Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Aqua(5-nitro-1*H*-benzimidazole)-(oxydiacetato)copper(II)

Wan-Ju Zhang,[a] Yan-Tuan Li[a]* and Zhi-Yong Wu[b]

[a]Marine Drug and Food Institute, Ocean University of China, 266003 Qingdao, People's Republic of China, and [b]Key Laboratory of Marine Drugs, Chinese Ministry of Education, Ocean University of China, 266003 Qingdao, People's Republic of China
Correspondence e-mail: yantuanli@ouc.edu.cn

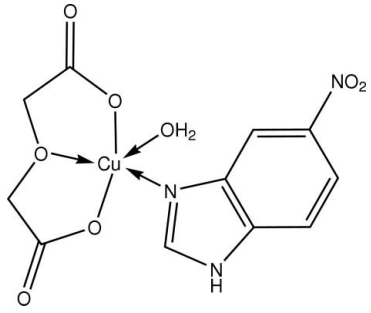
Received 27 October 2007; accepted 1 November 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.031; wR factor = 0.082; data-to-parameter ratio = 11.9.

In the molecule of the title compound, $[Cu(C_4H_4O_5)(C_7H_5N_3O_2)(H_2O)]$, the Cu^{II} atom is coordinated by one tridentate oxydiacetate (ODA) dianion, one monodentate nitrobenzimidazole (NBZIM) molecule and one H_2O molecule, in a distorted square-based pyramidal geometry. In the crystal structure, O—H···O, N—H···O and C—H···O hydrogen bonds link the molecules, forming a three-dimensional network. π–π Stacking interactions between parallel NBZIM rings consolidate the supramolecular structure [the shortest interplanar distances are 3.360 (3) and 3.269 (3) Å].

Related literature

For general background, see: Vigato *et al.* (1990); Bouwman *et al.* (1990); Ruttimann *et al.* (1992). For related structures, see: Cao *et al.* (2004).



Experimental

Crystal data

$[Cu(C_4H_4O_5)(C_7H_5N_3O_2)(H_2O)]$
M_r = 376.77
Triclinic, $P\overline{1}$
a = 6.961 (3) Å
b = 9.190 (4) Å
c = 11.691 (5) Å
α = 68.694 (5)°
β = 87.316 (5)°
γ = 84.623 (5)°
V = 693.6 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.62 mm^{-1}
T = 298 (2) K
0.48 × 0.31 × 0.27 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.509, T_{max} = 0.668
3708 measured reflections
2470 independent reflections
2007 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.082
S = 1.06
2470 reflections
208 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9450 (19)	Cu1—O4	1.957 (2)
Cu1—N1	1.945 (2)	Cu1—O8	2.321 (2)
Cu1—O3	1.955 (2)		
O1—Cu1—N1	98.39 (8)	O3—Cu1—O4	81.33 (8)
O1—Cu1—O3	82.00 (8)	O1—Cu1—O8	94.16 (9)
N1—Cu1—O3	176.16 (9)	N1—Cu1—O8	94.12 (8)
O1—Cu1—O4	159.71 (9)	O3—Cu1—O8	89.66 (9)
N1—Cu1—O4	97.48 (8)	O4—Cu1—O8	97.21 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H1W···O5^{i}	0.79	2.00	2.788 (3)	170
O8—H2W···O5^{ii}	0.79	2.03	2.810 (3)	172
N2—H2···O2^{iii}	0.86	1.85	2.708 (3)	179
C7—H7···O8^{iv}	0.93	2.59	3.322 (3)	135

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the National Natural Science Foundation of China (grant No. 30672515) and the Natural Science Foundation of Qingdao City (grant No. 06–2-2–11-jch).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2356).

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supplementary materials

Acta Cryst. (2007). E**63**, m2962-m2963 [**doi:10.1107/S1600536807055225**]

Aqua(5-nitro-1*H*-benzimidazole)(oxydiacetato)copper(II)

W.-J. Zhang, Y.-T. Li and Z.-Y. Wu

Comment

Benzimidazole transition metal complexes are of great interest of relevance to metalloproteins such as haemoglobin, haemocyanin and blue-copper proteins (Vigato *et al.*, 1990; Bouwman *et al.*, 1990). They are also used as mimics of the self-assembling process (Ruttimann *et al.*, 1992). These potential and versatile applications are stimulating researchers to synthesize new complexes containing benzimidazoles with potential chemical and biological properties. We report herein the crystal structure of the title compound, (I), a Cu^{II} complex with oxydiacetate (ODA) and nitrobenzimidazole (NBZIM).

In the molecule of (I) (Fig. 1), the Cu^{II} atom is coordinated by one (ODA) dianion, one NBZIM molecule and one H_2O molecule, in a distorted square base pyramidal coordination geometry (Table 1). The O1, O3 and O4 donor atoms from the tridentate ODA ligand and N1 atom of NBZIM define the square base, whereas the apical position is occupied by O8 oxygen atom of water. N1, O1, O3 and O4 are similarly displaced from the mean plane of such base [deviations from 0.0600 (9) to 0.0796 (12) Å]. The Cu^{II} atom displaces 0.1334 (11) Å from the plane towards O8 oxygen atom.

Different from another similar complex $[Cu(BZIM)(ODA)(H_2O)]_n$ (BZIM = benzimidazole) (Cao *et al.*, 2004), the ODA ion in (I) behaves as a tridentate ligand and the chelating Cu^{II} atom is in a meridional coordination mode. It forms two five-membered chelating rings; A (Cu1/O1/O3/C1/C2) and B (Cu1/O3/O4/C3/C4) around the Cu^{II} atom. Ring A is nearly planar, [the maximum deviation being 0.008 (2) Å (for atom C2)], whereas ring B has an envelope conformation with atom Cu1 displaced by 0.266(%) Å from the plane of the other ring atoms. The NBZIM molecule coordinates to the Cu^{II} atom in a monodentate fashion. The nitro group is co-planar with the benzimidazole ring [the maximum atomic deviation is 0.514 (4) Å (for atom O7)].

In the crystal structure, O—H···O, N—H···O and C—H···O hydrogen bonds (Table 2, Fig. 2) link the molecules to form a three-dimensional network. A supramolecular structure is consolidated by two types of strong π-π stacking interactions between neighboring parallel NBZIM ring systems [symmetry codes: 1 − *x*, 1 − *y*, −*z* and −*x*, 1 − *y*, −*z*.]. The shortest interplanar distances are 3.360 (3) Å and 3.269 (3) Å, respectively.

Experimental

For the preparation of the title compound, oxydiacetic acid (27 mg, 0.2 mmol) and sodium carbonate (21 mg, 0.2 mmol) were dissolved in water (5 ml). A methanol solution containing copper dichloride dihydrate (34 mg, 0.2 mmol) was then slowly added with continuous stirring. After 30 min, 5 ml me thanol solution of nitrobenzimidazole (33 mg, 0.2 mmol) was added dropwise to the reaction solution. The mixture was refluxed for 5 h and then slowly filtered. Blue single crystals of the title compound were obtained from the filtrate after 7 d. Analysis calculated for $C_{11}H_{11}CuN_3O_8$: C 35.07, H 2.94, N 11.15%; found: C 35.10, H 3.00, N 11.21%.

Refinement

H atoms (for H_2O) were located in difference syntheses and constrained to ride on their parent atom [O—H = 0.7950, 0.7851 Å and U_{iso}(H) = 1.95U_{eq}(O)]. The remaining H atoms were positioned geometrically, with N—H = 0.86 Å (for NH) and C—H = 0.93 and 0.97 Å, for aromatic and methylene H atoms and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C,*N*).

Figures

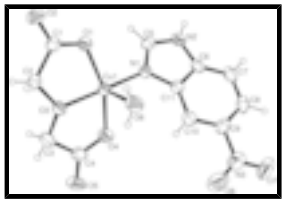

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level

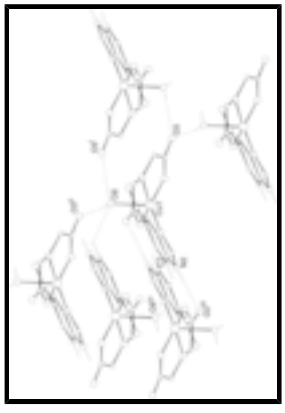

Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding were omitted for clarity [symmetry codes: (i) −*x*, 1 − *y*, 1 − *z*; (ii) 1 + *x*, *y*, *z*; (iii) 1 − *x*, 2 − *y*, −*z*; (iv) 1 − *x*, 1 − *y*, −*z*].

Aqua(6-nitro-1*H*-benzimidazole)(oxydiacetato)copper(II)

Crystal data

$[Cu(C_4H_4O_5)(C_7H_5N_3O_2)(H_2O)]$	$Z = 2$
$M_r = 376.77$	$F_{000} = 382$
Triclinic, $P\overline{1}$	$D_x = 1.804$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
$a = 6.961$ (3) Å	Cell parameters from 1984 reflections
$b = 9.190$ (4) Å	θ = 2.4–27.9º
$c = 11.691$ (5) Å	μ = 1.62 mm^{-1}
α = 68.694 (5)º	$T = 298$ (2) K
β = 87.316 (5)º	Block, green
γ = 84.623 (5)º	0.48 × 0.31 × 0.27 mm
$V = 693.6$ (5) Å^3	

Data collection

Bruker CCD area-detector diffractometer	2470 independent reflections
Radiation source: fine-focus sealed tube	2007 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.015$
$T = 298(2)$ K	$\theta_{max} = 25.2^{o}$
φ and ω scans	$\theta_{min} = 1.9^{o}$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -8\rightarrow8$
$T_{min} = 0.510$, $T_{max} = 0.668$	$k = -5\rightarrow11$
3708 measured reflections	$l = -13\rightarrow14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.031$	H-atom parameters constrained
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.3047P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2470 reflections	$\Delta\rho_{max} = 0.52$ e Å^{-3}
208 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-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 $F^2 > 2$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	0.24432 (5)	0.75145 (4)	0.25300 (3)	0.03187 (13)
O1	0.4483 (3)	0.8870 (2)	0.24224 (16)	0.0340 (5)
O2	0.5871 (3)	1.0114 (3)	0.34360 (18)	0.0491 (6)
O3	0.2009 (3)	0.7724 (3)	0.41289 (19)	0.0483 (6)
O4	−0.0046 (3)	0.6608 (3)	0.29471 (18)	0.0417 (5)

O5	−0.2437 (3)	0.6150 (3)	0.43260 (18)	0.0455 (5)
O6	0.1047 (4)	0.1687 (3)	0.2491 (2)	0.0640 (7)
O7	0.1297 (4)	0.1101 (3)	0.0858 (3)	0.0603 (7)
O8	0.4380 (3)	0.5216 (2)	0.34517 (17)	0.0410 (5)
H1W	0.3824	0.4730	0.4061	0.080*
H2W	0.5309	0.5511	0.3624	0.080*
N1	0.2740 (3)	0.7418 (3)	0.08959 (19)	0.0281 (5)
N2	0.3290 (3)	0.8066 (3)	−0.1096 (2)	0.0337 (5)
N3	0.1424 (4)	0.2014 (3)	0.1398 (3)	0.0449 (7)
C1	0.4652 (4)	0.9264 (3)	0.3348 (2)	0.0333 (6)
C2	0.3239 (4)	0.8678 (3)	0.4418 (2)	0.0360 (7)
H2A	0.3932	0.8077	0.5166	0.043*
H2B	0.2491	0.9556	0.4541	0.043*
C3	0.0111 (4)	0.7501 (4)	0.4616 (3)	0.0388 (7)
H3A	−0.0585	0.8502	0.4520	0.047*
H3B	0.0150	0.6861	0.5483	0.047*
C4	−0.0883 (4)	0.6686 (3)	0.3913 (2)	0.0331 (6)
H2	0.3554	0.8634	−0.1842	0.040*
C5	0.3159 (4)	0.8532 (3)	−0.0143 (2)	0.0325 (6)
H5	0.3345	0.9547	−0.0204	0.039*
C6	0.2930 (4)	0.6519 (3)	−0.0676 (2)	0.0294 (6)
C7	0.2858 (4)	0.5453 (4)	−0.1271 (3)	0.0367 (7)
H7	0.3115	0.5737	−0.2108	0.044*
C8	0.2395 (4)	0.3980 (4)	−0.0573 (3)	0.0381 (7)
H8	0.2332	0.3234	−0.0932	0.046*
C9	0.2015 (4)	0.3589 (3)	0.0685 (3)	0.0330 (6)
C10	0.2107 (4)	0.4606 (3)	0.1305 (2)	0.0308 (6)
H10	0.1873	0.4305	0.2145	0.037*
C11	0.2573 (4)	0.6106 (3)	0.0590 (2)	0.0258 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0323 (2)	0.0444 (2)	0.0285 (2)	−0.01726 (15)	0.00659 (13)	−0.02199 (16)
O1	0.0370 (11)	0.0443 (12)	0.0268 (10)	−0.0188 (9)	0.0052 (8)	−0.0170 (9)
O2	0.0606 (14)	0.0634 (15)	0.0330 (11)	−0.0393 (12)	0.0052 (10)	−0.0213 (10)
O3	0.0463 (13)	0.0768 (16)	0.0457 (12)	−0.0397 (12)	0.0233 (10)	−0.0450 (12)
O4	0.0381 (11)	0.0596 (14)	0.0377 (11)	−0.0229 (10)	0.0080 (9)	−0.0265 (10)
O5	0.0327 (11)	0.0621 (14)	0.0394 (12)	−0.0206 (10)	0.0063 (9)	−0.0123 (11)
O6	0.0870 (19)	0.0435 (14)	0.0569 (16)	−0.0176 (13)	−0.0015 (14)	−0.0094 (12)
O7	0.0625 (16)	0.0414 (13)	0.0909 (19)	−0.0059 (12)	−0.0105 (14)	−0.0387 (13)
O8	0.0429 (12)	0.0513 (13)	0.0311 (10)	−0.0126 (10)	0.0020 (9)	−0.0158 (10)
N1	0.0294 (12)	0.0343 (13)	0.0265 (12)	−0.0094 (10)	0.0021 (9)	−0.0165 (10)
N2	0.0324 (13)	0.0458 (15)	0.0251 (12)	−0.0138 (11)	0.0050 (10)	−0.0136 (11)
N3	0.0357 (15)	0.0383 (15)	0.0616 (19)	0.0005 (12)	−0.0113 (13)	−0.0186 (14)
C1	0.0404 (16)	0.0359 (16)	0.0271 (14)	−0.0137 (13)	0.0002 (12)	−0.0132 (12)
C2	0.0459 (17)	0.0421 (17)	0.0285 (14)	−0.0191 (14)	0.0028 (12)	−0.0195 (13)
C3	0.0329 (16)	0.0543 (19)	0.0356 (16)	−0.0120 (14)	0.0113 (12)	−0.0232 (14)

C4	0.0283 (15)	0.0394 (17)	0.0304 (15)	−0.0086 (13)	0.0003 (12)	−0.0097 (13)
C5	0.0321 (15)	0.0350 (16)	0.0352 (16)	−0.0119 (12)	0.0016 (12)	−0.0163 (13)
C6	0.0191 (13)	0.0436 (17)	0.0314 (14)	−0.0059 (12)	0.0020 (10)	−0.0200 (13)
C7	0.0294 (15)	0.056 (2)	0.0343 (15)	−0.0065 (14)	0.0026 (12)	−0.0275 (15)
C8	0.0271 (15)	0.0507 (19)	0.0514 (18)	0.0000 (13)	−0.0055 (13)	−0.0364 (16)
C9	0.0219 (14)	0.0319 (15)	0.0496 (17)	−0.0035 (11)	−0.0052 (12)	−0.0193 (13)
C10	0.0266 (14)	0.0375 (16)	0.0305 (14)	−0.0045 (12)	−0.0017 (11)	−0.0142 (12)
C11	0.0204 (13)	0.0341 (15)	0.0281 (13)	−0.0054 (11)	−0.0023 (10)	−0.0162 (12)

Geometric parameters (Å, °)

Cu1—O1	1.9450 (19)	N2—C5	1.328 (3)
Cu1—N1	1.945 (2)	N2—C6	1.369 (4)
Cu1—O3	1.955 (2)	N2—H2	0.8600
Cu1—O4	1.957 (2)	C5—H5	0.9300
Cu1—O8	2.321 (2)	C6—C7	1.397 (4)
O1—C1	1.274 (3)	C6—C11	1.405 (4)
O2—C1	1.237 (3)	C7—C8	1.363 (4)
C1—C2	1.522 (4)	C7—H7	0.9300
C2—O3	1.414 (3)	C8—C9	1.400 (4)
C2—H2A	0.9700	C8—H8	0.9300
C2—H2B	0.9700	C9—C10	1.383 (4)
O3—C3	1.417 (3)	C9—N3	1.470 (4)
C3—C4	1.520 (4)	C10—C11	1.388 (4)
C3—H3A	0.9700	C10—H10	0.9300
C3—H3B	0.9700	N3—O6	1.223 (4)
C4—O5	1.234 (3)	N3—O7	1.231 (3)
C4—O4	1.269 (3)	O8—H2W	0.7851
N1—C5	1.314 (3)	O8—H1W	0.7950
N1—C11	1.392 (3)		
O1—Cu1—N1	98.39 (8)	C5—N1—C11	105.1 (2)
O1—Cu1—O3	82.00 (8)	C5—N1—Cu1	128.69 (19)
N1—Cu1—O3	176.16 (9)	C11—N1—Cu1	126.17 (17)
O1—Cu1—O4	159.71 (9)	C5—N2—C6	107.7 (2)
N1—Cu1—O4	97.48 (8)	C5—N2—H2	126.2
O3—Cu1—O4	81.33 (8)	C6—N2—H2	126.2
O1—Cu1—O8	94.16 (9)	N1—C5—N2	113.4 (2)
N1—Cu1—O8	94.12 (8)	N1—C5—H5	123.3
O3—Cu1—O8	89.66 (9)	N2—C5—H5	123.3
O4—Cu1—O8	97.21 (9)	N2—C6—C7	132.3 (3)
C1—O1—Cu1	116.08 (17)	N2—C6—C11	105.5 (2)
O2—C1—O1	124.6 (3)	C7—C6—C11	122.2 (3)
O2—C1—C2	117.2 (2)	C8—C7—C6	117.2 (3)
O1—C1—C2	118.1 (2)	C8—C7—H7	121.4
O3—C2—C1	107.5 (2)	C6—C7—H7	121.4
O3—C2—H2A	110.2	C7—C8—C9	120.0 (3)
C1—C2—H2A	110.2	C7—C8—H8	120.0
O3—C2—H2B	110.2	C9—C8—H8	120.0
C1—C2—H2B	110.2	C10—C9—C8	124.2 (3)

H2A—C2—H2B	108.5	C10—C9—N3	117.2 (3)
C2—O3—C3	122.8 (2)	C8—C9—N3	118.6 (3)
C2—O3—Cu1	116.24 (16)	C9—C10—C11	115.6 (2)
C3—O3—Cu1	115.29 (17)	C9—C10—H10	122.2
O3—C3—C4	107.4 (2)	C11—C10—H10	122.2
O3—C3—H3A	110.2	C10—C11—N1	131.0 (2)
C4—C3—H3A	110.2	C10—C11—C6	120.7 (2)
O3—C3—H3B	110.2	N1—C11—C6	108.3 (2)
C4—C3—H3B	110.2	O6—N3—O7	123.3 (3)
H3A—C3—H3B	108.5	O6—N3—C9	118.5 (3)
O5—C4—O4	125.1 (3)	O7—N3—C9	118.2 (3)
O5—C4—C3	117.6 (2)	Cu1—O8—H2W	103.3
O4—C4—C3	117.3 (2)	Cu1—O8—H1W	106.2
C4—O4—Cu1	116.29 (18)	H2W—O8—H1W	109.6

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H1W···O5^{i}	0.79	2.00	2.788 (3)	170
O8—H2W···O5^{ii}	0.79	2.03	2.810 (3)	172
N2—H2···O2^{iii}	0.86	1.85	2.708 (3)	179
C7—H7···O8^{iv}	0.93	2.59	3.322 (3)	135

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

Fig. 1

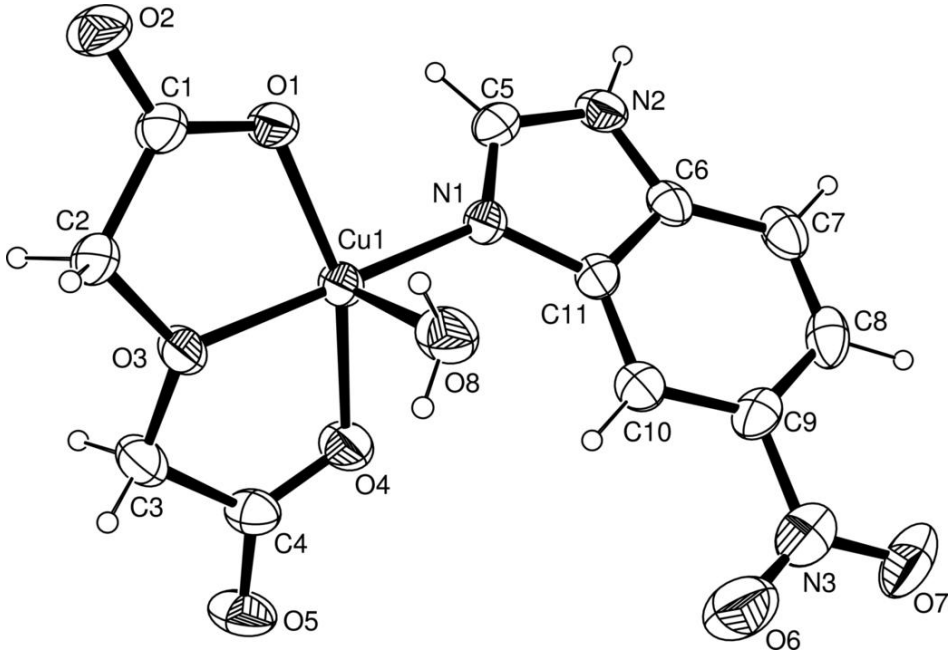

Fig. 2