C2—C1—C6—C5	-0.3 (4)	C12—C13—C16—C17	-157.2 (3)
C7—C1—C6—C5	-179.9 (2)	C13—C16—C17—C16 ⁱⁱ	62.0 (2)
Cu1—O1—C7—O2	3.4 (4)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A \cdots O2 ⁱⁱⁱ	0.85 (4)	1.86 (2)	2.668 (3)	158 (4)

Symmetry codes: (iii) $-x+1/2, -y+1/2, -z$.

Fig. 1

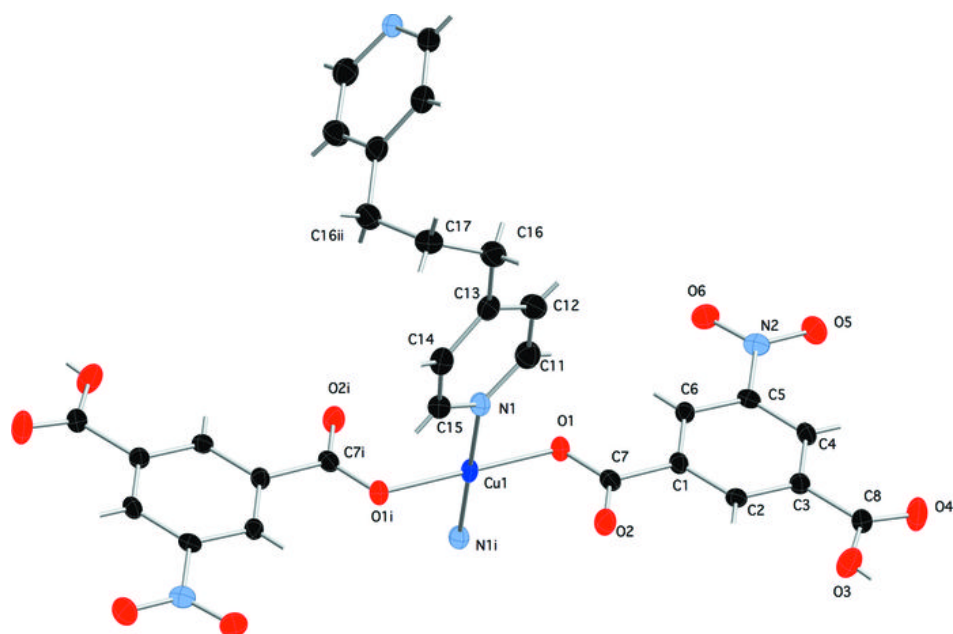


Fig. 2

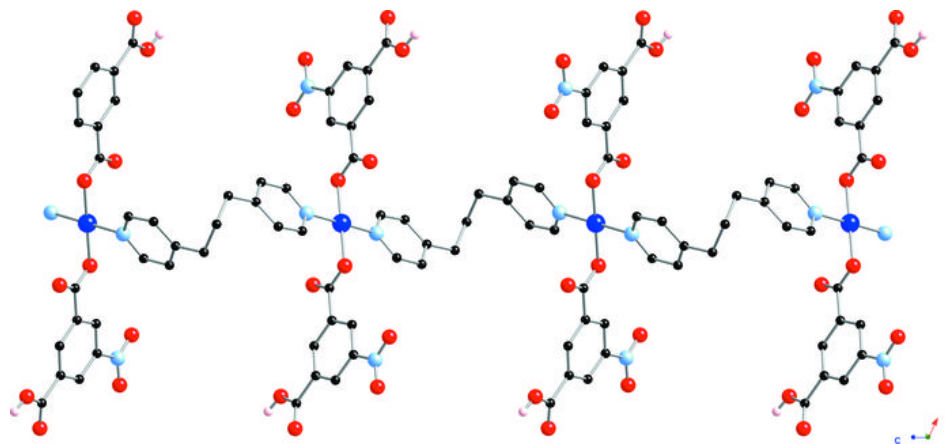


Fig. 3

