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catena-Poly[4,4′-bipyridinium [bis(μ_3-pyrazole-3,5-dicarboxylato-$\kappa^5O^5,N^1:N^2,O^3:O^3$)dicopper(II)]]

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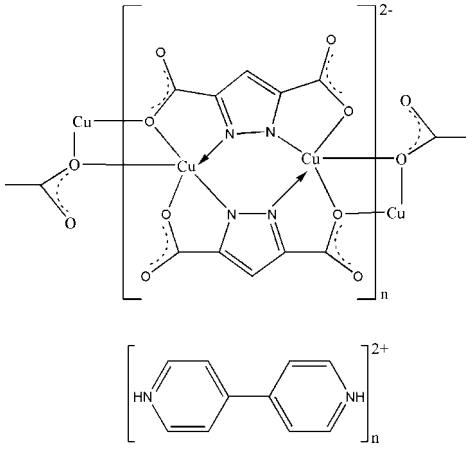
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.025; wR factor = 0.071; data-to-parameter ratio = 13.3.

The title compound, $\{(C_{10}H_{10}N_2)[Cu_2(C_5HN_2O_4)_2]\}_n$, has been synthesized under hydrothermal conditions. The self-assembly of the pyrazole-3,5-dicarboxylate ligands and Cu^{II} atoms results in a one-dimensional anionic chain, in which the Cu^{II} atom is five-coordinate in a square-pyramidal geometry. The doubly protonated 4,4′-bipyridine (bpy) cation lies on an inversion center. A two-dimensional supramolecular network is formed through N—H···O hydrogen bonds between the bpy cations and the uncoordinated carboxylate O atoms of the polymeric anions. The dinuclear repeat unit with two bridging pyrazole rings is centrosymmetric.

Related literature

For related literature, see: Chaudhuri (2003); Han *et al.* (2007); Koomen-Van Oudenniel *et al.* (1989); La Monica & Ardizzoia (1997); Sears & Wong (1999); Tanase *et al.* (2005); Thompson (2002).



Experimental

Crystal data

$(C_{10}H_{10}N_2)[Cu_2(C_5HN_2O_4)_2]$
M_r = 591.44
Monoclinic, $P2_1/c$
a = 8.1582 (18) Å
b = 6.3620 (12) Å
c = 18.679 (3) Å
β = 101.862 (15)°
V = 948.8 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.31 mm^{-1}
T = 293 (2) K
0.46 × 0.35 × 0.29 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.416, T_{max} = 0.554
(expected range = 0.384–0.511)
3105 measured reflections
2187 independent reflections
2032 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.071
S = 1.05
2187 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.9021 (16)	Cu1—O3^{i}	1.9889 (13)
Cu1—N2^{i}	1.9099 (15)	Cu1—O3^{ii}	2.7543 (15)
Cu1—O1	1.9647 (13)		
N1—Cu1—N2^{i}	93.64 (7)	O1—Cu1—O3^{i}	104.43 (6)
N1—Cu1—O1	81.29 (6)	N1—Cu1—O3^{ii}	92.88 (6)
N2^{i}—Cu1—O1	172.70 (6)	N2^{i}—Cu1—O3^{ii}	102.51 (6)
N1—Cu1—O3^{i}	173.89 (6)	O1—Cu1—O3^{ii}	83.08 (5)
N2^{i}—Cu1—O3^{i}	80.46 (6)	O3^{i}—Cu1—O3^{ii}	89.96 (5)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···O4	0.86	1.90	2.719 (2)	160

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); 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: HY2090).

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supplementary materials

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catena-Poly[4,4'-bipyridinium [bis(μ_3-pyrazole-3,5-dicarboxylato-$\kappa^5O^5,N^1:N^2,O^3:O^3$)dicopper(II)]]

Q.-Q. Dou, Y.-K. He, L.-T. Zhang and Z.-B. Han

Comment

Coordination chemistry of copper(II) complexes is a subject of continuing importance in connection with the structures and their magnetic properties (Tanase *et al.*, 2005). Particular interest has been directed towards the investigation of the copper(II) complexes, which have been intensively studied as a result of the efforts to understand the factors that are responsible for the magnetic-exchange interactions between uncoupled metal centers (Sears & Wong, 1999; Thompson, 2002; Chaudhuri, 2003; La Monica & Ardizzoia, 1997). We report here the synthesis and structure of a coordination polymer assembled by pyrazole-3,5-dicarboxylic acid (H_3pydc), 4,4'-bipyridine (bpy) and Cu^{II} ion.

The asymmetric unit of the title compound contains one Cu^{II} atom, one pydc ligand and a half protonated bpy ligand. Two centrosymmetric Cu^{II} atoms are bridged by a pair of anionic pydc ligands, forming a binuclear unit. The binuclear units are further connected by O3 atoms of adjacent units to form a one-dimensional zigzag chain (Han *et al.*, 2007). Each Cu^{II} atom is five-coordinated by three O atoms and two N atoms from three individual pydc ligands in a square-pyramidal coordination geometry (Fig. 1; Table 1). One intriguing feature of the structure is that there exist two bimetallic rings. One is a six-membered Cu_2N_4 ring with a Cu···Cu separation of 3.934 (3) Å. The other is a four-membered Cu_2O_2 ring with a Cu···Cu separation of 3.399 (3) Å. This short Cu···Cu separation is very similar to the distance observed in a structurally related copper complex recently reported (Koomen-Van Oudenniel *et al.*, 1989). Another interesting feature is that the zigzag chains are further extended into a three-dimensional supramolecular network (Fig. 2) though N—H···O hydrogen bonds between the carboxylate O atoms of the anionic $[Cu_2(pydc)_2]$ units and the protonated bpy molecules (Table 2).

Experimental

A mixture of $Cu(NO_3)_2{\cdot}3H_2O$(0.120 g, 0.5 mmol), pyrazole-3,5-dicarboxylic acid (0.087 g, 0.5 mmol), 4,4'-bipyridine (0.122 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and water (10 ml) was sealed in a 23 ml Teflon-lined reactor and heated at 473 K for 6 d. After cooled to room temperature at a rate of 5 K h^{-1}, black crystals of the title compound were obtained (yield 52%). Analysis calculated for $C_{20}H_{12}Cu_2N_6O_8$: C 40.60, H 2.00, N 14.25%; found: C 40.62, H 2.05, N 14.21%.

Refinement

H atoms were positioned geometrically and refined as riding, with C—H = 0.93 Å, N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(C,*N*).

Figures

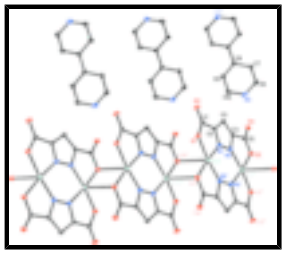

Fig. 1. One-dimensional chain structure in the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) −*x*, 2 − *y*, 1 − *z*; (ii) *x*, *y* − 1, *z*; (iii) −*x*, 1 − *y*, 1 − *z*.]

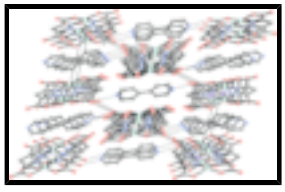

Fig. 2. Three-dimensional network of the title compound, showing the hydrogen-bonding interactions (dotted lines).

catena-Poly[4,4'-bipyridinium [bis(μ$_3$-pyrazole-3,5-dicarboxylato- $\kappa^5O^5,N^1:N^2,O^3:O^3$)dicopper(II)]]

Crystal data

$(C_{10}H_{10}N_2)[Cu_2(C_5HN_2O_4)_2]$	F_{000} = 592
M_r = 591.44	D_x = 2.070 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 2356 reflections
a = 8.1582 (18) Å	θ = 2.3–25.0º
b = 6.3620 (12) Å	μ = 2.31 mm^{-1}
c = 18.679 (3) Å	T = 293 (2) K
β = 101.862 (15)º	Block, black
V = 948.8 (3) Å^3	0.46 × 0.35 × 0.29 mm
Z = 2	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2187 independent reflections
Radiation source: fine-focus sealed tube	2032 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.018
T = 293(2) K	θ_{max} = 27.5º
φ and ω scan	θ_{min} = 2.2º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −10→1
T_{min} = 0.416, T_{max} = 0.554	k = −8→1
3105 measured reflections	l = −24→24

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.071$

$S = 1.05$

2187 reflections

164 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

$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.6043P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.38$ e Å^{-3}

$\Delta\rho_{min} = -0.36$ e Å^{-3}

Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0249 (13)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.11209 (3)	0.72576 (4)	0.501800 (11)	0.02128 (11)
C1	0.3356 (2)	0.7260 (3)	0.63644 (10)	0.0214 (4)
C2	0.2373 (2)	0.9262 (3)	0.63423 (9)	0.0197 (3)
C3	0.2260 (2)	1.1011 (3)	0.67817 (9)	0.0216 (4)
H3A	0.2843	1.1266	0.7256	0.026*
C4	0.1067 (2)	1.2288 (3)	0.63437 (10)	0.0201 (3)
C5	0.0225 (2)	1.4354 (3)	0.63753 (9)	0.0207 (3)
C6	0.3833 (3)	1.7140 (3)	0.85036 (11)	0.0309 (4)
H6A	0.4011	1.8292	0.8223	0.037*
C7	0.4729 (3)	1.6925 (3)	0.92106 (11)	0.0267 (4)
H7A	0.5494	1.7956	0.9413	0.032*
C8	0.4491 (2)	1.5165 (3)	0.96242 (9)	0.0202 (3)
C9	0.3284 (2)	1.3702 (3)	0.93080 (10)	0.0271 (4)
H9A	0.3078	1.2525	0.9571	0.033*
C10	0.2399 (3)	1.4006 (4)	0.86062 (10)	0.0303 (4)
H10A	0.1584	1.3043	0.8396	0.036*
N1	0.1315 (2)	0.9517 (2)	0.56971 (8)	0.0244 (3)
N2	0.0535 (2)	1.1346 (2)	0.56948 (8)	0.0248 (3)
N3	0.2707 (2)	1.5681 (3)	0.82268 (8)	0.0301 (4)
H3B	0.2158	1.5826	0.7785	0.036*
O1	0.29805 (16)	0.6162 (2)	0.57641 (7)	0.0238 (3)
O2	0.44127 (18)	0.6763 (3)	0.69028 (8)	0.0318 (3)
O3	−0.07916 (17)	1.4892 (2)	0.57719 (7)	0.0255 (3)
O4	0.04633 (18)	1.5447 (2)	0.69333 (7)	0.0278 (3)

Atomic displacement parameters (Å^2)

U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

Cu1	0.02635 (15)	0.01578 (14)	0.01696 (14)	0.00340 (8)	−0.00663 (9)	−0.00196 (7)
C1	0.0207 (8)	0.0222 (9)	0.0194 (8)	0.0004 (7)	0.0000 (7)	0.0038 (7)
C2	0.0210 (8)	0.0208 (8)	0.0147 (7)	−0.0008 (7)	−0.0027 (6)	0.0023 (6)
C3	0.0230 (8)	0.0251 (9)	0.0144 (7)	0.0003 (7)	−0.0018 (6)	0.0003 (7)
C4	0.0233 (8)	0.0193 (8)	0.0155 (8)	−0.0017 (7)	−0.0009 (7)	−0.0013 (6)
C5	0.0225 (8)	0.0202 (8)	0.0179 (7)	−0.0012 (7)	0.0006 (6)	−0.0021 (7)
C6	0.0363 (11)	0.0330 (11)	0.0225 (9)	0.0010 (9)	0.0040 (8)	0.0058 (8)
C7	0.0286 (9)	0.0272 (10)	0.0227 (9)	−0.0055 (8)	0.0013 (7)	0.0019 (8)
C8	0.0197 (8)	0.0250 (9)	0.0157 (8)	−0.0004 (7)	0.0029 (6)	−0.0009 (7)
C9	0.0274 (9)	0.0317 (10)	0.0207 (8)	−0.0073 (8)	0.0012 (7)	0.0009 (8)
C10	0.0287 (9)	0.0371 (11)	0.0225 (8)	−0.0053 (8)	−0.0010 (7)	−0.0052 (8)
N1	0.0309 (8)	0.0176 (7)	0.0194 (7)	0.0046 (6)	−0.0072 (6)	−0.0014 (6)
N2	0.0324 (8)	0.0170 (7)	0.0194 (7)	0.0051 (6)	−0.0079 (6)	−0.0018 (6)
N3	0.0312 (8)	0.0412 (10)	0.0150 (7)	0.0046 (8)	−0.0020 (6)	0.0002 (7)
O1	0.0253 (6)	0.0223 (7)	0.0205 (6)	0.0054 (5)	−0.0029 (5)	−0.0010 (5)
O2	0.0312 (7)	0.0358 (8)	0.0227 (6)	0.0097 (6)	−0.0075 (6)	0.0022 (6)
O3	0.0297 (7)	0.0214 (6)	0.0206 (6)	0.0056 (5)	−0.0062 (5)	−0.0051 (5)
O4	0.0327 (7)	0.0286 (7)	0.0189 (6)	0.0043 (6)	−0.0020 (5)	−0.0061 (5)

Geometric parameters (Å, °)

Cu1—N1	1.9021 (16)	C6—N3	1.333 (3)
Cu1—N2^{i}	1.9099 (15)	C6—C7	1.378 (3)
Cu1—O1	1.9647 (13)	C6—H6A	0.9300
Cu1—O3^{i}	1.9889 (13)	C7—C8	1.397 (3)
Cu1—O3^{ii}	2.7543 (15)	C7—H7A	0.9300
C1—O2	1.224 (2)	C8—C9	1.395 (3)
C1—O1	1.303 (2)	C8—C8^{iii}	1.492 (3)
C1—C2	1.501 (3)	C9—C10	1.374 (3)
C2—N1	1.340 (2)	C9—H9A	0.9300
C2—C3	1.397 (3)	C10—N3	1.332 (3)
C3—C4	1.396 (3)	C10—H10A	0.9300
C3—H3A	0.9300	N1—N2	1.326 (2)
C4—N2	1.342 (2)	N2—Cu1^{i}	1.9099 (15)
C4—C5	1.490 (2)	N3—H3B	0.8600
C5—O4	1.235 (2)	O3—Cu1^{i}	1.9889 (13)
C5—O3	1.300 (2)		
N1—Cu1—N2^{i}	93.64 (7)	N3—C6—H6A	120.3
N1—Cu1—O1	81.29 (6)	C7—C6—H6A	120.3
N2^{i}—Cu1—O1	172.70 (6)	C6—C7—C8	120.20 (19)
N1—Cu1—O3^{i}	173.89 (6)	C6—C7—H7A	119.9
N2^{i}—Cu1—O3^{i}	80.46 (6)	C8—C7—H7A	119.9
O1—Cu1—O3^{i}	104.43 (6)	C9—C8—C7	117.83 (16)
N1—Cu1—O3^{ii}	92.88 (6)	C9—C8—C8^{iii}	120.9 (2)
N2^{i}—Cu1—O3^{ii}	102.51 (6)	C7—C8—C8^{iii}	121.3 (2)
O1—Cu1—O3^{ii}	83.08 (5)	C10—C9—C8	119.79 (19)

$O3^{i}$—Cu1—$O3^{ii}$	89.96 (5)	C10—C9—H9A	120.1
O2—C1—O1	124.77 (18)	C8—C9—H9A	120.1
O2—C1—C2	121.57 (17)	N3—C10—C9	120.04 (19)
O1—C1—C2	113.66 (15)	N3—C10—H10A	120.0
N1—C2—C3	108.88 (16)	C9—C10—H10A	120.0
N1—C2—C1	111.66 (16)	N2—N1—C2	109.22 (15)
C3—C2—C1	139.41 (16)	N2—N1—Cu1	133.39 (12)
C4—C3—C2	103.99 (15)	C2—N1—Cu1	117.27 (13)
C4—C3—H3A	128.0	N1—N2—C4	108.85 (15)
C2—C3—H3A	128.0	N1—N2—$Cu1^{i}$	132.90 (12)
N2—C4—C3	109.06 (16)	C4—N2—$Cu1^{i}$	118.24 (13)
N2—C4—C5	111.32 (16)	C10—N3—C6	122.76 (17)
C3—C4—C5	139.62 (17)	C10—N3—H3B	118.6
O4—C5—O3	123.05 (17)	C6—N3—H3B	118.6
O4—C5—C4	122.45 (16)	C1—O1—Cu1	115.54 (12)
O3—C5—C4	114.50 (15)	C5—O3—$Cu1^{i}$	115.29 (12)
N3—C6—C7	119.33 (19)		
O2—C1—C2—N1	178.59 (18)	O1—Cu1—N1—N2	177.5 (2)
O1—C1—C2—N1	−0.8 (2)	$O3^{ii}$—Cu1—N1—N2	−99.92 (19)
O2—C1—C2—C3	1.8 (4)	$N2^{i}$—Cu1—N1—C2	178.31 (15)
O1—C1—C2—C3	−177.5 (2)	O1—Cu1—N1—C2	−6.97 (14)
N1—C2—C3—C4	−0.1 (2)	$O3^{ii}$—Cu1—N1—C2	75.58 (15)
C1—C2—C3—C4	176.7 (2)	C2—N1—N2—C4	−0.7 (2)
C2—C3—C4—N2	−0.3 (2)	Cu1—N1—N2—C4	175.05 (15)
C2—C3—C4—C5	−179.8 (2)	C2—N1—N2—$Cu1^{i}$	−179.60 (15)
N2—C4—C5—O4	176.42 (18)	Cu1—N1—N2—$Cu1^{i}$	−3.8 (3)
C3—C4—C5—O4	−4.0 (4)	C3—C4—N2—N1	0.6 (2)
N2—C4—C5—O3	−2.8 (2)	C5—C4—N2—N1	−179.69 (16)
C3—C4—C5—O3	176.8 (2)	C3—C4—N2—$Cu1^{i}$	179.69 (13)
N3—C6—C7—C8	1.8 (3)	C5—C4—N2—$Cu1^{i}$	−0.6 (2)
C6—C7—C8—C9	−2.5 (3)	C9—C10—N3—C6	−1.5 (3)
C6—C7—C8—$C8^{iii}$	176.7 (2)	C7—C6—N3—C10	0.3 (3)
C7—C8—C9—C10	1.2 (3)	O2—C1—O1—Cu1	175.90 (16)
$C8^{iii}$—C8—C9—C10	−178.0 (2)	C2—C1—O1—Cu1	−4.8 (2)
C8—C9—C10—N3	0.8 (3)	N1—Cu1—O1—C1	6.42 (14)
C3—C2—N1—N2	0.5 (2)	$O3^{i}$—Cu1—O1—C1	−175.75 (13)
C1—C2—N1—N2	−177.25 (16)	$O3^{ii}$—Cu1—O1—C1	−87.58 (13)
C3—C2—N1—Cu1	−176.01 (12)	O4—C5—O3—$Cu1^{i}$	−174.44 (14)
C1—C2—N1—Cu1	6.2 (2)	C4—C5—O3—$Cu1^{i}$	4.7 (2)
$N2^{i}$—Cu1—N1—N2	2.8 (2)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

N3—H3B···O4	0.86	1.90	2.719 (2)	160

Fig. 1

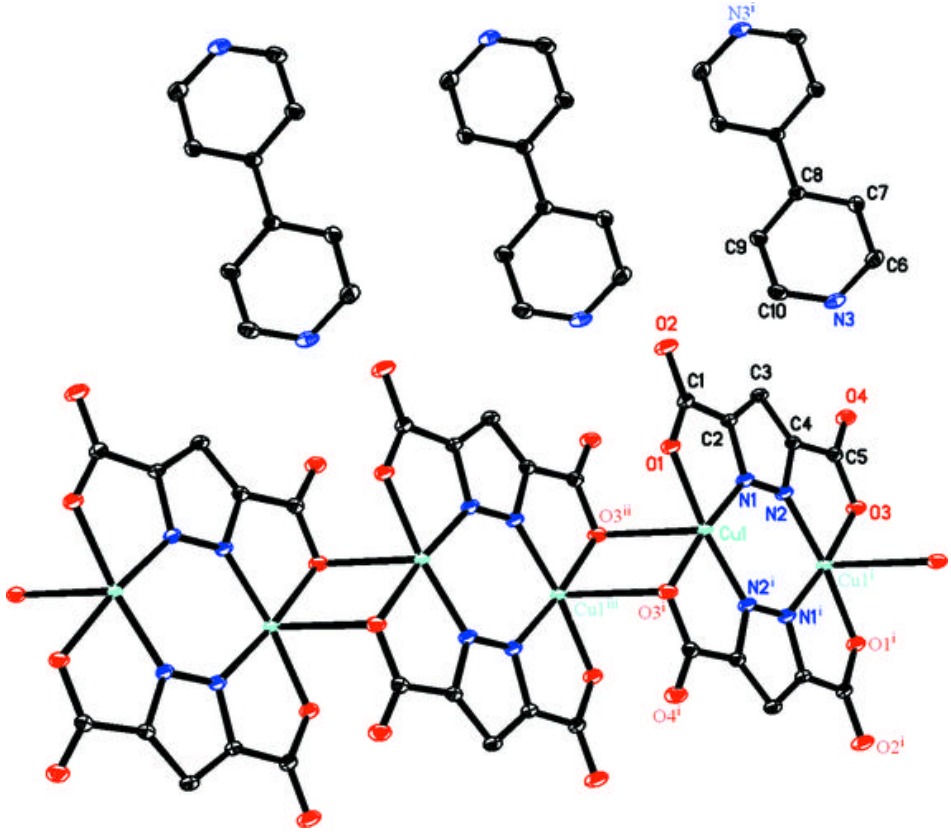

Fig. 2