

Poly[propane-1,3-diammonium [cuprate(II)-bis(μ_2 -pyridine-2,3-dicarboxylato)] trihydrate]

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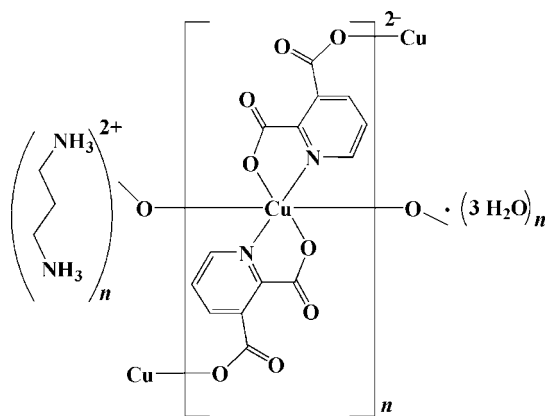
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; disorder in main residue; R factor = 0.063; wR factor = 0.176; data-to-parameter ratio = 12.4.

The title polymeric compound $\{(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)_2] \cdot 3\text{H}_2\text{O}\}_n$ or $\{(\text{pnH}_2)[\text{Cu}(\text{py-2,3-dc})_2] \cdot 3\text{H}_2\text{O}\}_n$ (pn is propane-1,3-diamine and py-2,3-dc is pyridine-2,3-dicarboxylic acid), was synthesized by reaction of copper(II) chloride dihydrate with a proton-transfer compound, propane-1,3-diammonium pyridine-2,3-dicarboxylate or $(\text{pnH}_2)(\text{py-2,3-dc})$, in aqueous solution. The anion is a six-coordinate complex (site symmetry $\bar{1}$), with a distorted octahedral geometry around Cu^{II} , consisting of two bidentate pyridine-2,3-dicarboxylate groups and two O atoms of bridging ligands from $(\text{py-2,3-dc})^{2-}$ fragments, which are located in *trans* positions. The $(\text{pnH}_2)^{2+}$ cation is disordered over two sites by the center of inversion. Intermolecular hydrogen bonds, $\pi-\pi$ [centroid-centroid distances of 3.539 (3) Å] and $\text{C}-\text{O} \cdots \pi$ stacking interactions [$\text{O} \cdots \text{Cg} = 3.240$ (5) Å; Cg is the center of the pyridine ring], connect the various components into a supramolecular structure.

Related literature

For related literature, see: Aghabozorg, Attar Gharamaleki, Ghadermazi *et al.* (2007); Aghabozorg, Attar Gharamaleki, Ghasemikhah *et al.* (2007); Aghabozorg, Daneshvar *et al.* (2007).



Experimental

Crystal data

$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)_2] \cdot 3\text{H}_2\text{O}$
 $M_r = 523.94$
 Triclinic, $P\bar{1}$
 $a = 6.6857$ (12) Å
 $b = 7.8251$ (18) Å
 $c = 9.9188$ (9) Å
 $\alpha = 82.6561$ (10)°
 $\beta = 84.0079$ (13)°

$\gamma = 71.9520$ (17)°
 $V = 488.20$ (15) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.19$ mm⁻¹
 $T = 100$ (2) K
 $0.21 \times 0.16 \times 0.15$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\text{min}} = 0.775$, $T_{\text{max}} = 0.836$

10997 measured reflections
 2348 independent reflections
 2310 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.176$
 $S = 1.01$
 2348 reflections

189 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.69$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.93$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.960 (4)	Cu1—O4 ⁱ	2.549 (4)
Cu1—N1	1.970 (4)		
O1 ⁱⁱ —Cu1—N1 ⁱⁱ	83.39 (16)	O4 ⁱ —Cu1—O4 ⁱⁱⁱ	180
O1—Cu1—N1 ⁱⁱ	96.61 (16)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2A \cdots O3	0.91	1.96	2.854 (1)	167
N2—H2B \cdots O2 ^{iv}	0.91	2.01	2.830 (1)	150
N3—H3B \cdots N2 ^v	0.91	1.56	2.283 (1)	134
N3—H3B \cdots O2W ^{vi}	0.91	1.95	2.852 (13)	174
N3—H3C \cdots O3 ^{iv}	0.91	2.42	3.041 (10)	126
N3—H3C \cdots O4 ^{iv}	0.91	2.08	2.991 (1)	174
N3—H3D \cdots O1WA ^{vii}	0.91	2.03	2.934 (1)	170
N3—H3D \cdots O1WB ^{viii}	0.91	2.51	3.407 (15)	170
O1WA—H3W \cdots O1 ^{viii}	0.89	2.11	2.764 (1)	130

metal-organic compounds

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1WA-H4W\cdots O3^i$	0.97	1.74	2.696 (1)	168
$O2W-H1W\cdots O1WA$	0.87	2.00	2.779 (15)	148
$O2W-H1W\cdots O1WB$	0.87	1.59	2.350 (1)	145
$O2W-H2W\cdots O3^{ix}$	0.85	1.92	2.768 (1)	179
$C5-H5\cdots O1WA^x$	0.95	2.60	3.534 (13)	169
$C8-H8A\cdots O2$	0.99	2.37	2.891 (11)	112
$C8-H8B\cdots O4^i$	0.99	2.49	3.396 (11)	153

Symmetry codes: (i) $x-1, y, z$; (iv) $-x+1, -y+2, -z+1$; (v) $-x, -y+2, -z+1$; (vi) $x-1, y+1, z$; (vii) $x, y+1, z$; (viii) $x, y-1, z$; (ix) $-x+1, -y+1, -z+1$; (x) $-x, -y+1, -z+2$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

Financial support from Ilam University and the Teacher Training University is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2184).

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supplementary materials

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Poly[propane-1,3-diammonium [cuprate(II)-bis(μ_2 -pyridine-2,3-dicarboxylato)] trihydrate]

H. Aghabozorg, R. Khadivi, M. Ghadermazi, H. Pasdar and S. Hooshmand

Comment

Intermolecular interactions, such as hydrogen bonding, π - π stacking, ion pairing and donor-acceptor interactions, are famous for making aggregates of molecules. One or more of these interactions may result in the formation of specific and spontaneous self-associations or self-associated compounds. Research has shown that hydrogen bonding plays the key role in preparation of self-assembled compounds. There is a very close relationship between hydrogen bonding and formation of proton transfer compounds (Aghabozorg, Attar Gharamaleki, Ghadermazi *et al.*, 2007; Aghabozorg, Attar Gharamaleki, Ghasemikhah *et al.*, 2007; Aghabozorg, Daneshvar *et al.*, 2007).

Here, we report on the synthesis and X-ray crystal structure of the title compound. Selected bond lengths, bond angles are given in Table 1. The Cu^{II} compound is composed of an anionic complex, [Cu(py-2,3-dc)₂]²⁻, propane-1,3-diammonium as a counter-ion, (pnH₂)²⁺, and three uncoordinated water molecules (Fig. 1). The Cu^{II} atom resides on a center of symmetry and is six-coordinated by two pyridine-2,3-dicarboxylate, (py-2,3-dc)²⁻, groups which act as a bidentate ligand through one O atom and one N atom and two O atoms of bridging (py-2,3-dc)²⁻ ligands that occupy *trans* positions with [O4ⁱⁱ—Cu1—O4ⁱⁱⁱ = 180°; ii: $x - 1, y, z$ and iii: $-x + 1, -y + 2, -z + 2$] which create the title polymeric structure. On the other hand, O1—Cu1—N1—C1 and N1—Cu1—O1—C6 torsion angles are 175.1 (3)° and -176.7 (4)°, respectively indicate that two (py-2,3-dc)²⁻ units are in the plane. In the crystal structure, the spaces between two layers of [Cu(py-2,3-dc)₂]²⁻ are filled with a layers of (pnH₂)²⁺ cations and water molecules (Fig 2). Solvate water molecules are disordered over two sites: O1WA and O1WB with equal occupancies and O2W by the center of inversion.

A notable feature of this compound is the presence of π - π and C—O \cdots π stacking interactions. The π - π stacking between two aromatic rings of (py-2,3-dc)²⁻ fragments with distances of 3.539 (3) Å ($1 - x, 1 - y, 2 - z$) are observed (Fig. 3). The C—O \cdots π distances are 3.240 (5) Å (C6—O2 \cdots Cg1($1 - x, 2 - y, 2 - z$); Cg1 is the centroid for the N1/C1—C5 ring) (Fig. 4). Intermolecular O—H \cdots O, O—H \cdots N, N—H \cdots O, C—H \cdots O and C—H \cdots N hydrogen bonds with D \cdots A ranging from 2.283 (1) Å to 3.534 (13) Å (Table 2) seem to be effective in the stabilization of the crystal structure, resulting in the formation of an interesting supramolecular structure.

Experimental

A solution of CuCl₂.2H₂O (85 mg, 0.5 mmol) in water (5 ml) was added to an aqueous solution of (pnH₂)(py-2,3-dc) (242 mg, 1 mmol) in water (10 ml) in a 1:2 molar ratio. Blue crystals of title compound were obtained after allowing the mixture to stand for four weeks at room temperature.

Refinement

The H(C) atom positions were calculated. H(N) and H(O) atom positions were found in difference Fourier synthesis. All hydrogen atoms were refined with use of a riding model with the $U_{\text{iso}}(\text{H})$ parameters equal to $1.2 U_{\text{eq}}(\text{C})$ and to $1.5 U_{\text{eq}}(\text{N})$, $1.5 U_{\text{eq}}(\text{O})$, where $U(\text{C})$, $U_{\text{eq}}(\text{O})$ and $U(\text{N})$ are equivalent isotropic thermal parameters of the atoms to which corresponding H atoms are bonded.

The cation is disordered over two sites by a center of inversion.

Water molecules are disordered over two sites: O1WA and O1WB with equal occupancies and O2W by the center of inversion.

Figures

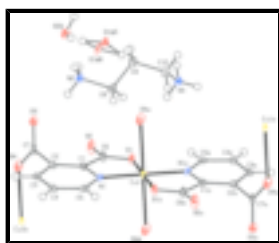


Fig. 1. The molecular structure of the title complex, with displacement ellipsoids drawn at the 50% probability level. [The labels a, b, c and d denote atoms generated by the symmetry operators $(-1 + x, y, z)$, $(1 + x, y, z)$, $(-x, 2 - y, 2 - z)$ and $(1 - x, 2 - y, 2 - z)$, respectively].

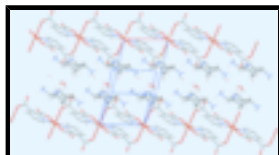


Fig. 2. A layered packing diagram viewed down the b axis. The space between the two layers of $[\text{Cu}(\text{py-2,3-dc})_2]^{2-}$ fragments is filled with a layer of $(\text{pnH}_2)^{2+}$ cations and water molecules.

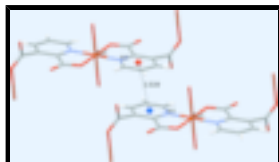


Fig. 3. π - π Stacking interactions between two aromatic rings. The average distance between the planes is $3.539(3) \text{ \AA}$ $(1 - x, 1 - y, 2 - z)$.

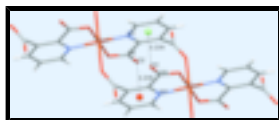


Fig. 4. The stacking interactions of the carbonyl groups of $(\text{py-2,3-dc})^{2-}$ fragments. The $\text{C}=\text{O}\cdots\pi$ distances (measured to the center of ring (N1/C1—C5)) are $3.239(5) \text{ \AA}$ $(1 - x, 2 - y, 2 - z)$.

Poly[propane-1,3-diammonium [cuprate(II)-bis(μ_2 -pyridine-2,3-dicarboxylato)] tetrahydrate]

Crystal data

$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)_2]\cdot 3\text{H}_2\text{O}$

$M_r = 523.94$

Triclinic, PT

$a = 6.6857(12) \text{ \AA}$

$b = 7.8251(18) \text{ \AA}$

$Z = 1$

$F_{000} = 271$

$D_x = 1.782 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1234 reflections

$c = 9.9188$ (9) Å	$\theta = 3\text{--}20^\circ$
$\alpha = 82.6561$ (10) $^\circ$	$\mu = 1.19$ mm $^{-1}$
$\beta = 84.0079$ (13) $^\circ$	$T = 100$ (2) K
$\gamma = 71.9520$ (17) $^\circ$	Prism, blue
$V = 488.20$ (15) Å 3	$0.21 \times 0.16 \times 0.15$ mm

Data collection

Bruker SMART APEXII CCD diffractometer	2348 independent reflections
Radiation source: fine-focus sealed tube	2310 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.026$
$T = 100$ (2) K	$\theta_{\text{max}} = 28.0^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.8^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.775$, $T_{\text{max}} = 0.836$	$k = -10 \rightarrow 10$
10997 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.063$	H-atom parameters constrained
$wR(F^2) = 0.176$	$w = 1/[\sigma^2(F_o^2) + (0.010P)^2 + 9.P]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
2348 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
189 parameters	$\Delta\rho_{\text{max}} = 0.69$ e Å $^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.93$ e Å $^{-3}$
	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 (Å 2)

x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
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supplementary materials

Cu1	0.0000	1.0000	1.0000	0.0083 (2)	
O1	0.1529 (5)	1.0909 (5)	0.8418 (4)	0.0137 (7)	
O2	0.4743 (6)	1.0337 (6)	0.7330 (4)	0.0233 (9)	
O3	0.7857 (6)	0.6603 (5)	0.7152 (4)	0.0189 (8)	
O4	0.9507 (6)	0.7923 (5)	0.8365 (4)	0.0184 (8)	
N1	0.2805 (6)	0.8300 (5)	1.0351 (4)	0.0099 (8)	
C1	0.4291 (7)	0.8457 (6)	0.9349 (5)	0.0098 (9)	
C2	0.6352 (8)	0.7332 (6)	0.9342 (5)	0.0108 (9)	
C3	0.6889 (8)	0.6039 (6)	1.0472 (5)	0.0119 (9)	
H3	0.8292	0.5260	1.0525	0.014*	
C4	0.5387 (8)	0.5903 (6)	1.1494 (5)	0.0113 (9)	
H4	0.5743	0.5031	1.2259	0.014*	
C5	0.3353 (8)	0.7039 (6)	1.1406 (5)	0.0111 (9)	
H5	0.2314	0.6924	1.2112	0.013*	
C6	0.3515 (8)	1.0015 (7)	0.8261 (5)	0.0135 (9)	
C7	0.8024 (7)	0.7337 (7)	0.8180 (5)	0.0135 (10)	
N2	0.4757 (13)	0.7636 (12)	0.5189 (9)	0.0129 (16)	0.50
H2A	0.5574	0.7319	0.5913	0.019*	0.50
H2B	0.5369	0.8236	0.4504	0.019*	0.50
H2C	0.4627	0.6624	0.4892	0.019*	0.50
C8	0.2618 (16)	0.8836 (14)	0.5611 (10)	0.0139 (19)	0.50
H8A	0.2673	1.0086	0.5610	0.017*	0.50
H8B	0.2188	0.8415	0.6549	0.017*	0.50
C9	0.1014 (16)	0.8816 (14)	0.4648 (11)	0.014 (2)	0.50
H9A	0.0884	0.7582	0.4704	0.017*	0.50
H9B	0.1506	0.9140	0.3702	0.017*	0.50
C10	-0.1138 (17)	1.0139 (15)	0.4993 (11)	0.017 (2)	0.50
H10A	-0.2226	0.9832	0.4550	0.020*	0.50
H10B	-0.1467	1.0008	0.5990	0.020*	0.50
N3	-0.1232 (14)	1.2052 (12)	0.4541 (9)	0.0135 (16)	0.50
H3B	-0.2596	1.2764	0.4603	0.020*	0.50
H3C	-0.0696	1.2138	0.3662	0.020*	0.50
H3D	-0.0461	1.2422	0.5083	0.020*	0.50
O1WA	0.0811 (17)	0.3649 (16)	0.6306 (12)	0.015 (2)	0.50
O1WB	0.1490 (17)	0.3949 (16)	0.6312 (13)	0.018 (2)	0.50
H3W	0.1276	0.3321	0.7141	0.027*	
H4W	-0.0108	0.4794	0.6569	0.027*	
O2W	0.4409 (12)	0.4057 (11)	0.4800 (8)	0.0171 (15)	0.50
H1W	0.3664	0.3585	0.5422	0.026*	0.50
H2W	0.3701	0.3870	0.4201	0.026*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0047 (4)	0.0081 (4)	0.0105 (4)	-0.0008 (3)	0.0010 (3)	0.0011 (3)
O1	0.0095 (16)	0.0141 (17)	0.0131 (17)	0.0005 (13)	0.0002 (13)	0.0039 (13)
O2	0.0120 (18)	0.029 (2)	0.019 (2)	0.0007 (16)	0.0054 (15)	0.0113 (16)
O3	0.0152 (18)	0.024 (2)	0.0127 (18)	-0.0001 (15)	0.0009 (14)	-0.0029 (15)

O4	0.0134 (17)	0.0167 (18)	0.023 (2)	-0.0041 (14)	0.0063 (15)	-0.0012 (15)
N1	0.0093 (18)	0.0090 (18)	0.0103 (19)	-0.0011 (15)	0.0015 (15)	-0.0022 (14)
C1	0.008 (2)	0.012 (2)	0.010 (2)	-0.0044 (17)	-0.0004 (16)	-0.0005 (17)
C2	0.011 (2)	0.011 (2)	0.011 (2)	-0.0048 (17)	-0.0024 (17)	0.0010 (17)
C3	0.013 (2)	0.010 (2)	0.013 (2)	-0.0022 (17)	-0.0039 (18)	-0.0027 (17)
C4	0.014 (2)	0.009 (2)	0.012 (2)	-0.0034 (17)	-0.0036 (17)	0.0005 (17)
C5	0.016 (2)	0.010 (2)	0.010 (2)	-0.0061 (18)	-0.0015 (17)	-0.0026 (17)
C6	0.006 (2)	0.017 (2)	0.013 (2)	-0.0005 (18)	0.0021 (17)	0.0030 (18)
C7	0.007 (2)	0.015 (2)	0.012 (2)	0.0036 (17)	-0.0006 (17)	0.0041 (18)
N2	0.011 (4)	0.016 (4)	0.010 (4)	-0.003 (3)	0.002 (3)	0.000 (3)
C8	0.014 (5)	0.014 (5)	0.012 (4)	-0.002 (4)	0.004 (4)	-0.004 (4)
C9	0.012 (5)	0.012 (5)	0.017 (5)	-0.003 (4)	0.002 (4)	0.000 (4)
C10	0.018 (5)	0.013 (5)	0.016 (5)	-0.004 (4)	0.004 (4)	0.000 (4)
N3	0.015 (4)	0.012 (4)	0.012 (4)	-0.002 (3)	0.000 (3)	0.001 (3)
O1WA	0.014 (6)	0.018 (5)	0.010 (4)	-0.002 (4)	0.005 (4)	0.000 (3)
O1WB	0.016 (6)	0.016 (5)	0.016 (4)	0.001 (4)	0.006 (4)	0.001 (3)
O2W	0.014 (3)	0.020 (4)	0.017 (4)	-0.007 (3)	0.002 (3)	-0.002 (3)

Geometric parameters (Å, °)

Cu1—O1 ⁱ	1.960 (4)	C5—H5	0.9500
Cu1—O1	1.960 (4)	N2—C8	1.499 (12)
Cu1—N1 ⁱ	1.970 (4)	N2—H2A	0.9100
Cu1—N1	1.970 (4)	N2—H2B	0.9100
Cu1—O4 ⁱⁱ	2.549 (4)	N2—H2C	0.9100
Cu1—O4 ⁱⁱⁱ	2.549 (4)	C8—C9	1.513 (14)
O1—C6	1.298 (6)	C8—H8A	0.9900
O2—C6	1.225 (6)	C8—H8B	0.9900
O3—C7	1.263 (7)	C9—C10	1.524 (14)
O4—C7	1.252 (7)	C9—H9A	0.9900
O4—Cu1 ^{iv}	2.549 (4)	C9—H9B	0.9900
N1—C5	1.340 (6)	C10—N3	1.491 (13)
N1—C1	1.352 (6)	C10—H10A	0.9900
C1—C2	1.386 (7)	C10—H10B	0.9900
C1—C6	1.520 (7)	N3—H3B	0.9100
C2—C3	1.406 (7)	N3—H3C	0.9100
C2—C7	1.520 (7)	N3—H3D	0.9100
C3—C4	1.369 (7)	O1WA—H3W	0.8934
C3—H3	0.9500	O1WA—H4W	0.9660
C4—C5	1.379 (7)	O2W—H1W	0.8700
C4—H4	0.9500	O2W—H2W	0.8498
O1 ⁱ —Cu1—O1	180.000 (1)	N1—C5—C4	121.7 (5)
O1 ⁱ —Cu1—N1 ⁱ	83.39 (16)	C4—C5—Cu1	152.8 (4)
O1—Cu1—N1 ⁱ	96.61 (16)	N1—C5—H5	119.1
O1 ⁱ —Cu1—N1	96.61 (16)	C4—C5—H5	119.1
O1—Cu1—N1	83.39 (16)	Cu1—C5—H5	88.0
N1 ⁱ —Cu1—N1	180.000 (1)	O2—C6—O1	125.3 (5)

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O1 ⁱ —Cu1—O4 ⁱⁱ	96.02 (14)	O2—C6—C1	119.8 (4)
O1—Cu1—O4 ⁱⁱ	83.98 (14)	O1—C6—C1	114.9 (4)
N1 ⁱ —Cu1—O4 ⁱⁱ	90.52 (15)	O2—C6—Cu1	165.3 (4)
N1—Cu1—O4 ⁱⁱ	89.48 (15)	C1—C6—Cu1	74.8 (3)
O1 ⁱ —Cu1—O4 ⁱⁱⁱ	83.98 (14)	O4—C7—O3	126.2 (5)
O1—Cu1—O4 ⁱⁱⁱ	96.02 (14)	O4—C7—C2	118.0 (5)
N1 ⁱ —Cu1—O4 ⁱⁱⁱ	89.48 (15)	O3—C7—C2	115.5 (4)
N1—Cu1—O4 ⁱⁱⁱ	90.52 (15)	N2—C8—C9	110.5 (8)
O4 ⁱⁱ —Cu1—O4 ⁱⁱⁱ	180.000 (1)	N2—C8—H8A	109.5
C6—O1—Cu1	114.8 (3)	C9—C8—H8A	109.5
C7—O4—Cu1 ^{iv}	134.2 (3)	N2—C8—H8B	109.5
C5—N1—C1	118.9 (4)	C9—C8—H8B	109.5
C5—N1—Cu1	128.3 (3)	H8A—C8—H8B	108.1
C1—N1—Cu1	112.8 (3)	C8—C9—C10	111.4 (9)
N1—C1—C2	122.9 (4)	C8—C9—H9A	109.3
N1—C1—C6	113.9 (4)	C10—C9—H9A	109.3
C2—C1—C6	123.2 (4)	C8—C9—H9B	109.3
C2—C1—Cu1	163.3 (4)	C10—C9—H9B	109.3
C6—C1—Cu1	73.4 (3)	H9A—C9—H9B	108.0
C1—C2—C3	116.9 (4)	N3—C10—C9	112.5 (8)
C1—C2—C7	124.9 (4)	N3—C10—H10A	109.1
C3—C2—C7	118.1 (4)	C9—C10—H10A	109.1
C4—C3—C2	119.9 (5)	N3—C10—H10B	109.1
C4—C3—H3	120.0	C9—C10—H10B	109.1
C2—C3—H3	120.0	H10A—C10—H10B	107.8
C3—C4—C5	119.6 (5)	H3W—O1WA—H4W	91.9
C3—C4—H4	120.2	H1W—O2W—H2W	88.7
C5—C4—H4	120.2		
N1 ⁱ —Cu1—O1—C6	-176.6 (4)	C3—C4—C5—Cu1	1.2 (10)
N1—Cu1—O1—C6	3.4 (4)	O1 ⁱ —Cu1—C5—N1	176.7 (4)
O4 ⁱⁱ —Cu1—O1—C6	-86.8 (4)	O1—Cu1—C5—N1	-3.3 (4)
O4 ⁱⁱⁱ —Cu1—O1—C6	93.2 (4)	N1 ⁱ —Cu1—C5—N1	180.000 (3)
O1 ⁱ —Cu1—N1—C5	-3.2 (4)	O4 ⁱⁱ —Cu1—C5—N1	81.2 (4)
O1—Cu1—N1—C5	176.8 (4)	O4 ⁱⁱⁱ —Cu1—C5—N1	-98.8 (4)
O4 ⁱⁱ —Cu1—N1—C5	-99.2 (4)	O1 ⁱ —Cu1—C5—C4	173.2 (8)
O4 ⁱⁱⁱ —Cu1—N1—C5	80.8 (4)	O1—Cu1—C5—C4	-6.8 (8)
O1 ⁱ —Cu1—N1—C1	175.0 (3)	N1 ⁱ —Cu1—C5—C4	176.5 (7)
O1—Cu1—N1—C1	-5.0 (3)	N1—Cu1—C5—C4	-3.5 (7)
O4 ⁱⁱ —Cu1—N1—C1	79.0 (3)	O4 ⁱⁱ —Cu1—C5—C4	77.6 (7)
O4 ⁱⁱⁱ —Cu1—N1—C1	-101.0 (3)	O4 ⁱⁱⁱ —Cu1—C5—C4	-102.4 (7)
C5—N1—C1—C2	2.0 (7)	Cu1—O1—C6—O2	178.7 (5)
Cu1—N1—C1—C2	-176.4 (4)	Cu1—O1—C6—C1	-1.2 (6)
C5—N1—C1—C6	-176.0 (4)	N1—C1—C6—O2	177.1 (5)
Cu1—N1—C1—C6	5.6 (5)	C2—C1—C6—O2	-1.0 (8)

C5—N1—C1—Cu1	178.4 (6)	Cu1—C1—C6—O2	-179.1 (6)
O1 ⁱ —Cu1—C1—N1	-5.9 (4)	N1—C1—C6—O1	-3.0 (7)
O1—Cu1—C1—N1	174.1 (4)	C2—C1—C6—O1	179.0 (5)
N1 ⁱ —Cu1—C1—N1	180.000 (3)	Cu1—C1—C6—O1	0.8 (4)
O4 ⁱⁱ —Cu1—C1—N1	-99.6 (3)	N1—C1—C6—Cu1	-3.8 (4)
O4 ⁱⁱⁱ —Cu1—C1—N1	80.4 (3)	C2—C1—C6—Cu1	178.2 (5)
O1 ⁱ —Cu1—C1—C2	4.7 (13)	O1 ⁱ —Cu1—C6—O2	176.0 (15)
O1—Cu1—C1—C2	-175.3 (13)	O1—Cu1—C6—O2	-4.0 (15)
N1 ⁱ —Cu1—C1—C2	-169.4 (11)	N1 ⁱ —Cu1—C6—O2	-0.1 (18)
N1—Cu1—C1—C2	10.6 (11)	N1—Cu1—C6—O2	179.9 (18)
O4 ⁱⁱ —Cu1—C1—C2	-89.0 (12)	O4 ⁱⁱ —Cu1—C6—O2	86.3 (17)
O4 ⁱⁱⁱ —Cu1—C1—C2	91.0 (12)	O4 ⁱⁱⁱ —Cu1—C6—O2	-93.7 (17)
O1 ⁱ —Cu1—C1—C6	179.4 (3)	O1 ⁱ —Cu1—C6—O1	180.000 (2)
O1—Cu1—C1—C6	-0.6 (3)	N1 ⁱ —Cu1—C6—O1	3.9 (4)
N1 ⁱ —Cu1—C1—C6	5.3 (5)	N1—Cu1—C6—O1	-176.1 (4)
N1—Cu1—C1—C6	-174.7 (5)	O4 ⁱⁱ —Cu1—C6—O1	90.3 (4)
O4 ⁱⁱ —Cu1—C1—C6	85.7 (3)	O4 ⁱⁱⁱ —Cu1—C6—O1	-89.7 (4)
O4 ⁱⁱⁱ —Cu1—C1—C6	-94.3 (3)	O1 ⁱ —Cu1—C6—C1	-1.1 (5)
N1—C1—C2—C3	-2.9 (7)	O1—Cu1—C6—C1	178.9 (5)
C6—C1—C2—C3	175.0 (4)	N1 ⁱ —Cu1—C6—C1	-177.2 (3)
Cu1—C1—C2—C3	-11.1 (15)	N1—Cu1—C6—C1	2.8 (3)
N1—C1—C2—C7	174.0 (5)	O4 ⁱⁱ —Cu1—C6—C1	-90.8 (3)
C6—C1—C2—C7	-8.2 (8)	O4 ⁱⁱⁱ —Cu1—C6—C1	89.2 (3)
Cu1—C1—C2—C7	165.8 (10)	Cu1 ^{iv} —O4—C7—O3	164.8 (4)
C1—C2—C3—C4	1.8 (7)	Cu1 ^{iv} —O4—C7—C2	-21.4 (7)
C7—C2—C3—C4	-175.3 (4)	C1—C2—C7—O4	109.8 (6)
C2—C3—C4—C5	0.0 (7)	C3—C2—C7—O4	-73.4 (6)
C1—N1—C5—C4	0.0 (7)	C1—C2—C7—O3	-75.7 (6)
Cu1—N1—C5—C4	178.1 (4)	C3—C2—C7—O3	101.1 (5)
C1—N1—C5—Cu1	-178.1 (7)	N2—C8—C9—C10	-175.6 (8)
C3—C4—C5—N1	-1.0 (7)	C8—C9—C10—N3	76.1 (11)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots O3	0.91	1.96	2.854 (1)	167
N2—H2B \cdots O2 ^v	0.91	2.01	2.830 (1)	150
N3—H3B \cdots N2 ^{vi}	0.91	1.56	2.283 (1)	134
N3—H3B \cdots O2W ^{vii}	0.91	1.95	2.852 (13)	174
N3—H3C \cdots O3 ^v	0.91	2.42	3.041 (10)	126
N3—H3C \cdots O4 ^v	0.91	2.08	2.991 (1)	174
N3—H3D \cdots O1WA ^{viii}	0.91	2.03	2.934 (1)	170
N3—H3D \cdots O1WB ^{viii}	0.91	2.51	3.407 (15)	170

supplementary materials

O1WA—H3W…O1 ^{ix}	0.89	2.11	2.764 (1)	130
O1WA—H4W…O3 ⁱⁱ	0.97	1.74	2.696 (1)	168
O2W—H1W…O1WA	0.87	2.00	2.779 (15)	148
O2W—H1W…O1WB	0.87	1.59	2.350 (1)	145
O2W—H2W…O3 ^x	0.85	1.92	2.768 (1)	179
C5—H5…O1WA ^{xi}	0.95	2.60	3.534 (13)	169
C8—H8A…O2	0.99	2.37	2.891 (11)	112
C8—H8B…O4 ⁱⁱ	0.99	2.49	3.396 (11)	153

Symmetry codes: (v) $-x+1, -y+2, -z+1$; (vi) $-x, -y+2, -z+1$; (vii) $x-1, y+1, z$; (viii) $x, y+1, z$; (ix) $x, y-1, z$; (ii) $x-1, y, z$; (x) $-x+1, -y+1, -z+1$; (xi) $-x, -y+1, -z+2$.

Fig. 1

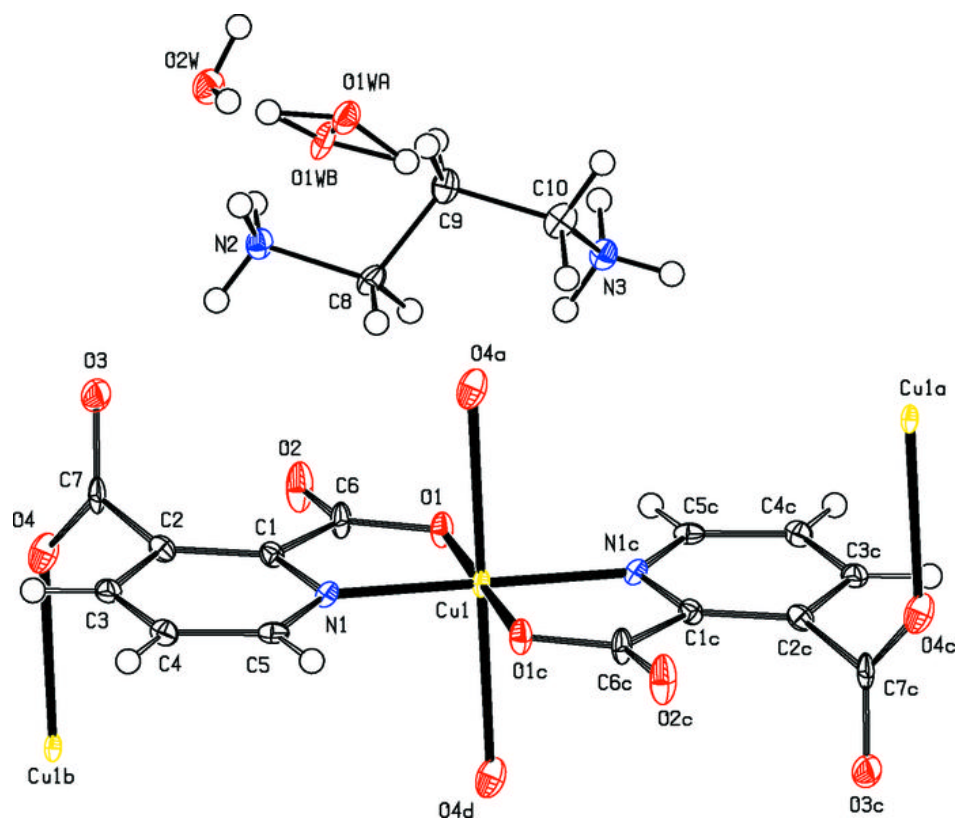


Fig. 2

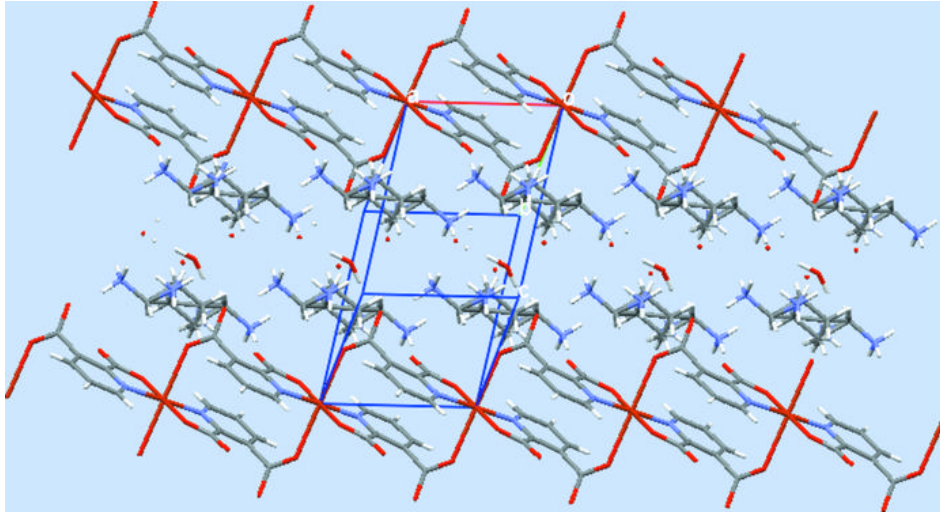


Fig. 3

