Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

(2,9-Dimethyl-1,10-phenanthroline-κ^2N,N')bis(3-hydroxybenzoato-κO)copper(II)

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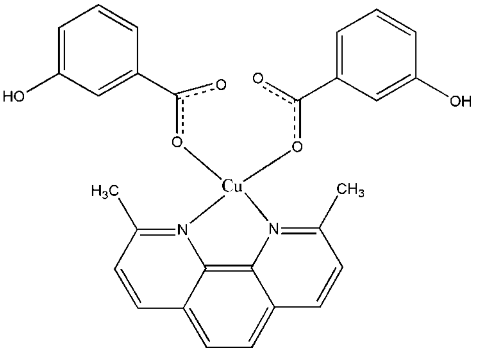
Received 16 August 2007; accepted 5 September 2007

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.004 Å; R factor = 0.038; wR factor = 0.105; data-to-parameter ratio = 13.4.

In the title compound, $[Cu(C_7H_5O_3)_2(C_{14}H_{12}N_2)]$, the Cu^{II} ion is located on a twofold rotation axis and is coordinated by a 2,9-dimethyl-1,10-phenanthroline (dmphen) molecule and two 3-hydroxybenzoate anions in a distorted tetrahedral geometry. Molecules are linked into a one-dimensional framework by O—H⋯O hydrogen bonding. The packing is further stabilized by π–π stacking between parallel dmphen rings of neighboring molecules, with a face-to-face distance of 3.385 (18) Å.

Related literature

For related literature, see: Wang *et al.* (1996); Wall *et al.* (1999); Naing *et al.* (1995).



Experimental

Crystal data

$[Cu(C_7H_5O_3)_2(C_{14}H_{12}N_2)]$
M_r = 546.02
Monoclinic, $C2/c$
a = 17.623 (3) Å
b = 14.587 (2) Å
c = 9.7581 (15) Å
β = 94.199 (2)°
V = 2501.8 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.92 mm^{-1}
T = 291 (2) K
0.44 × 0.33 × 0.24 mm

Data collection

Bruker SMART CCD area detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.690, T_{max} = 0.809
7268 measured reflections
2275 independent reflections
1766 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.105
S = 1.01
2275 reflections
170 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9509 (18)	Cu1—N1	2.022 (2)
O1—Cu1—O1^i	97.05 (11)	O1^i—Cu1—N1	102.00 (8)
O1—Cu1—N1	141.50 (8)	N1—Cu1—N1^i	83.20 (12)

Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3⋯O2^{ii}	0.82	1.90	2.688 (3)	160

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); 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, 1997); software used to prepare material for publication: *SHELXTL*.

Financial support of this work by the Science Fund of Henan Province for Distinguished Young Scholars (No. 074100510005) is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2313).

References

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doi:10.1107/S1600536807043449

supplementary materials

Acta Cryst. (2007). E**63**, m2523 [**doi:10.1107/S1600536807043449**]

(2,9-Dimethyl-1,10-phenanthroline-$\kappa^2 N,N'$)bis(3-hydroxybenzoato-κO) copper(II)

P.-Z. Zhao, F.-M. Yan, X.-P. Xuan and **Q.-H. Tang**

Comment

Metal-phenanthroline complexes and its derivatives have attracted much attention because of their peculiar features (Wang *et al.*, 1996; Wall *et al.*, 1999; Naing *et al.*, 1995). Recently, we obtained the title mononuclear copper(II) complex (I), by reaction of 2,9-dimethyl-1,10-phenanthroline, *m*-hydroxybenzoic acid and $Cu(NO_3)_2$ in an ethanol/water mixture. Here we report its crystal structure.

Each Cu^{II} ion is four-coordinated by two N atoms from a 2,9-dimethyl-1,10-phenanthroline ligand, and two O atoms from two *m*-hydroxybenzoic anions. The Cu^{II} ion locates on a twofold rotation axis, and CuO_2N_2 unit forms a distorted tetrahedral geometry (Fig. 1). The Cu1–N1 bond length is slightly longer than Cu1—O1 bond length (Table 1).

In the crystal structure, molecules are linked into a two dimensional framework by intermolecular O—H···O hydrogen bonds (Fig. 2). The crystal further stabilized by π-π interactions between the dmphen ring systems (Fig. 3). These intermolecular interactions occur between the parallel rings within offset face-to-face packing. The face-to-face distance of the parallel ring planes between the neighboring molecules related by $1 - x, 2 - y, 1 - z$ is 3.385 (18) Å.

Experimental

An aqueous solution (10 ml) of 3-hydroxybenzoic acid (0.0698 g, 0.5 mmol), NaOH (0.0198 g, 0.5 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.1212 g, 0.5 mmol) was mixed with an ethanol solution (10 ml) of 2,9-dimethyl-1,10-phenanthroline hemihydrate (0.1088 g, 0.5 mmol). The mixture was refluxed for 4 h. After cooling to room temperature the solution was filtered. The single crystals of the title compound were obtained after 3 weeks at room temperature.

Refinement

Methyl H and hydroxy H atoms were placed in calculated positions with C—H = 0.96 and O—H = 0.82 Å, and refined with free torsion angles to fit the electron density, $U_{iso}(H) = 1.5U_{eq}$(carrier). Other H atoms were placed in calculated positions with C—H = 0.93 Å and refined in the riding model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

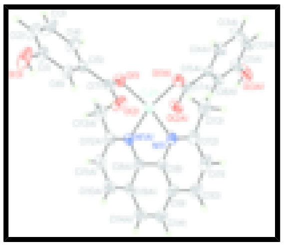

Fig. 1. The molecular structure of the title complex(I),with atom labels and 30% probability displacement ellipsoids for non-H atoms. Symmetry code for the symbol 'A': $-x + 1, y, -z + 3/2$

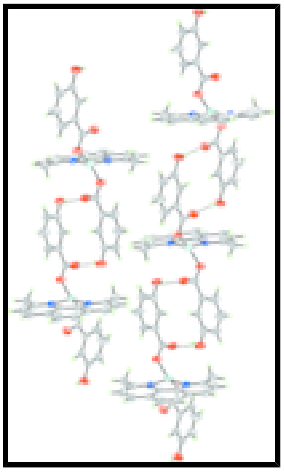

Fig. 2. The hydrogen-bonding motifs in the crystal structure of (I). Dashed lines indicate the hydrogen.

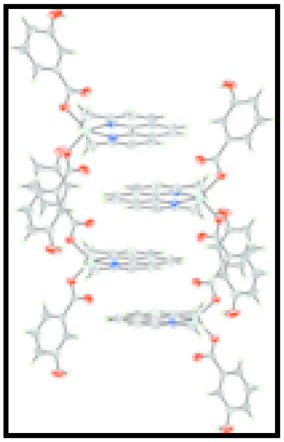

Fig. 3. The π-π interaction between the dmphen rings of neighboring molecules in the crystal structure of (I). Symmetry code: $-x + 1, y, -z + 3/2$

(2,9-Dimethyl-1,10-phenanthroline-κ^2*N*,*N*')bis(3-hydroxybenzoato-κ*O*) copper(II)

Crystal data

$[Cu(C_7H_5O_3)_2(C_{14}H_{12}N_2)]$	F_{000} = 1124
M_r = 546.02	D_x = 1.450 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 1908 reflections
a = 17.623 (3) Å	θ = 2.3–24.8°
b = 14.587 (2) Å	μ = 0.92 mm^{-1}

c = 9.7581 (15) Å
β = 94.199 (2)°
V = 2501.8 (7) Å^3
Z = 4

T = 291 (2) K
Block, yellow
0.44 × 0.33 × 0.24 mm

Data collection

Bruker SMART CCD area detector diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
T = 291(2) K
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1997)
T_{min} = 0.690, T_{max} = 0.809
7268 measured reflections

2275 independent reflections
1766 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 25.5°
θ_{min} = 2.3°
$h = -21 \rightarrow 21$
$k = -12 \rightarrow 17$
$l = -8 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.105
S = 1.01
2275 reflections
170 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
$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 1.4781P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$ = 0.001
$\Delta\rho_{\text{max}}$ = 0.28 e Å^{-3}
$\Delta\rho_{\text{min}}$ = −0.33 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	0.76339 (3)	0.7500	0.0548 (2)

O1	0.48033 (10)	0.67482 (13)	0.89294 (19)	0.0591 (5)
O2	0.37612 (12)	0.75613 (14)	0.8785 (2)	0.0708 (6)
O3	0.22168 (12)	0.6282 (2)	1.2567 (3)	0.0946 (9)
H3	0.2009	0.6713	1.2151	0.142*
N1	0.44985 (11)	0.86705 (14)	0.6396 (2)	0.0475 (5)
C1	0.28890 (14)	0.6092 (2)	1.2022 (3)	0.0569 (7)
C2	0.32881 (17)	0.5350 (2)	1.2543 (3)	0.0758 (9)
H2	0.3098	0.4999	1.3236	0.091*
C3	0.3970 (2)	0.5128 (2)	1.2036 (4)	0.0938 (13)
H3A	0.4242	0.4623	1.2389	0.113*
C4	0.42579 (18)	0.5645 (2)	1.1005 (3)	0.0761 (10)
H4	0.4725	0.5494	1.0680	0.091*
C5	0.38563 (14)	0.63782 (16)	1.0463 (2)	0.0443 (6)
C6	0.31729 (14)	0.66047 (19)	1.0984 (3)	0.0515 (6)
H6	0.2900	0.7109	1.0632	0.062*
C7	0.41479 (14)	0.69351 (17)	0.9321 (2)	0.0455 (6)
C8	0.47227 (14)	0.95027 (18)	0.6924 (2)	0.0480 (6)
C9	0.44369 (17)	1.0339 (2)	0.6395 (3)	0.0588 (7)
C10	0.38814 (19)	1.0287 (2)	0.5295 (3)	0.0714 (9)
H10	0.3674	1.0822	0.4908	0.086*
C11	0.36452 (17)	0.9460 (3)	0.4793 (3)	0.0687 (9)
H11	0.3272	0.9432	0.4069	0.082*
C12	0.39594 (15)	0.8639 (2)	0.5356 (3)	0.0560 (7)
C13	0.36969 (19)	0.7725 (2)	0.4826 (3)	0.0752 (9)
H13A	0.4130	0.7357	0.4642	0.113*
H13B	0.3378	0.7804	0.3994	0.113*
H13C	0.3414	0.7424	0.5501	0.113*
C14	0.47253 (19)	1.1177 (2)	0.6983 (3)	0.0738 (9)
H14	0.4530	1.1732	0.6646	0.089*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0702 (3)	0.0494 (3)	0.0457 (3)	0.000	0.0106 (2)	0.000
O1	0.0571 (11)	0.0621 (12)	0.0615 (12)	0.0067 (9)	0.0269 (9)	0.0056 (9)
O2	0.0672 (13)	0.0720 (14)	0.0761 (14)	0.0143 (10)	0.0260 (11)	0.0323 (11)
O3	0.0623 (13)	0.139 (2)	0.0871 (16)	0.0299 (13)	0.0399 (12)	0.0534 (15)
N1	0.0468 (11)	0.0572 (14)	0.0403 (11)	−0.0009 (10)	0.0155 (9)	0.0027 (10)
C1	0.0466 (14)	0.0730 (19)	0.0524 (16)	0.0042 (13)	0.0124 (12)	0.0153 (14)
C2	0.070 (2)	0.086 (2)	0.074 (2)	0.0079 (17)	0.0206 (17)	0.0384 (18)
C3	0.096 (3)	0.082 (2)	0.108 (3)	0.037 (2)	0.040 (2)	0.055 (2)
C4	0.078 (2)	0.073 (2)	0.083 (2)	0.0322 (17)	0.0380 (18)	0.0270 (17)
C5	0.0506 (14)	0.0424 (14)	0.0413 (13)	0.0013 (11)	0.0121 (11)	−0.0004 (11)
C6	0.0513 (14)	0.0554 (16)	0.0489 (15)	0.0092 (12)	0.0111 (12)	0.0128 (12)
C7	0.0508 (14)	0.0440 (15)	0.0429 (13)	−0.0012 (12)	0.0110 (11)	−0.0038 (11)
C8	0.0549 (15)	0.0510 (16)	0.0410 (13)	0.0027 (12)	0.0239 (11)	0.0029 (11)
C9	0.0705 (18)	0.0584 (18)	0.0513 (16)	0.0077 (14)	0.0311 (15)	0.0102 (14)
C10	0.081 (2)	0.077 (2)	0.0592 (19)	0.0209 (18)	0.0271 (17)	0.0202 (17)

C11	0.0601 (18)	0.096 (3)	0.0507 (17)	0.0072 (17)	0.0110 (14)	0.0189 (17)
C12	0.0492 (14)	0.073 (2)	0.0478 (15)	−0.0022 (13)	0.0183 (12)	0.0058 (14)
C13	0.0652 (19)	0.096 (3)	0.064 (2)	−0.0180 (17)	−0.0016 (16)	−0.0019 (17)
C14	0.106 (3)	0.0518 (18)	0.069 (2)	0.0085 (16)	0.0412 (17)	0.0083 (14)

Geometric parameters (Å, °)

Cu1—O1	1.9509 (18)	C5—C6	1.381 (3)
Cu1—O1^{i}	1.9509 (18)	C5—C7	1.500 (3)
Cu1—N1	2.022 (2)	C6—H6	0.9300
Cu1—N1^{i}	2.022 (2)	C8—C9	1.403 (4)
O1—C7	1.272 (3)	C8—C8^{i}	1.434 (5)
O2—C7	1.233 (3)	C9—C10	1.400 (4)
O3—C1	1.362 (3)	C9—C14	1.428 (4)
O3—H3	0.8200	C10—C11	1.356 (4)
N1—C12	1.339 (3)	C10—H10	0.9300
N1—C8	1.366 (3)	C11—C12	1.413 (4)
C1—C2	1.367 (4)	C11—H11	0.9300
C1—C6	1.382 (4)	C12—C13	1.492 (4)
C2—C3	1.372 (4)	C13—H13A	0.9600
C2—H2	0.9300	C13—H13B	0.9600
C3—C4	1.383 (4)	C13—H13C	0.9600
C3—H3A	0.9300	C14—C14^{i}	1.346 (7)
C4—C5	1.367 (4)	C14—H14	0.9300
C4—H4	0.9300		

O1—Cu1—O1^{i}	97.05 (11)	C1—C6—H6	119.6
O1—Cu1—N1	141.50 (8)	O2—C7—O1	121.2 (2)
O1^{i}—Cu1—N1	102.00 (8)	O2—C7—C5	120.5 (2)
O1—Cu1—N1^{i}	102.00 (8)	O1—C7—C5	118.3 (2)
O1^{i}—Cu1—N1^{i}	141.50 (8)	N1—C8—C9	123.2 (2)
N1—Cu1—N1^{i}	83.20 (12)	N1—C8—C8^{i}	117.22 (14)
C7—O1—Cu1	106.58 (16)	C9—C8—C8^{i}	119.62 (17)
C1—O3—H3	109.5	C10—C9—C8	116.6 (3)
C12—N1—C8	119.1 (2)	C10—C9—C14	124.2 (3)
C12—N1—Cu1	129.51 (19)	C8—C9—C14	119.2 (3)
C8—N1—Cu1	111.12 (16)	C11—C10—C9	120.2 (3)
O3—C1—C2	117.1 (2)	C11—C10—H10	119.9
O3—C1—C6	123.2 (2)	C9—C10—H10	119.9
C2—C1—C6	119.8 (2)	C10—C11—C12	120.8 (3)
C1—C2—C3	119.6 (3)	C10—C11—H11	119.6
C1—C2—H2	120.2	C12—C11—H11	119.6
C3—C2—H2	120.2	N1—C12—C11	120.1 (3)
C2—C3—C4	120.7 (3)	N1—C12—C13	118.6 (3)
C2—C3—H3A	119.6	C11—C12—C13	121.3 (3)
C4—C3—H3A	119.6	C12—C13—H13A	109.5
C5—C4—C3	120.1 (3)	C12—C13—H13B	109.5
C5—C4—H4	120.0	H13A—C13—H13B	109.5

C3—C4—H4	120.0	C12—C13—H13C	109.5
C4—C5—C6	119.0 (2)	H13A—C13—H13C	109.5
C4—C5—C7	121.0 (2)	H13B—C13—H13C	109.5
C6—C5—C7	120.0 (2)	C14^{i}—C14—C9	121.10 (18)
C5—C6—C1	120.8 (2)	C14^{i}—C14—H14	119.4
C5—C6—H6	119.6	C9—C14—H14	119.4

O1^{i}—Cu1—O1—C7	−124.17 (18)	C6—C5—C7—O2	−4.3 (4)
N1—Cu1—O1—C7	−4.7 (2)	C4—C5—C7—O1	−4.7 (4)
N1^{i}—Cu1—O1—C7	89.48 (17)	C6—C5—C7—O1	175.2 (2)
O1—Cu1—N1—C12	−74.0 (2)	C12—N1—C8—C9	−2.6 (3)
O1^{i}—Cu1—N1—C12	43.9 (2)	Cu1—N1—C8—C9	−177.13 (18)
N1^{i}—Cu1—N1—C12	−174.8 (2)	C12—N1—C8—C8^{i}	177.4 (2)
O1—Cu1—N1—C8	99.75 (19)	Cu1—N1—C8—C8^{i}	2.8 (3)
O1^{i}—Cu1—N1—C8	−142.29 (15)	N1—C8—C9—C10	1.7 (4)
N1^{i}—Cu1—N1—C8	−1.00 (11)	C8^{i}—C8—C9—C10	−178.3 (3)
O3—C1—C2—C3	−179.8 (4)	N1—C8—C9—C14	−177.8 (2)
C6—C1—C2—C3	0.5 (5)	C8^{i}—C8—C9—C14	2.3 (4)
C1—C2—C3—C4	0.0 (6)	C8—C9—C10—C11	0.0 (4)
C2—C3—C4—C5	−1.1 (6)	C14—C9—C10—C11	179.4 (3)
C3—C4—C5—C6	1.6 (5)	C9—C10—C11—C12	−0.7 (4)
C3—C4—C5—C7	−178.5 (3)	C8—N1—C12—C11	1.8 (3)
C4—C5—C6—C1	−1.1 (4)	Cu1—N1—C12—C11	175.13 (17)
C7—C5—C6—C1	179.0 (2)	C8—N1—C12—C13	−177.5 (2)
O3—C1—C6—C5	−179.6 (3)	Cu1—N1—C12—C13	−4.2 (3)
C2—C1—C6—C5	0.0 (5)	C10—C11—C12—N1	−0.2 (4)
Cu1—O1—C7—O2	1.7 (3)	C10—C11—C12—C13	179.1 (3)
Cu1—O1—C7—C5	−177.83 (17)	C10—C9—C14—C14^{i}	−178.2 (3)
C4—C5—C7—O2	175.8 (3)	C8—C9—C14—C14^{i}	1.2 (5)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2^{ii}	0.82	1.90	2.688 (3)	160

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

Fig. 1

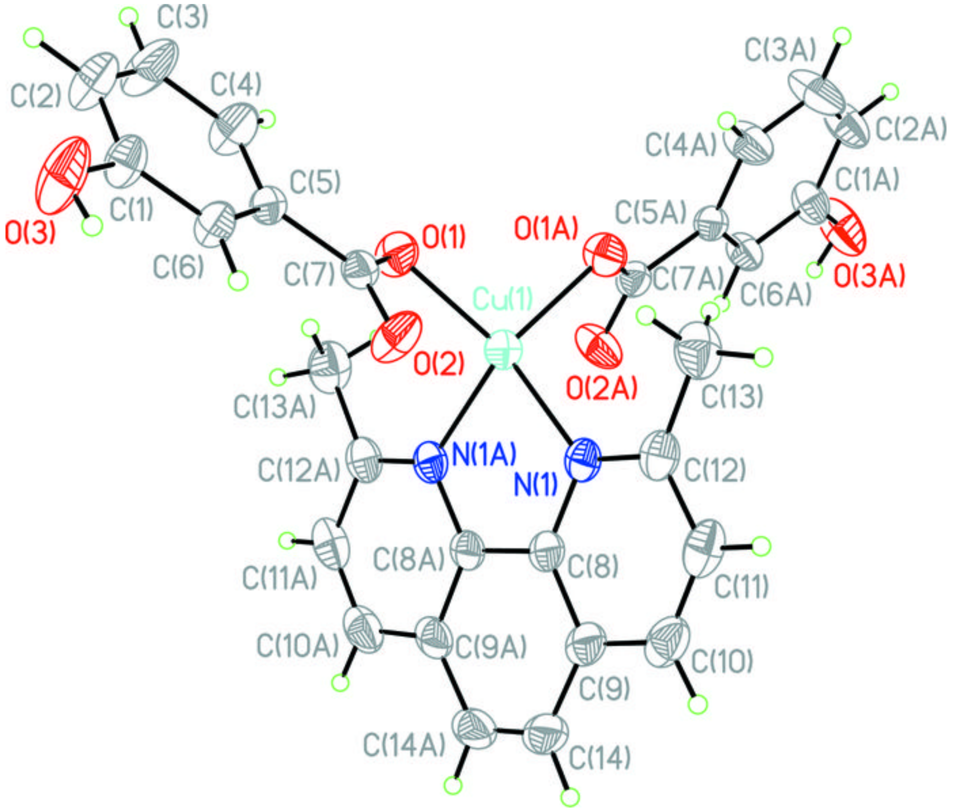
C(3)
C(2)
C(4)
C(1)
O(3)
C(5)
C(6)
C(7)
O(1)
O(2)
C(13A)
C(3A)
C(2A)
C(4A)
C(1A)
C(5A)
O(1A)
C(7A)
C(6A)
O(3A)
Cu(1)
O(2A)
C(13)
C(12A)
N(1A)
N(1)
C(12)
C(11A)
C(8A)
C(8)
C(11)
C(10A)
C(9A)
C(9)
C(10)
C(14A)
C(14)

Fig. 2

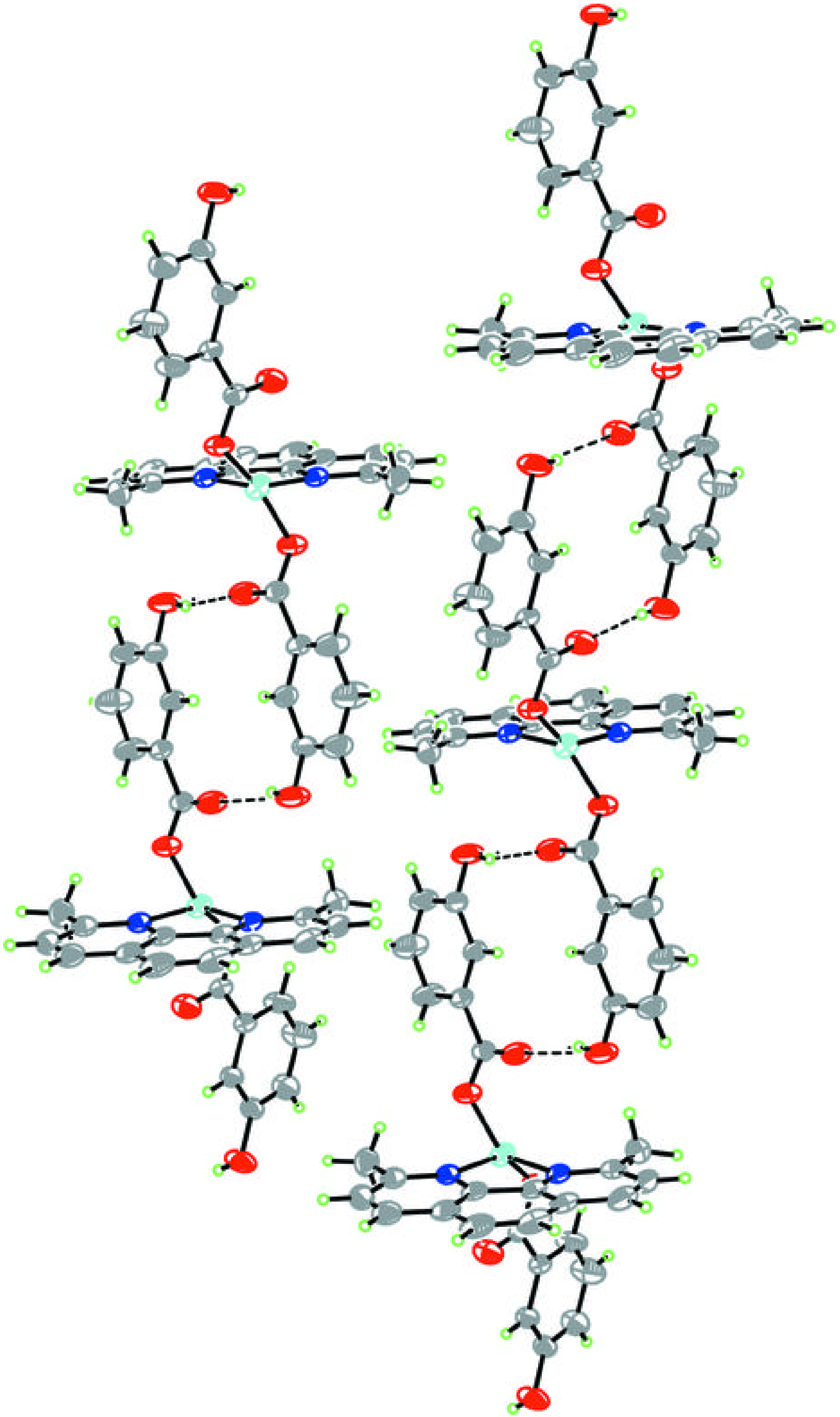

Fig. 3