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Poly[*trans*-diaquabis(μ_2-3-pyridylacetato)copper(II)]

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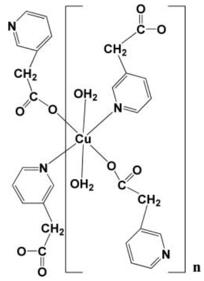
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.008 Å; R factor = 0.047; wR factor = 0.117; data-to-parameter ratio = 12.1.

The title copper^{II} coordination polymer, *trans*-$[Cu(C_7H_6NO_2)_2(H_2O)_2]_n$, was obtained from a solvothermal reaction of 3-pyridylacetic acid hydrochloride with $Cu(ClO_4)_2\cdot 6H_2O$. The molecule is centrosymmetric, so pairs of equivalent ligands lie *trans* to each other in a slightly distorted octahedral geometry. The Cu^{II} center is coordinated by two water molecules [Cu—O = 2.424 (4) Å], two pyridyl N atoms [Cu—N = 2.031 (4) Å], and two carboxylate O atoms [Cu—O1 = 1.968 (4) Å]. All $O_{carboxylate}$—Cu—$O_{carboxylate}$, O_{water}—Cu—O_{water} and N—Cu—N bond angles are 180° due to the inversion symmetry of the complexes. Each 3-pyridylacetate anion uses its pyridine N atom and one carboxylate O atom to connect two Cu^{II} ions, generating two-dimensional sheets parallel to (212). Each complex exhibits two intramolecular O—H···O hydrogen bonds with angles at hydrogen of 156°. Adjacent two-dimensional layers are connected *via* intermolecular O—H···O and weak C—H···O hydrogen-bonding contacts, resulting in a three-dimensional framework structure with oxygen as a trifurcated acceptor atom.

Related literature

The six-coordinate complex with 4-pyridylacetate and 3-pyridylacetate ligands have similar octahedral geometry (Li *et al.*, 2004; Du *et al.*, 2006; Martin *et al.*, 2007).

For related literature, see: Aakeröy *et al.* (1999); Evans & Lin (2002); Tong *et al.* (2003).



Experimental

Crystal data

$[Cu(C_7H_6NO_2)_2(H_2O)_2]$
M_r = 371.83
Monoclinic, $P2_1/n$
a = 9.0672 (18) Å
b = 8.6022 (17) Å
c = 9.601 (2) Å
β = 101.335 (3)°
V = 734.2 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.52 mm^{-1}
T = 298 (2) K
0.70 × 0.38 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.416, T_{max} = 0.875
3558 measured reflections
1284 independent reflections
821 reflections with $I > \sigma(I)$
R_{int} = 0.071

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.117
S = 1.07
1284 reflections
106 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.968 (4)	Cu1—O3	2.424 (4)
Cu1—N1	2.031 (4)		
O1^i—Cu1—O1	180	N1—Cu1—O3	87.45 (15)
O1—Cu1—N1^i	89.41 (17)	O3^i—Cu1—O3	180
O1—Cu1—N1	90.59 (17)	C3—N1—Cu1	120.7 (4)
N1^i—Cu1—N1	180	C7—N1—Cu1	120.8 (4)
N1—Cu1—O3^i	92.55 (15)	C1—O1—Cu1	129.9 (4)
O1^i—Cu1—O3	84.15 (14)	Cu1—O3—H1	94.7
O1—Cu1—O3	95.85 (14)	Cu1—O3—H2	125.9

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O2	0.85	1.96	2.762 (6)	156
O3—H2···O2^{ii}	0.85	1.98	2.826 (6)	170
C5—H5···O2^{iii}	0.93	2.52	3.366 (7)	151

Symmetry codes: (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x-1, y, z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2011).

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supplementary materials

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Poly[*trans*-diaquabis(μ_2-3-pyridylacetato)copper(II)]

S.-N. Qin, F.-P. Liang, Z.-L. Chen and **W.-H. Yan**

Comment

Pyridinecarboxylic acids have been extensively used in the preparation of metal complexes because of their versatile coordination modes. These ligands can connect different metal ions to form robust networks or some porous coordination polymers. Though various metal-pyridinepolycarboxylate complexes have been reported (Evans *et al.*, 2002; Aakeröy *et al.*, 1999; Tong *et al.*, 2003; Li *et al.*, 2004; Du *et al.*, 2006), complexes of 3-pyridylacetate are very limited. Only complexes of nickel and cobalt have been published recently up to now (Martin *et al.*, 2007). In this paper, we report a new two-dimensional coordination polymer, [Cu(3-pyridylacetato)$_2$(H$_2$O)$_2$]$_n$, (I).

The molecule of the title complex, which is similar to that previously described for [M(Hpya)$_2$(H$_2$O)$_2$]$_n$ (M = Cu, Co, Mn, Ni, Zn, Cd; Hpya = 4-pyridylacetic acid) (Li *et al.*, 2004; Du *et al.*, 2006) and [M(3-pyridylacetato)$_2$(H$_2$O)$_2$]$_n$ (M = Ni, Co) (Martin *et al.*, 2007), is centrosymmetric, so pairs of equivalent ligands lie *trans* to each other in a slightly distorted octahedral geometry. The Cu^{II} center is six-coordinated by two water molecules in the axial positions, two pyridyl nitrogen atoms and two carboxylate oxygen atoms from four 3-pyridylacetate ligands in the equatorial plane. Each 3-pyridylacetate anion uses its pyridine nitrogen atom and one carboxylate oxygen atom to connect two Cu^{II} ions. Four 3-pyridylacetate anionic ligands and four Cu^{II} ions form a tetragon with a side length of 8.405 Å and a diagonal measurement of 14.443 * 8.602 Å based on the Cu—Cu distances. The tetragon is further extended into a two-dimensional framework parallel to (212) with a rhombic grid through sharing Cu^{II} ions, 3-pyridylacetate anionic ligands and intramolecular O3—H1···O2 hydrogen bonds (Fig. 1).

Adjacent two-dimensional layers are connected *via* intermolecular O—H···O and weak C—H···O hydrogen-bonding contacts, resulting in a three-dimensional framework structure with oxygen as a trifurcated acceptor atom (Fig. 2).

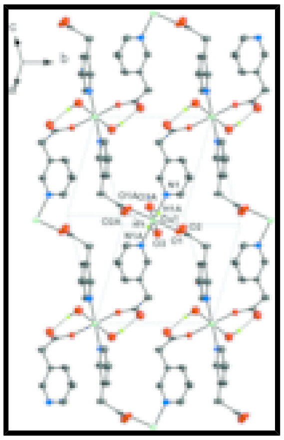
Experimental

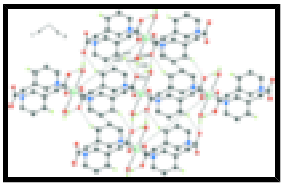
A mixture of 3-pyridylacetic acid hydrochloride (0.0434 g, 0.25 mmol), Cu(ClO$_4$)$_2$·6H$_2$O(0.0555 g, 0.15 mmol), NaClO$_4$·6H$_2$O (0.0300 g, 0.13 mmol), NaOH (0.0200 g, 0.5 mmol), THF (10 ml) and water (5 ml) was sealed in a 25 ml Teflon-lined stainless-steel reactor and heated to 333 K for 96 h, yielding blue crystals of (I) suitable for X-ray analysis. Elemental analysis for C$_{14}$H$_{16}$CuN$_2$O$_6$, calculated: C 45.22, H 4.34, N 7.53%; found: C 44.61, H 5.44, N 7.13%.

Refinement

H atoms of the water molecules were located in a difference map. H atoms bonded to C atoms were placed at calulated positions and treated using a riding-model approximation [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C)].

Figures





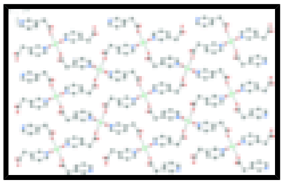


Fig. 1. Principal connectivity of the coordination polymer two-dimensional structure (I) on (2 1 2), showing 50% probability displacement ellipsoids. All H atoms except H1 have been omitted for clarity. Symmetry codes: (i) $-x + 1,-y + 1,-z + 1$.

Fig. 2. Intermolecular hydrogen bonding contacts between the two-dimensional polymer layers in *ac* plane. For clarity, only H1, H2, and H5 were used. Symmetry codes: (ii) $x - 1/2,-y + 3/2,z - 1/2$; (iii) $1 - x,2 - y,1 - z$; (iv) $-x,2 - y,1 - z$..

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Crystal data

$[Cu(C_7H_6NO_2)_2(H_2O)_2]n$

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Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 9.0672$ (18) Å

$b = 8.6022$ (17) Å

$c = 9.601$ (2) Å

$\beta = 101.335$ (3)°

$V = 734.2$ (3) Å^3

$Z = 2$

$F_{000} = 382$

$D_x = 1.682$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 748 reflections

$\theta = 2.8$–25.1°

$\mu = 1.52$ mm^{-1}

$T = 298$ (2) K

Block, blue

0.70 × 0.38 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

1284 independent reflections

821 reflections with $I > \sigma(I)$

Monochromator: graphite

T = 298(2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 1998)

$T_{\min}$ = 0.416, $T_{\max}$ = 0.875

3558 measured reflections

R_{int} = 0.071

$\theta_{\max}$ = 25.0°

$\theta_{\min}$ = 2.8°

$h = -10 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -9 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.047

$wR(F^2)$ = 0.117

S = 1.07

1284 reflections

106 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.9264P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max}$ = 0.79 e Å^{-3}

$\Delta\rho_{\min}$ = −0.72 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_{iso}*/U_{eq}
Cu1	0.5000	0.5000	0.5000	0.0263 (3)
N1	0.3098 (5)	0.5766 (6)	0.5596 (5)	0.0278 (11)
O1	0.5329 (4)	0.7068 (4)	0.4238 (4)	0.0316 (10)
O2	0.6976 (4)	0.8160 (5)	0.5997 (4)	0.0444 (11)
O3	0.6312 (4)	0.5530 (5)	0.7405 (4)	0.0418 (12)
H1	0.6716	0.6365	0.7190	0.063*
H2	0.6890	0.4905	0.7941	0.063*
C1	0.6225 (6)	0.8136 (7)	0.4763 (6)	0.0280 (14)
C2	0.6336 (7)	0.9518 (7)	0.3801 (6)	0.0384 (17)
H2A	0.5428	1.0136	0.3719	0.046*
H2B	0.7176	1.0163	0.4244	0.046*

C3	0.2837 (6)	0.5449 (7)	0.6883 (5)	0.0293 (15)
H3	0.3553	0.4885	0.7509	0.035*
C4	0.1545 (6)	0.5920 (6)	0.7331 (6)	0.0263 (13)
C5	0.0475 (6)	0.6698 (7)	0.6372 (6)	0.0353 (15)
H5	−0.0428	0.6987	0.6620	0.042*
C6	0.0737 (6)	0.7049 (8)	0.5056 (6)	0.0402 (16)
H6	0.0037	0.7614	0.4415	0.048*
C7	0.2058 (6)	0.6550 (7)	0.4693 (6)	0.0338 (15)
H7	0.2228	0.6767	0.3789	0.041*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0300 (5)	0.0278 (6)	0.0254 (5)	−0.0014 (6)	0.0157 (4)	−0.0012 (5)
N1	0.029 (3)	0.029 (3)	0.027 (3)	−0.002 (2)	0.011 (2)	−0.002 (2)
O1	0.041 (2)	0.027 (3)	0.029 (2)	−0.009 (2)	0.0141 (18)	−0.0047 (18)
O2	0.048 (2)	0.044 (3)	0.039 (3)	−0.005 (2)	0.003 (2)	0.003 (2)
O3	0.043 (2)	0.045 (3)	0.035 (2)	−0.003 (2)	0.0032 (19)	−0.0014 (18)
C1	0.029 (3)	0.035 (4)	0.026 (3)	0.008 (3)	0.019 (3)	0.002 (3)
C2	0.044 (3)	0.044 (5)	0.034 (3)	−0.004 (3)	0.022 (3)	−0.002 (3)
C3	0.030 (3)	0.036 (4)	0.023 (3)	0.004 (3)	0.008 (2)	0.003 (2)
C4	0.031 (3)	0.021 (3)	0.032 (3)	−0.003 (3)	0.017 (3)	−0.002 (3)
C5	0.027 (3)	0.043 (4)	0.038 (4)	0.002 (3)	0.013 (3)	−0.004 (3)
C6	0.034 (3)	0.049 (5)	0.038 (4)	0.010 (3)	0.008 (3)	0.005 (3)
C7	0.041 (3)	0.038 (4)	0.024 (3)	−0.001 (3)	0.010 (3)	0.001 (3)

Geometric parameters (Å, °)

Cu1—O1^{i}	1.968 (4)	C2—C4^{ii}	1.508 (7)
Cu1—O1	1.968 (4)	C2—H2A	0.9700
Cu1—N1^{i}	2.031 (4)	C2—H2B	0.9700
Cu1—N1	2.031 (4)	C3—C4	1.385 (7)
Cu1—O3^{i}	2.424 (4)	C3—H3	0.9300
Cu1—O3	2.424 (4)	C4—C5	1.373 (7)
N1—C3	1.331 (6)	C4—C2^{iii}	1.508 (7)
N1—C7	1.332 (7)	C5—C6	1.364 (7)
O1—C1	1.263 (7)	C5—H5	0.9300
O2—C1	1.245 (6)	C6—C7	1.380 (7)
O3—H1	0.8500	C6—H6	0.9300
O3—H2	0.8500	C7—H7	0.9300
C1—C2	1.521 (8)		
O1^{i}—Cu1—O1	180.00 (10)	O2—C1—C2	118.4 (5)
O1^{i}—Cu1—N1^{i}	90.59 (17)	O1—C1—C2	116.1 (5)
O1—Cu1—N1^{i}	89.41 (17)	C4^{ii}—C2—C1	114.1 (5)
O1^{i}—Cu1—N1	89.41 (17)	C4^{ii}—C2—H2A	108.7
O1—Cu1—N1	90.59 (17)	C1—C2—H2A	108.7
N1^{i}—Cu1—N1	180.000 (1)	C4^{ii}—C2—H2B	108.7

O1$^{\text{i}}$—Cu1—O3$^{\text{i}}$	95.85 (14)	C1—C2—H2B	108.7
O1—Cu1—O3$^{\text{i}}$	84.15 (14)	H2A—C2—H2B	107.6
N1$^{\text{i}}$—Cu1—O3$^{\text{i}}$	87.45 (15)	N1—C3—C4	122.9 (5)
N1—Cu1—O3$^{\text{i}}$	92.55 (15)	N1—C3—H3	118.5
O1$^{\text{i}}$—Cu1—O3	84.15 (14)	C4—C3—H3	118.5
O1—Cu1—O3	95.85 (14)	C5—C4—C3	117.6 (5)
N1$^{\text{i}}$—Cu1—O3	92.55 (15)	C5—C4—C2$^{\text{iii}}$	123.2 (5)
N1—Cu1—O3	87.45 (15)	C3—C4—C2$^{\text{iii}}$	119.1 (5)
O3$^{\text{i}}$—Cu1—O3	180.000 (1)	C6—C5—C4	120.0 (5)
C3—N1—C7	118.4 (5)	C6—C5—H5	120.0
C3—N1—Cu1	120.7 (4)	C4—C5—H5	120.0
C7—N1—Cu1	120.8 (4)	C5—C6—C7	118.8 (6)
C1—O1—Cu1	129.9 (4)	C5—C6—H6	120.6
Cu1—O3—H1	94.7	C7—C6—H6	120.6
Cu1—O3—H2	125.9	N1—C7—C6	122.1 (5)
H1—O3—H2	116.0	N1—C7—H7	118.9
O2—C1—O1	125.5 (5)	C6—C7—H7	118.9
O1$^{\text{i}}$—Cu1—N1—C3	46.4 (4)	Cu1—O1—C1—C2	172.3 (3)
O1—Cu1—N1—C3	−133.6 (4)	O2—C1—C2—C4$^{\text{ii}}$	133.6 (5)
O3$^{\text{i}}$—Cu1—N1—C3	142.2 (4)	O1—C1—C2—C4$^{\text{ii}}$	−48.2 (7)
O3—Cu1—N1—C3	−37.8 (4)	C7—N1—C3—C4	−1.2 (8)
O1$^{\text{i}}$—Cu1—N1—C7	−131.1 (4)	Cu1—N1—C3—C4	−178.8 (4)
O1—Cu1—N1—C7	48.9 (4)	N1—C3—C4—C5	2.5 (8)
O3$^{\text{i}}$—Cu1—N1—C7	−35.3 (4)	N1—C3—C4—C2$^{\text{iii}}$	179.0 (5)
O3—Cu1—N1—C7	144.7 (4)	C3—C4—C5—C6	−3.2 (9)
N1$^{\text{i}}$—Cu1—O1—C1	−78.0 (4)	C2$^{\text{iii}}$—C4—C5—C6	−179.6 (6)
N1—Cu1—O1—C1	102.0 (4)	C4—C5—C6—C7	2.8 (9)
O3$^{\text{i}}$—Cu1—O1—C1	−165.5 (4)	C3—N1—C7—C6	0.6 (9)
O3—Cu1—O1—C1	14.5 (4)	Cu1—N1—C7—C6	178.2 (4)
Cu1—O1—C1—O2	−9.7 (8)	C5—C6—C7—N1	−1.4 (9)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*+1/2, −*y*+3/2, *z*−1/2; (iii) *x*−1/2, −*y*+3/2, *z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O2	0.85	1.96	2.762 (6)	156
O3—H2···O2$^{\text{iv}}$	0.85	1.98	2.826 (6)	170
C5—H5···O2$^{\text{v}}$	0.93	2.52	3.366 (7)	151

Symmetry codes: (iv) −*x*+3/2, *y*−1/2, −*z*+3/2; (v) *x*−1, *y*, *z*.

Fig. 1

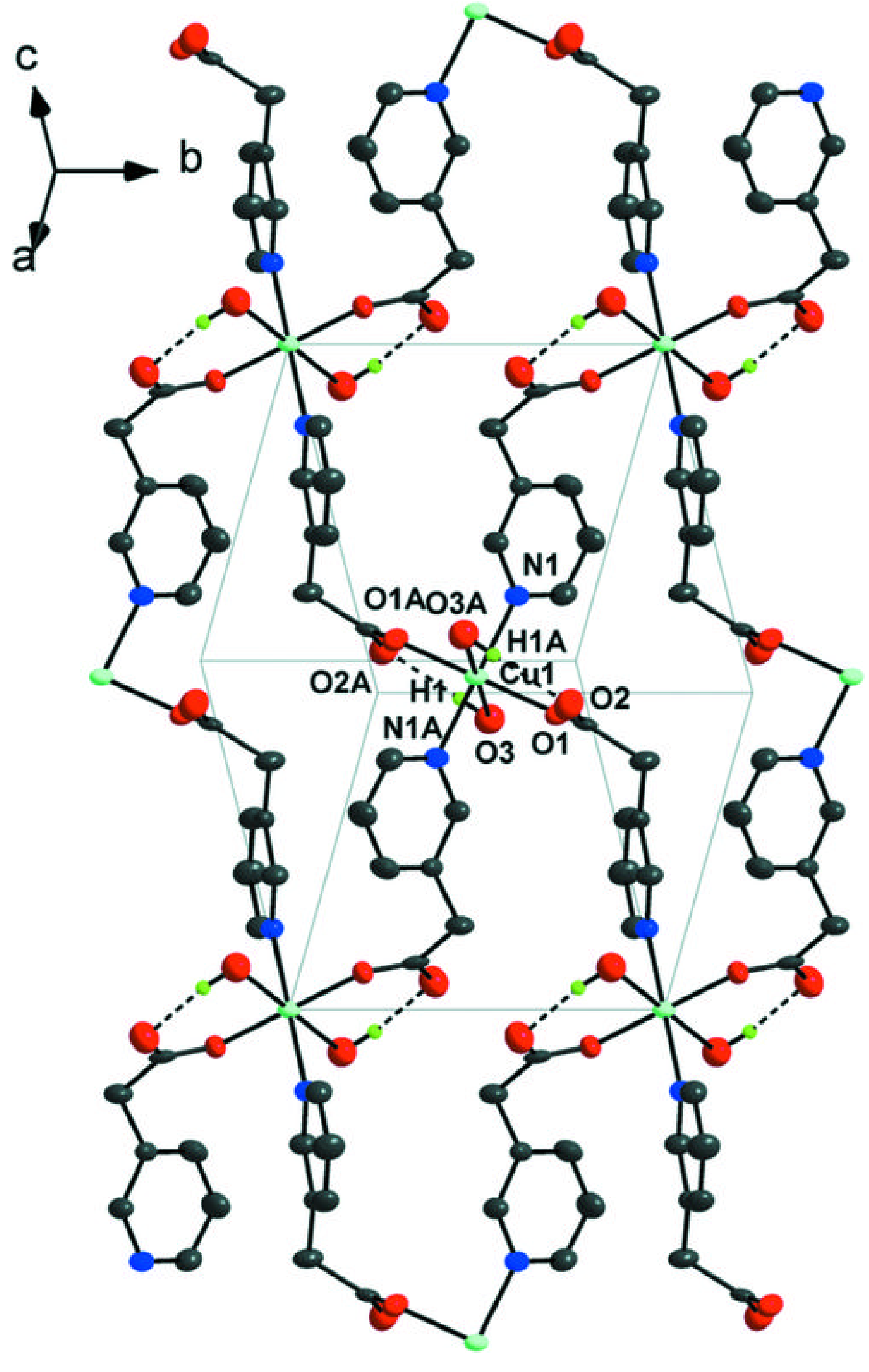

Fig. 2

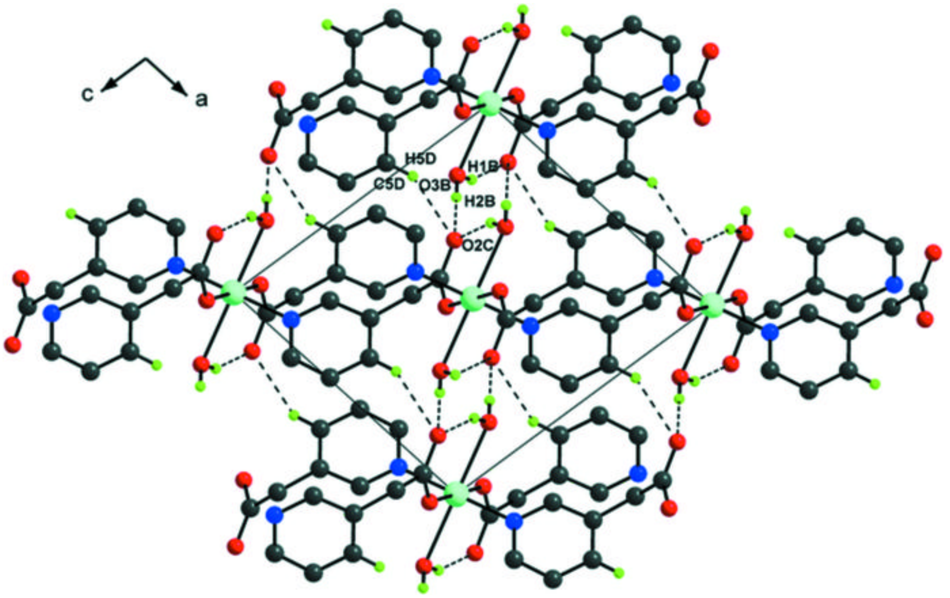

Fig. 3