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[(*E*)-2-(3-Methoxy-2-oxidobenzylidene-amino)ethanesulfonato](1,10-phenanthroline)copper(II)

Liang-Gui Wang

Department of C,hemistry, Lishui University, 323000 Lishui, Zhejiang, People's Republic of China
Correspondence e-mail: zjlswgl@126.com

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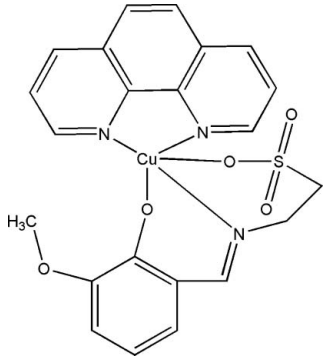
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.035; wR factor = 0.089; data-to-parameter ratio = 15.4.

In the mononuclear title complex, $[Cu(C_{10}H_{11}NO_5S)(C_{12}H_8N_2)]$, the Cu^{II} cation has a slightly distorted square-pyramidal environment, with a basal plane formed by two N atoms of the 1,10-phenanthroline (phen) ligand, one O atom and one N atom of the 2-(3-methoxy-2-oxidobenzylidene-amino)ethanesulfonate (*L*) ligand. The apical position is occupied by one O atom from the same *L* ligand. The asymmetric unit contains two such complexes, which are interconnected by weak π–π interactions between the phenanthroline planes, with an interplanar distance of 3.675 Å and centroid-to-centroid vector of 3.455 Å. The crystal structure contains a certain amount of solvent water which could not be unambiguously located, and the best structure refinement was obtained by removing the solvent contribution from the intensity data and refining against a solvent-free model.

Related literature

For related literature, see: Casella & Gullotti (1981, 1986); van der Sluis & Spek (1990); Spek (2003); Wang *et al.* (1994); Zhang & Jiang (2002).



Experimental

Crystal data

$[Cu(C_{10}H_{11}NO_5S)(C_{12}H_8N_2)]$
M_r = 501.00
Monoclinic, $P2_1/c$
a = 14.932 (1) Å
b = 26.6371 (17) Å
c = 13.1937 (9) Å
β = 114.032 (1)°
V = 4792.8 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.03 mm^{-1}
T = 298 (2) K
0.20 × 0.18 × 0.18 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.817, T_{max} = 0.833
30244 measured reflections
8898 independent reflections
4855 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.089
S = 0.79
8898 reflections
579 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Data collection: *SMART* (Bruker,1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2173).

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supplementary materials

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[(*E*)-2-(3-Methoxy-2-oxidobenzylideneamino)ethanesulfonato](1,10-phenanthroline)copper(II)

L.-G. Wang

Comment

Studies of Schiff base complexes containing sulfur and complexes of amino acid Schiff bases (Casella & Gullotti, 1981; Wang *et al.*, 1994; Casella & Gullotti, 1986) have attracted increasing interest because of their antiviral, anticancer and antibacterial activities. Recently, Zhang & Jiang (2002) have reported a Schiff base complex derived from taurine, an amino acid containing sulfur. Compound (I) reported here represents a new Schiff base copper(II) complex.

The Cu1 atom in the title complex has a distorted square-pyramidal environment with the basal plane formed by two N atoms of the 2,2'-pyridine ligand [Cu1—N = 2.06 (3) Å] and one O atom and one N atom of the *L* ligand. [Cu1—O1 = 1.914 (3) Å and Cu1—N3 = 1.958 (3) Å]. The apical position is occupied by another O atom from the same *L* ligand. [Cu1—O2 = 2.286 (3) Å]. The asymmetric unit contains two such complexes which are interconnected by weak π-π interaction between the phenanthroline planes with interplanar distance of 3.675Å and centroid to centroid vector of 3.455Å leading to an offset of 19.9° (Fig. 1).

The unit cell contains a certain amount of water molecules. However, these water molecules appear to be highly disordered and it was difficult to model their positions and distribution reliably. Therefore, the SQUEEZE function of *PLATON* (van der Sluis & Spek, 1990; Spek, 2003) was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was emplyed from the final refinement. Further details are given in the experimental section. Due to the omission of the water molecules from the model, it was not possible to analyse the hydrogen- bonding interactions.

Experimental

H_2L(0.05 g, 8 mmol), $Cu(CH_3COO)_2$ (0.18 g, 12 mmol) and phen(0.23 g,15 mmol), were added in a mixed solvent of dry ethanol and acetonitrile, the mixture was heated for 5 h under reflux and stirring. The resultant was then filtered to give a pure solution which was treated by diethyl ether. A week later, single crystals suitable for X-Ray diffraction analysis formed.

Refinement

All H atoms were placed in calculated positions and treated as riding on their parent atoms with C—H = 0.93 Å ($C_{aromatic}$), 0.97 Å ($C_{methylene}$) or 0.98Å (C_{methyl}) and with $U_{iso}(H) = 1.2U_{eq}(C_{aromatic}, C_{methylene})$ or $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$.

Figures

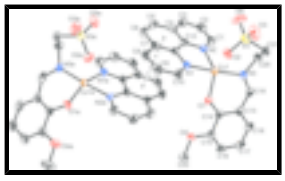


Fig. 1. Molecular view of compound (I), showing the atomic numbering scheme. For the sake of clarity, only heavier atoms are labelled for molecule A. Ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. The π-π interaction is represented as dashed line.

[(*E*)-2-(3-Methoxy-2-oxidobenzylideneamino)ethanesulfonato](1,10- phenanthroline)copper(II)

Crystal data

$[Cu(C_{10}H_{11}N_1O_5S_1)(C_{12}H_8N_2)]$	F_{000} = 2056
M_r = 501.00	D_x = 1.389 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 8898 reflections
a = 14.9320 (10) Å	θ = 3.1–25.1º
b = 26.6371 (17) Å	μ = 1.04 mm^{-1}
c = 13.1937 (9) Å	T = 298 (2) K
β = 114.0320 (10)º	Block, blue
V = 4792.8 (6) Å^3	0.20 × 0.18 × 0.18 mm
Z = 8	

Data collection

Bruker APEX area-detector diffractometer	8898 independent reflections
Radiation source: fine-focus sealed tube	4855 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.045
T = 298(2) K	θ_{max} = 25.5º
φ and ω scans	θ_{min} = 3.1º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −18→18
T_{min} = 0.817, T_{max} = 0.833	k = −32→31
30244 measured reflections	l = −15→15

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.035	H-atom parameters constrained
$wR(F^2)$ = 0.089	$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.79	$(\Delta/\sigma)_{max}$ = 0.002
8898 reflections	$\Delta\rho_{max}$ = 0.25 e Å^{-3}

579 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. There is one cavity of 820 Å^3 per unitl cell. *PLATON* estimated that the cavity contains 105 electrons which may correspond to roughly 10 water molecules within the cell. This is contradictory with the size of the cavity in which we could expect to introduce roughly 40 water molecules *i.e.* roughly 10 water molecules within each asymmetric unit. It is well known that the SQUEEZE procedure is very dependent on the low-angle reflections and that the electron count may be underestimated if those reflections are missing which could be the case when data are collected on CCD machine.

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.06716 (3)	0.858157 (14)	0.41746 (3)	0.04569 (13)
S3	−0.03709 (7)	0.76293 (3)	0.47713 (7)	0.0608 (3)
N1	0.19477 (18)	0.85975 (9)	0.5512 (2)	0.0433 (6)
N2	0.15521 (18)	0.81301 (9)	0.3600 (2)	0.0454 (7)
N3	−0.06083 (18)	0.85115 (9)	0.29555 (19)	0.0421 (6)
O1	0.06101 (14)	0.93005 (7)	0.41949 (17)	0.0497 (6)
O2	0.02223 (16)	0.80818 (8)	0.51816 (17)	0.0620 (7)
O3	−0.0761 (2)	0.74568 (11)	0.5538 (2)	0.0974 (10)
O4	0.09579 (16)	1.02724 (8)	0.4369 (2)	0.0657 (7)
O5	0.0147 (2)	0.72467 (10)	0.4458 (2)	0.1085 (11)
C1	0.1363 (3)	0.79042 (12)	0.2629 (3)	0.0562 (9)
H1	0.0725	0.7916	0.2086	0.067*
C2	0.2064 (3)	0.76553 (13)	0.2390 (3)	0.0673 (11)
H2	0.1891	0.7504	0.1701	0.081*
C3	0.2997 (3)	0.76306 (13)	0.3153 (3)	0.0672 (11)
H3	0.3475	0.7468	0.2992	0.081*
C4	0.3235 (2)	0.78553 (12)	0.4195 (3)	0.0529 (9)
C5	0.4197 (3)	0.78579 (13)	0.5064 (4)	0.0685 (11)
H5	0.4703	0.7699	0.4952	0.082*
C6	0.4389 (3)	0.80842 (14)	0.6038 (3)	0.0655 (11)
H6	0.5024	0.8077	0.6588	0.079*
C7	0.3642 (2)	0.83352 (12)	0.6249 (3)	0.0480 (8)
C8	0.3787 (3)	0.85810 (13)	0.7246 (3)	0.0608 (10)
H8	0.4403	0.8580	0.7832	0.073*

C9	0.3027 (3)	0.88202 (13)	0.7350 (3)	0.0592 (10)
H9	0.3113	0.8979	0.8011	0.071*
C10	0.2115 (2)	0.88243 (12)	0.6452 (3)	0.0539 (9)
H10	0.1602	0.8996	0.6525	0.065*
C11	0.2698 (2)	0.83488 (11)	0.5410 (2)	0.0403 (8)
C12	0.2492 (2)	0.81033 (11)	0.4373 (3)	0.0429 (8)
C13	−0.0865 (2)	0.94087 (11)	0.2543 (2)	0.0412 (8)
C14	−0.0023 (2)	0.95869 (11)	0.3425 (2)	0.0417 (8)
C15	0.0137 (2)	1.01168 (11)	0.3467 (3)	0.0466 (8)
C16	−0.0475 (2)	1.04272 (12)	0.2673 (3)	0.0520 (9)
H16	−0.0344	1.0770	0.2716	0.062*
C17	−0.1294 (3)	1.02408 (13)	0.1798 (3)	0.0581 (10)
H17	−0.1702	1.0457	0.1251	0.070*
C18	−0.1499 (2)	0.97418 (13)	0.1740 (3)	0.0544 (9)
H18	−0.2061	0.9619	0.1168	0.065*
C19	−0.1122 (2)	0.88848 (12)	0.2405 (2)	0.0434 (8)
H19	−0.1733	0.8807	0.1852	0.052*
C20	−0.1069 (2)	0.80149 (11)	0.2676 (3)	0.0519 (9)
H20A	−0.0610	0.7782	0.2580	0.062*
H20B	−0.1639	0.8036	0.1976	0.062*
C21	−0.1380 (2)	0.78127 (12)	0.3548 (3)	0.0564 (9)
H21A	−0.1806	0.7526	0.3249	0.068*
H21B	−0.1752	0.8068	0.3732	0.068*
C22	0.1063 (3)	1.07918 (12)	0.4594 (3)	0.0679 (11)
H22A	0.0482	1.0918	0.4650	0.102*
H22B	0.1158	1.0962	0.4004	0.102*
H22C	0.1619	1.0849	0.5281	0.102*
Cu1A	0.64785 (3)	0.963637 (14)	0.76034 (3)	0.04578 (12)
S3A	0.68734 (7)	0.85167 (4)	0.89860 (9)	0.0639 (3)
N1A	0.5971 (2)	0.93262 (9)	0.6028 (2)	0.0478 (7)
N2A	0.50451 (18)	0.97952 (9)	0.7082 (2)	0.0437 (6)
N3A	0.78552 (19)	0.94433 (10)	0.8101 (2)	0.0486 (7)
O1A	0.68059 (15)	1.02090 (7)	0.85712 (17)	0.0492 (6)
O2A	0.62862 (16)	0.89728 (8)	0.8594 (2)	0.0717 (7)
O3A	0.69166 (19)	0.83556 (10)	1.0061 (2)	0.0919 (9)
O4A	0.67704 (19)	1.11313 (8)	0.9188 (2)	0.0728 (7)
O5A	0.6580 (2)	0.81301 (10)	0.8164 (2)	0.1016 (10)
C1A	0.6446 (3)	0.91202 (13)	0.5493 (3)	0.0636 (10)
H1A	0.7125	0.9096	0.5842	0.076*
C2A	0.5959 (3)	0.89336 (14)	0.4402 (3)	0.0721 (11)
H2A	0.6318	0.8786	0.4048	0.087*
C3A	0.4992 (3)	0.89691 (13)	0.3882 (3)	0.0656 (11)
H3A	0.4674	0.8846	0.3163	0.079*
C4A	0.4457 (3)	0.91880 (12)	0.4403 (3)	0.0524 (9)
C5A	0.3416 (3)	0.92501 (13)	0.3925 (3)	0.0654 (11)
H5A	0.3056	0.9124	0.3217	0.078*
C6A	0.2941 (3)	0.94820 (13)	0.4455 (3)	0.0630 (10)
H6A	0.2264	0.9518	0.4107	0.076*
C7A	0.3460 (2)	0.96773 (12)	0.5555 (3)	0.0499 (9)

C8A	0.3022 (3)	0.99224 (13)	0.6163 (3)	0.0613 (10)
H8A	0.2345	0.9962	0.5868	0.074*
C9A	0.3587 (3)	1.01060 (13)	0.7198 (3)	0.0594 (10)
H9A	0.3300	1.0275	0.7606	0.071*
C10A	0.4595 (2)	1.00356 (12)	0.7630 (3)	0.0541 (9)
H10A	0.4974	1.0162	0.8333	0.065*
C11A	0.4485 (2)	0.96168 (11)	0.6052 (2)	0.0417 (8)
C12A	0.4978 (2)	0.93712 (11)	0.5483 (2)	0.0423 (8)
C13A	0.8456 (2)	1.02885 (12)	0.8696 (3)	0.0456 (8)
C14A	0.7607 (2)	1.04753 (12)	0.8784 (2)	0.0441 (8)
C15A	0.7620 (3)	1.09791 (12)	0.9134 (3)	0.0513 (9)
C16A	0.8427 (3)	1.12763 (14)	0.9370 (3)	0.0677 (11)
H16A	0.8420	1.1606	0.9598	0.081*
C17A	0.9265 (3)	1.10881 (16)	0.9272 (3)	0.0790 (13)
H17A	0.9807	1.1294	0.9424	0.095*
C18A	0.9283 (3)	1.05996 (16)	0.8951 (3)	0.0680 (11)
H18A	0.9844	1.0473	0.8902	0.082*
C19A	0.8546 (2)	0.97739 (14)	0.8474 (3)	0.0554 (10)
H19A	0.9175	0.9662	0.8612	0.066*
C20A	0.8158 (3)	0.89156 (13)	0.8196 (3)	0.0638 (10)
H20C	0.8830	0.8894	0.8269	0.077*
H20D	0.7745	0.8736	0.7529	0.077*
C21A	0.8076 (2)	0.86740 (12)	0.9202 (3)	0.0568 (10)
H21C	0.8339	0.8904	0.9825	0.068*
H21D	0.8475	0.8372	0.9398	0.068*
C22A	0.6742 (3)	1.16233 (14)	0.9612 (4)	0.1031 (16)
H22D	0.7251	1.1654	1.0346	0.155*
H22E	0.6116	1.1677	0.9638	0.155*
H22F	0.6840	1.1870	0.9136	0.155*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0392 (2)	0.0416 (2)	0.0400 (2)	0.00257 (19)	−0.00042 (18)	−0.00068 (18)
S3	0.0617 (6)	0.0527 (6)	0.0482 (6)	−0.0084 (5)	0.0022 (5)	0.0131 (5)
N1	0.0420 (16)	0.0432 (15)	0.0336 (15)	−0.0023 (13)	0.0041 (13)	−0.0023 (13)
N2	0.0447 (17)	0.0425 (15)	0.0376 (16)	0.0022 (13)	0.0053 (13)	−0.0015 (13)
N3	0.0419 (16)	0.0423 (16)	0.0326 (14)	−0.0017 (13)	0.0056 (12)	0.0019 (12)
O1	0.0420 (13)	0.0384 (12)	0.0523 (14)	0.0025 (10)	0.0024 (11)	0.0036 (10)
O2	0.0586 (15)	0.0613 (15)	0.0440 (13)	−0.0193 (12)	−0.0019 (12)	0.0098 (11)
O3	0.089 (2)	0.123 (2)	0.0590 (17)	−0.0396 (18)	0.0090 (16)	0.0348 (16)
O4	0.0532 (15)	0.0359 (14)	0.0852 (18)	0.0046 (11)	0.0048 (14)	−0.0028 (12)
O5	0.129 (3)	0.0715 (19)	0.092 (2)	0.0495 (19)	0.011 (2)	0.0101 (16)
C1	0.053 (2)	0.054 (2)	0.053 (2)	−0.0012 (19)	0.0121 (19)	−0.0049 (19)
C2	0.078 (3)	0.061 (2)	0.063 (3)	0.002 (2)	0.028 (2)	−0.018 (2)
C3	0.062 (3)	0.057 (2)	0.081 (3)	0.010 (2)	0.027 (2)	−0.009 (2)
C4	0.047 (2)	0.042 (2)	0.065 (2)	0.0038 (17)	0.0168 (19)	0.0019 (18)
C5	0.049 (2)	0.060 (2)	0.089 (3)	0.015 (2)	0.020 (2)	0.003 (2)

C6	0.041 (2)	0.066 (3)	0.069 (3)	0.0058 (19)	0.001 (2)	0.008 (2)
C7	0.037 (2)	0.0455 (19)	0.046 (2)	−0.0023 (17)	0.0009 (17)	0.0078 (17)
C8	0.049 (2)	0.064 (2)	0.047 (2)	−0.012 (2)	−0.0034 (18)	0.0110 (19)
C9	0.062 (3)	0.067 (2)	0.035 (2)	−0.010 (2)	0.0066 (19)	−0.0051 (17)
C10	0.049 (2)	0.060 (2)	0.046 (2)	−0.0028 (18)	0.0119 (18)	−0.0044 (18)
C11	0.0384 (19)	0.0325 (17)	0.041 (2)	−0.0019 (15)	0.0074 (16)	0.0053 (15)
C12	0.0387 (19)	0.0364 (18)	0.045 (2)	−0.0009 (15)	0.0081 (17)	0.0070 (15)
C13	0.0371 (18)	0.047 (2)	0.0353 (18)	0.0059 (16)	0.0103 (15)	0.0061 (15)
C14	0.0407 (19)	0.0435 (19)	0.0399 (19)	0.0064 (16)	0.0155 (16)	0.0068 (16)
C15	0.042 (2)	0.043 (2)	0.053 (2)	0.0030 (17)	0.0172 (18)	0.0033 (17)
C16	0.055 (2)	0.0415 (19)	0.061 (2)	0.0106 (18)	0.025 (2)	0.0106 (18)
C17	0.060 (2)	0.053 (2)	0.055 (2)	0.0226 (19)	0.018 (2)	0.0174 (18)
C18	0.045 (2)	0.064 (2)	0.046 (2)	0.0144 (18)	0.0101 (17)	0.0103 (18)
C19	0.0333 (18)	0.056 (2)	0.0326 (18)	0.0023 (17)	0.0046 (15)	0.0030 (16)
C20	0.051 (2)	0.048 (2)	0.039 (2)	−0.0059 (17)	−0.0001 (17)	−0.0016 (16)
C21	0.048 (2)	0.051 (2)	0.051 (2)	−0.0115 (17)	0.0008 (17)	0.0095 (17)
C22	0.063 (3)	0.046 (2)	0.089 (3)	−0.0012 (19)	0.025 (2)	−0.002 (2)
Cu1A	0.0351 (2)	0.0491 (2)	0.0476 (2)	−0.00128 (19)	0.01125 (19)	−0.00943 (19)
S3A	0.0467 (6)	0.0552 (6)	0.0697 (7)	−0.0005 (5)	0.0031 (5)	0.0013 (5)
N1A	0.0500 (18)	0.0486 (17)	0.0471 (17)	−0.0013 (14)	0.0222 (15)	−0.0049 (13)
N2A	0.0374 (15)	0.0434 (15)	0.0457 (17)	0.0016 (13)	0.0123 (14)	−0.0012 (13)
N3A	0.0394 (16)	0.0530 (17)	0.0519 (17)	0.0025 (14)	0.0171 (14)	−0.0069 (14)
O1A	0.0411 (13)	0.0499 (13)	0.0587 (14)	−0.0110 (11)	0.0224 (11)	−0.0146 (11)
O2A	0.0488 (15)	0.0647 (16)	0.099 (2)	0.0157 (13)	0.0271 (14)	0.0239 (14)
O3A	0.0751 (19)	0.107 (2)	0.083 (2)	0.0028 (17)	0.0221 (16)	0.0364 (17)
O4A	0.081 (2)	0.0526 (16)	0.0906 (19)	−0.0076 (14)	0.0406 (16)	−0.0209 (14)
O5A	0.078 (2)	0.0791 (19)	0.107 (2)	−0.0147 (16)	−0.0043 (17)	−0.0279 (18)
C1A	0.067 (3)	0.070 (3)	0.057 (3)	0.004 (2)	0.028 (2)	−0.004 (2)
C2A	0.100 (4)	0.070 (3)	0.057 (3)	0.003 (3)	0.043 (3)	−0.011 (2)
C3A	0.084 (3)	0.060 (2)	0.045 (2)	−0.011 (2)	0.019 (2)	−0.0082 (19)
C4A	0.066 (3)	0.045 (2)	0.040 (2)	−0.0118 (19)	0.016 (2)	0.0037 (17)
C5A	0.074 (3)	0.063 (3)	0.037 (2)	−0.021 (2)	0.000 (2)	0.0060 (19)
C6A	0.051 (2)	0.064 (2)	0.051 (2)	−0.010 (2)	−0.002 (2)	0.014 (2)
C7A	0.042 (2)	0.049 (2)	0.048 (2)	−0.0034 (17)	0.0075 (18)	0.0126 (17)
C8A	0.039 (2)	0.070 (3)	0.065 (3)	0.0055 (19)	0.012 (2)	0.020 (2)
C9A	0.050 (2)	0.064 (2)	0.070 (3)	0.0131 (19)	0.030 (2)	0.008 (2)
C10A	0.046 (2)	0.063 (2)	0.047 (2)	0.0052 (18)	0.0130 (18)	0.0007 (18)
C11A	0.0404 (19)	0.0383 (18)	0.0389 (19)	−0.0056 (16)	0.0084 (16)	0.0051 (15)
C12A	0.045 (2)	0.0391 (18)	0.037 (2)	−0.0091 (16)	0.0117 (17)	0.0044 (15)
C13A	0.0373 (19)	0.052 (2)	0.0427 (19)	−0.0088 (17)	0.0113 (16)	0.0041 (16)
C14A	0.043 (2)	0.050 (2)	0.0319 (18)	−0.0062 (17)	0.0082 (16)	0.0042 (15)
C15A	0.054 (2)	0.051 (2)	0.043 (2)	−0.0094 (19)	0.0141 (18)	−0.0037 (17)
C16A	0.071 (3)	0.052 (2)	0.060 (2)	−0.016 (2)	0.005 (2)	0.0029 (18)
C17A	0.050 (3)	0.072 (3)	0.089 (3)	−0.022 (2)	0.001 (2)	0.018 (2)
C18A	0.042 (2)	0.085 (3)	0.065 (3)	−0.007 (2)	0.0101 (19)	0.019 (2)
C19A	0.035 (2)	0.086 (3)	0.045 (2)	0.009 (2)	0.0172 (17)	0.006 (2)
C20A	0.050 (2)	0.069 (3)	0.071 (3)	0.009 (2)	0.023 (2)	−0.018 (2)
C21A	0.040 (2)	0.049 (2)	0.068 (2)	0.0081 (17)	0.0073 (18)	−0.0059 (18)
C22A	0.134 (4)	0.054 (3)	0.138 (4)	−0.008 (3)	0.072 (4)	−0.030 (3)

Geometric parameters (Å, °)

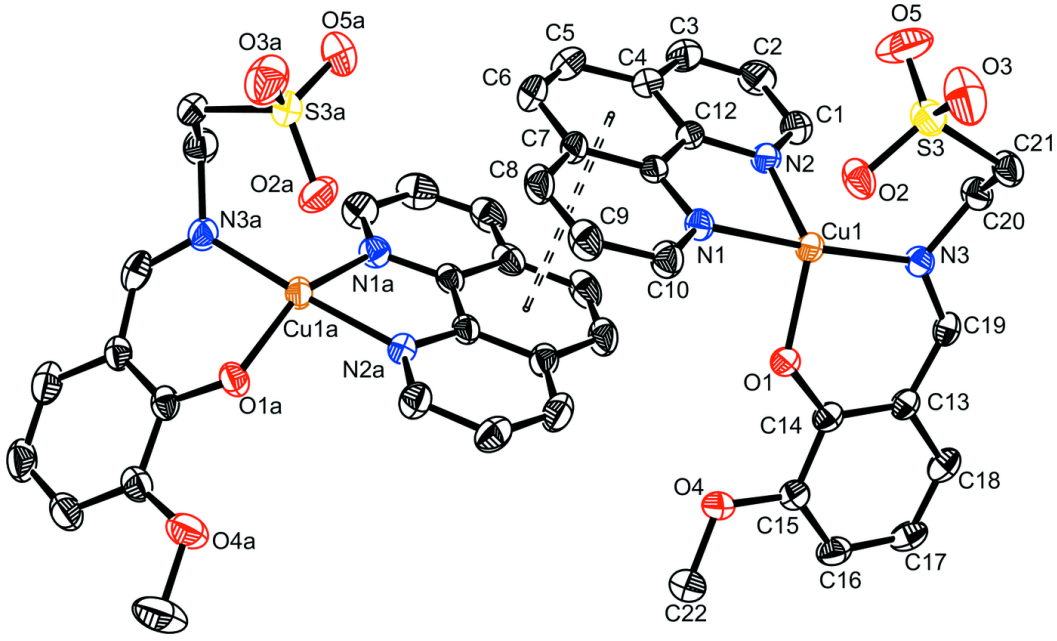
Cu1—O1	1.918 (2)	Cu1A—O1A	1.9204 (19)
Cu1—N3	1.942 (2)	Cu1A—N3A	1.955 (3)
Cu1—N1	2.002 (2)	Cu1A—N2A	2.008 (3)
Cu1—N2	2.136 (3)	Cu1A—N1A	2.072 (3)
Cu1—O2	2.171 (2)	Cu1A—O2A	2.285 (2)
S3—O3	1.433 (3)	S3A—O5A	1.429 (3)
S3—O5	1.438 (3)	S3A—O3A	1.457 (3)
S3—O2	1.463 (2)	S3A—O2A	1.464 (2)
S3—C21	1.770 (3)	S3A—C21A	1.751 (3)
N1—C10	1.310 (4)	N1A—C1A	1.307 (4)
N1—C11	1.355 (4)	N1A—C12A	1.364 (4)
N2—C1	1.337 (4)	N2A—C10A	1.334 (4)
N2—C12	1.360 (4)	N2A—C11A	1.359 (4)
N3—C19	1.285 (3)	N3A—C19A	1.292 (4)
N3—C20	1.467 (4)	N3A—C20A	1.466 (4)
O1—C14	1.314 (3)	O1A—C14A	1.318 (3)
O4—C15	1.380 (4)	O4A—C15A	1.360 (4)
O4—C22	1.410 (3)	O4A—C22A	1.432 (4)
C1—C2	1.379 (4)	C1A—C2A	1.413 (5)
C1—H1	0.9300	C1A—H1A	0.9300
C2—C3	1.348 (5)	C2A—C3A	1.326 (5)
C2—H2	0.9300	C2A—H2A	0.9300
C3—C4	1.407 (5)	C3A—C4A	1.378 (5)
C3—H3	0.9300	C3A—H3A	0.9300
C4—C12	1.391 (4)	C4A—C12A	1.405 (4)
C4—C5	1.427 (5)	C4A—C5A	1.429 (5)
C5—C6	1.340 (5)	C5A—C6A	1.333 (5)
C5—H5	0.9300	C5A—H5A	0.9300
C6—C7	1.422 (5)	C6A—C7A	1.436 (5)
C6—H6	0.9300	C6A—H6A	0.9300
C7—C11	1.393 (4)	C7A—C8A	1.388 (5)
C7—C8	1.405 (5)	C7A—C11A	1.408 (4)
C8—C9	1.357 (5)	C8A—C9A	1.370 (5)
C8—H8	0.9300	C8A—H8A	0.9300
C9—C10	1.394 (4)	C9A—C10A	1.388 (4)
C9—H9	0.9300	C9A—H9A	0.9300
C10—H10	0.9300	C10A—H10A	0.9300
C11—C12	1.432 (4)	C11A—C12A	1.408 (4)
C13—C14	1.403 (4)	C13A—C18A	1.409 (4)
C13—C18	1.410 (4)	C13A—C14A	1.411 (4)
C13—C19	1.439 (4)	C13A—C19A	1.420 (4)
C14—C15	1.429 (4)	C14A—C15A	1.417 (4)
C15—C16	1.354 (4)	C15A—C16A	1.368 (4)
C16—C17	1.388 (4)	C16A—C17A	1.402 (5)
C16—H16	0.9300	C16A—H16A	0.9300
C17—C18	1.359 (4)	C17A—C18A	1.372 (5)

C17—H17	0.9300	C17A—H17A	0.9300
C18—H18	0.9300	C18A—H18A	0.9300
C19—H19	0.9300	C19A—H19A	0.9300
C20—C21	1.505 (4)	C20A—C21A	1.525 (4)
C20—H20A	0.9700	C20A—H20C	0.9700
C20—H20B	0.9700	C20A—H20D	0.9700
C21—H21A	0.9700	C21A—H21C	0.9700
C21—H21B	0.9700	C21A—H21D	0.9700
C22—H22A	0.9600	C22A—H22D	0.9600
C22—H22B	0.9600	C22A—H22E	0.9600
C22—H22C	0.9600	C22A—H22F	0.9600
O1—Cu1—N3	94.07 (9)	O1A—Cu1A—N3A	92.14 (10)
O1—Cu1—N1	90.02 (9)	O1A—Cu1A—N2A	90.44 (10)
N3—Cu1—N1	174.02 (10)	N3A—Cu1A—N2A	176.90 (11)
O1—Cu1—N2	127.37 (9)	O1A—Cu1A—N1A	150.90 (9)
N3—Cu1—N2	101.09 (10)	N3A—Cu1A—N1A	97.89 (11)
N1—Cu1—N2	79.75 (10)	N2A—Cu1A—N1A	80.62 (11)
O1—Cu1—O2	125.12 (9)	O1A—Cu1A—O2A	106.94 (9)
N3—Cu1—O2	90.16 (9)	N3A—Cu1A—O2A	87.95 (10)
N1—Cu1—O2	83.92 (9)	N2A—Cu1A—O2A	89.66 (9)
N2—Cu1—O2	105.09 (9)	N1A—Cu1A—O2A	100.69 (9)
O3—S3—O5	113.38 (19)	O5A—S3A—O3A	113.86 (18)
O3—S3—O2	111.21 (16)	O5A—S3A—O2A	112.07 (16)
O5—S3—O2	111.99 (18)	O3A—S3A—O2A	111.78 (16)
O3—S3—C21	107.01 (16)	O5A—S3A—C21A	105.85 (18)
O5—S3—C21	106.94 (17)	O3A—S3A—C21A	106.01 (17)
O2—S3—C21	105.80 (14)	O2A—S3A—C21A	106.63 (15)
C10—N1—C11	118.2 (3)	C1A—N1A—C12A	117.7 (3)
C10—N1—Cu1	126.2 (2)	C1A—N1A—Cu1A	130.7 (2)
C11—N1—Cu1	115.6 (2)	C12A—N1A—Cu1A	111.6 (2)
C1—N2—C12	116.5 (3)	C10A—N2A—C11A	118.0 (3)
C1—N2—Cu1	132.3 (2)	C10A—N2A—Cu1A	128.1 (2)
C12—N2—Cu1	111.1 (2)	C11A—N2A—Cu1A	113.9 (2)
C19—N3—C20	116.4 (2)	C19A—N3A—C20A	116.8 (3)
C19—N3—Cu1	123.6 (2)	C19A—N3A—Cu1A	121.1 (2)
C20—N3—Cu1	119.82 (19)	C20A—N3A—Cu1A	121.8 (2)
C14—O1—Cu1	126.34 (19)	C14A—O1A—Cu1A	122.17 (19)
S3—O2—Cu1	124.76 (13)	S3A—O2A—Cu1A	130.35 (14)
C15—O4—C22	117.4 (3)	C15A—O4A—C22A	118.0 (3)
N2—C1—C2	123.4 (3)	N1A—C1A—C2A	122.1 (4)
N2—C1—H1	118.3	N1A—C1A—H1A	119.0
C2—C1—H1	118.3	C2A—C1A—H1A	119.0
C3—C2—C1	120.2 (4)	C3A—C2A—C1A	120.1 (4)
C3—C2—H2	119.9	C3A—C2A—H2A	119.9
C1—C2—H2	119.9	C1A—C2A—H2A	119.9
C2—C3—C4	118.8 (3)	C2A—C3A—C4A	120.2 (4)
C2—C3—H3	120.6	C2A—C3A—H3A	119.9
C4—C3—H3	120.6	C4A—C3A—H3A	119.9
C12—C4—C3	117.8 (3)	C3A—C4A—C12A	117.4 (3)

C12—C4—C5	118.2 (3)	C3A—C4A—C5A	125.2 (4)
C3—C4—C5	123.9 (3)	C12A—C4A—C5A	117.4 (3)
C6—C5—C4	121.7 (4)	C6A—C5A—C4A	122.5 (3)
C6—C5—H5	119.2	C6A—C5A—H5A	118.7
C4—C5—H5	119.2	C4A—C5A—H5A	118.7
C5—C6—C7	121.3 (3)	C5A—C6A—C7A	121.0 (3)
C5—C6—H6	119.3	C5A—C6A—H6A	119.5
C7—C6—H6	119.3	C7A—C6A—H6A	119.5
C11—C7—C8	116.9 (3)	C8A—C7A—C11A	117.6 (3)
C11—C7—C6	118.5 (3)	C8A—C7A—C6A	124.6 (3)
C8—C7—C6	124.6 (3)	C11A—C7A—C6A	117.8 (3)
C9—C8—C7	119.8 (3)	C9A—C8A—C7A	120.0 (3)
C9—C8—H8	120.1	C9A—C8A—H8A	120.0
C7—C8—H8	120.1	C7A—C8A—H8A	120.0
C8—C9—C10	119.0 (3)	C8A—C9A—C10A	119.1 (3)
C8—C9—H9	120.5	C8A—C9A—H9A	120.5
C10—C9—H9	120.5	C10A—C9A—H9A	120.5
N1—C10—C9	123.0 (3)	N2A—C10A—C9A	122.9 (3)
N1—C10—H10	118.5	N2A—C10A—H10A	118.5
C9—C10—H10	118.5	C9A—C10A—H10A	118.5
N1—C11—C7	123.0 (3)	N2A—C11A—C12A	117.0 (3)
N1—C11—C12	116.9 (3)	N2A—C11A—C7A	122.3 (3)
C7—C11—C12	120.1 (3)	C12A—C11A—C7A	120.7 (3)
N2—C12—C4	123.3 (3)	N1A—C12A—C4A	122.6 (3)
N2—C12—C11	116.6 (3)	N1A—C12A—C11A	116.9 (3)
C4—C12—C11	120.1 (3)	C4A—C12A—C11A	120.6 (3)
C14—C13—C18	120.7 (3)	C18A—C13A—C14A	120.2 (3)
C14—C13—C19	122.4 (3)	C18A—C13A—C19A	118.0 (3)
C18—C13—C19	116.9 (3)	C14A—C13A—C19A	121.5 (3)
O1—C14—C13	124.4 (3)	O1A—C14A—C13A	124.1 (3)
O1—C14—C15	119.2 (3)	O1A—C14A—C15A	118.0 (3)
C13—C14—C15	116.4 (3)	C13A—C14A—C15A	117.9 (3)
C16—C15—O4	124.5 (3)	O4A—C15A—C16A	124.7 (3)
C16—C15—C14	121.6 (3)	O4A—C15A—C14A	114.2 (3)
O4—C15—C14	113.9 (3)	C16A—C15A—C14A	121.1 (4)
C15—C16—C17	120.9 (3)	C15A—C16A—C17A	120.6 (4)
C15—C16—H16	119.6	C15A—C16A—H16A	119.7
C17—C16—H16	119.6	C17A—C16A—H16A	119.7
C18—C17—C16	119.9 (3)	C18A—C17A—C16A	119.9 (4)
C18—C17—H17	120.1	C18A—C17A—H17A	120.1
C16—C17—H17	120.1	C16A—C17A—H17A	120.1
C17—C18—C13	120.4 (3)	C17A—C18A—C13A	120.4 (4)
C17—C18—H18	119.8	C17A—C18A—H18A	119.8
C13—C18—H18	119.8	C13A—C18A—H18A	119.8
N3—C19—C13	127.7 (3)	N3A—C19A—C13A	127.5 (3)
N3—C19—H19	116.1	N3A—C19A—H19A	116.3
C13—C19—H19	116.1	C13A—C19A—H19A	116.3
N3—C20—C21	112.9 (3)	N3A—C20A—C21A	110.3 (3)
N3—C20—H20A	109.0	N3A—C20A—H20C	109.6

C21—C20—H20A	109.0	C21A—C20A—H20C	109.6
N3—C20—H20B	109.0	N3A—C20A—H20D	109.6
C21—C20—H20B	109.0	C21A—C20A—H20D	109.6
H20A—C20—H20B	107.8	H20C—C20A—H20D	108.1
C20—C21—S3	112.5 (2)	C20A—C21A—S3A	113.6 (2)
C20—C21—H21A	109.1	C20A—C21A—H21C	108.9
S3—C21—H21A	109.1	S3A—C21A—H21C	108.9
C20—C21—H21B	109.1	C20A—C21A—H21D	108.9
S3—C21—H21B	109.1	S3A—C21A—H21D	108.9
H21A—C21—H21B	107.8	H21C—C21A—H21D	107.7
O4—C22—H22A	109.5	O4A—C22A—H22D	109.5
O4—C22—H22B	109.5	O4A—C22A—H22E	109.5
H22A—C22—H22B	109.5	H22D—C22A—H22E	109.5
O4—C22—H22C	109.5	O4A—C22A—H22F	109.5
H22A—C22—H22C	109.5	H22D—C22A—H22F	109.5
H22B—C22—H22C	109.5	H22E—C22A—H22F	109.5

Fig. 1


O5a
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C22