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Aqua[1-(1,10-phenanthrolin-2-yl-κ^2N,N')-1*H*-pyrazol-3-amine-κN^2]-(sulfato-κO)copper(II) methanol monosolvate dihydrate

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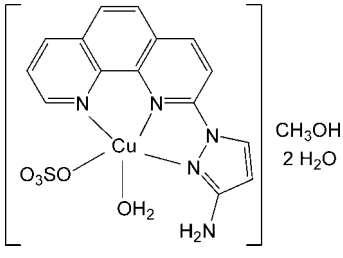
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.047; wR factor = 0.119; data-to-parameter ratio = 15.6.

In the title compound, $[Cu(SO_4)(C_{15}H_{11}N_5)(H_2O)]\cdot CH_3OH\cdot 2H_2O$, the Cu^{II} ion is in a distorted square-pyramidal geometry, in which three N atoms from the chelating 1-(1,10-phenanthrolin-2-yl)-1*H*-pyrazol-3-amine ligand and one O atom from a sulfate anion define the basal plane and the O atom from the coordinating water molecule is located at the apex. In the crystal, hydrogen-bonding interactions involving the coordinating and solvent water molecules, the methanol solvent molecule and the amine group (one with an intramolecular interaction to one of the sulfate O atoms) of the complex are observed. π–π interactions between symmetry-related phenantroline moieties, with a shortest centroid–centroid interaction of 3.573 (2)°, are also present.

Related literature

For related structures, see: Li *et al.* (2011*a*,*b*).



Experimental

Crystal data

$[Cu(SO_4)(C_{15}H_{11}N_5)(H_2O)]\cdot CH_4O\cdot 2H_2O$
M_r = 506.98
Monoclinic, $P2_1/n$
a = 8.0190 (13) Å
b = 18.489 (3) Å
c = 14.086 (2) Å
β = 104.551 (2)°
V = 2021.4 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.24 mm^{-1}
T = 298 K
0.22 × 0.15 × 0.11 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.772, T_{max} = 0.876
11702 measured reflections
4394 independent reflections
3434 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.119
S = 1.03
4394 reflections
281 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O3	1.906 (2)	Cu1—N1	2.090 (2)
Cu1—N2	1.934 (2)	Cu1—O5	2.220 (2)
Cu1—N3	2.068 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H4···O7	0.89	1.79	2.671 (4)	167
O5—H5···O8	0.89	1.90	2.774 (4)	164
O6—H12···O1	0.85	1.89	2.668 (4)	152
O7—H6···O6	0.84	2.10	2.878 (5)	153
O7—H7···O4^{i}	0.89	1.84	2.726 (4)	173
O8—H17···O6^{ii}	0.90	2.07	2.906 (5)	154
O8—H18···O2^{iii}	0.90	2.09	2.957 (4)	163
N5—H5*A*···O4	0.86	2.19	2.916 (4)	143
N5—H5*B*···O2^{ii}	0.86	2.17	3.022 (4)	175

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT* (Bruker, 200); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: WM2604).

References

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Li, H., Zhang, S. D., Xie, L. M., Yu, L. & Shi, J. M. (2011*b*). *J. Coord. Chem.* **64**, 3595–3608.
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supporting information

Acta Cryst. (2012). E**68**, m558–m559 [doi:10.1107/S1600536812014134]

Aqua[1-(1,10-phenanthrolin-2-yl-κ^2N,N')-1*H*-pyrazol-3-amine-κN^2](sulfato-κO)copper(II) methanol monosolvate dihydrate

Liang Yuan, Liu Shu Lian, Chi Yan Hui, Zhao Yan Xia and Shi Jing Min

S1. Comment

Derivatives of 1,10-phenanthroline play an important role in coordination chemistry and many of such complexes have been reported with these types of derivatives as ligands, e.g. Li *et al.* (2011*a,b*) for closely related Cu^{II} complexes. To the best of our knowledge, there is no report for a complex with 1-(1,10-phenanthrolin-9-yl)-1*H*-pyrazol-3-amine as ligand. Herein we report the crystal of the solvated title complex, (I).

The molecular structure of (I) is shown in Fig. 1. The Cu^{II} ion is is a distorted square-pyramidal coordination geometry with the O atom of the water molecule at the apex and three N atoms from the ligand and one O atoms from the sulfate anion in the basal plane. The non-hydrogen atoms from the 1-(1,10-phenanthrolin-9-yl)-1*H*-pyrazol-3-amine ligand make an approximate plane within 0.074 Å (rms deviation) with a maximum deviation of 0.145 (3) Å for the N5 atom.

In the crystal, the uncoordinated water molecules, the methanol molecule and the metal complex are connected to each other by hydrogen bonding interactions as shown in Table 2 and Figure 2. The coordinating water molecule and the solvent water molecule (O5—H4···O7 and O5—H5···O8) interact, as well as the solvent water molecules with the methanol molecule (O7—H6···O6 and O8—H17···O6). The solvent water molecules are also donors to the free sulfate O atoms of the complex (O7—H7···O4; O8—H18···O2). The complex is also connected *via* its amine function as donor molecule to an the adjacent complex (N5—H5···O2).There is also an intramolecular hydrogen bond in the complex, which involves the amine group and the O atom from sulfate anion (N5—H5A···O4).

π—π interactions between symmetry-related phenantroline moieties with a shortest centroid to centroid interaction of 3.573 (2) Å may consolidate the crystal packing.

S2. Experimental

A 10 mL methanol solution of 1-(1,10-phenanthrolin-9-yl)-1H-pyrazol-3-amine (0.0549 g, 0.21 mmol) was added into a 10 mL water solution containing $CuSO_4{\cdot}5H_2O$ (0.0549 g, 0.22 mmol), and the resulting solution was stirred for a few minutes. Yellow single crystals were obtained after the filtrate had been allowed to stand at room temperature for about one week.

S3. Refinement

The positions of the H atoms of the water molecule and hydroxyl group were located in a difference map; other H atoms were placed in calculated positions. All H atoms were refined as riding with C—H = 0.96 Å, U_{iso} = 1.5U_{eq}(C) for methyl group; C—H = 0.93 Å, U_{iso} = 1.2U_{eq}(C) for aromatic groups; N—H = 0.86 Å, U_{iso} = 1.2U_{eq}(N); O—H = 0.84-0.90 Å, U_{iso} = 1.5U_{eq}(O).

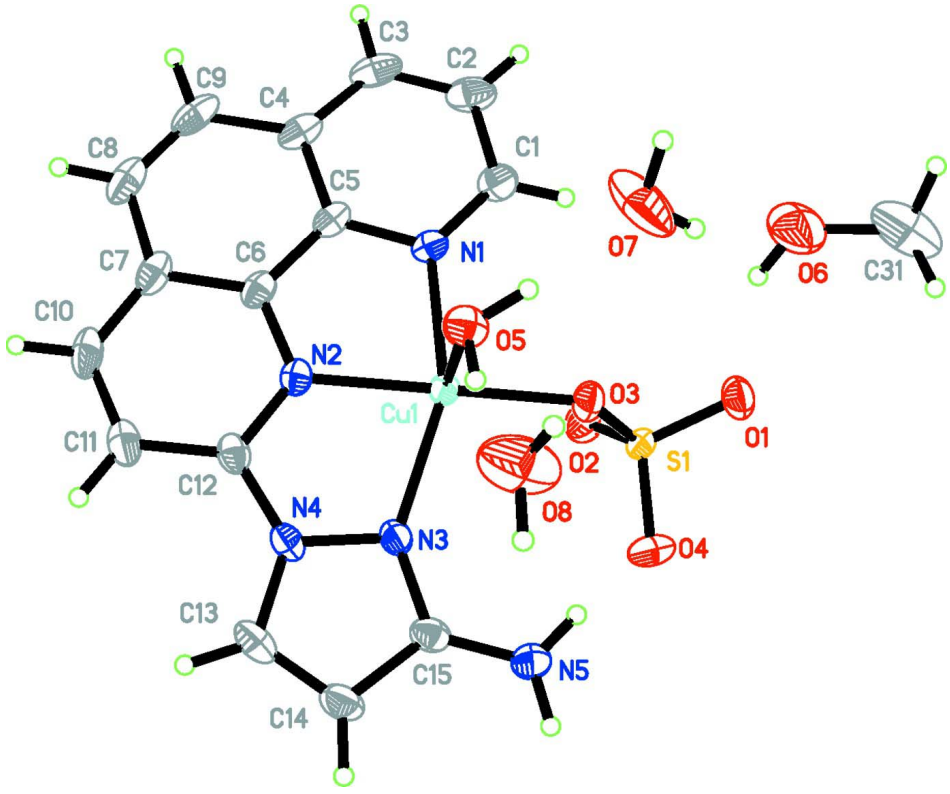

Figure 1

The asymmetric unit of the title compound with displacement ellipsoids shown at the 30% probability level.

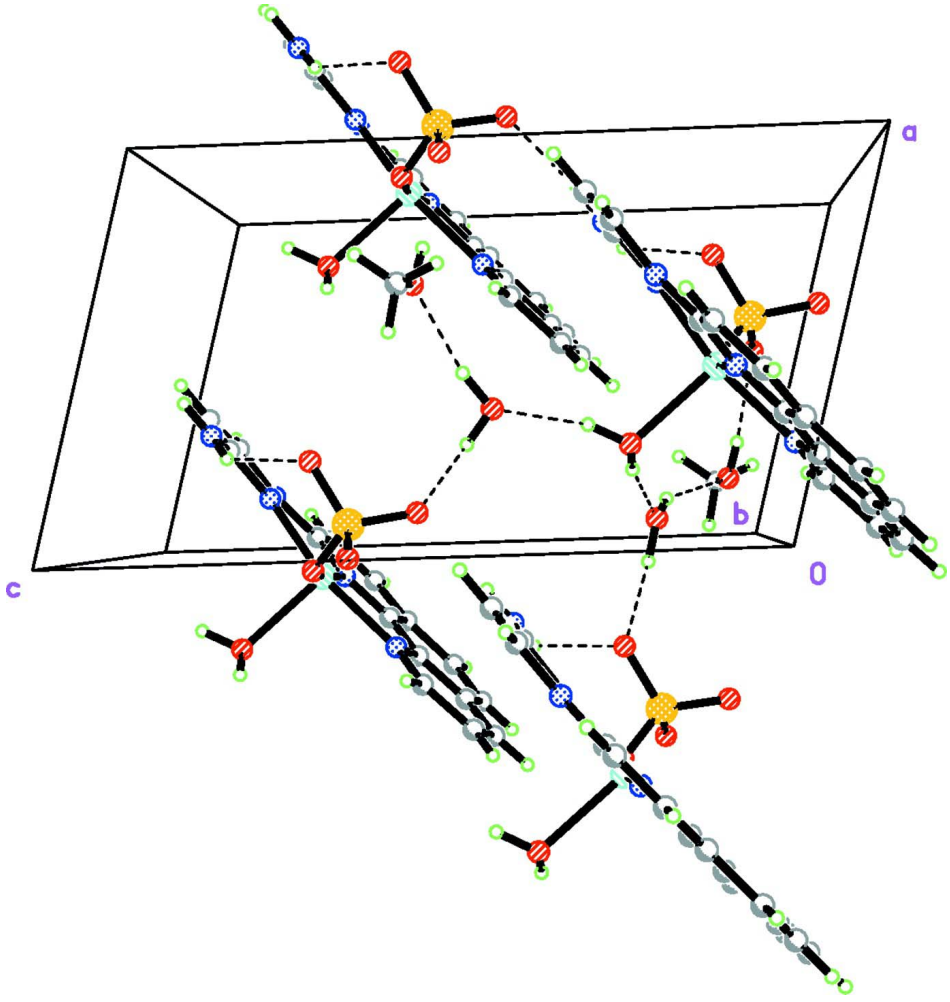

Figure 2

Unit cell of (I), showing the packing features consolidated by hydrogen bonding interactions

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Crystal data

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Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 8.0190\ (13)$ Å
$b = 18.489\ (3)$ Å
$c = 14.086\ (2)$ Å
$\beta = 104.551\ (2)°$
$V = 2021.4\ (6)$ Å^3
$Z = 4$

$F(000) = 1044$
$D_x = 1.666$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2683 reflections
$\theta = 2.7–23.6°$
$\mu = 1.24$ mm^{-1}
$T = 298$ K
Prism, yellow
0.22 × 0.15 × 0.11 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.772, T_{max} = 0.876
11702 measured reflections
4394 independent reflections
3434 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.0°, θ_{min} = 1.9°
h = −10→7
k = −23→19
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.119
S = 1.03
4394 reflections
281 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.2654P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1583 (4)	0.18352 (19)	−0.0328 (3)	0.0448 (8)
H1	0.1747	0.2313	−0.0121	0.054*
C2	0.0344 (5)	0.1677 (2)	−0.1206 (3)	0.0554 (10)
H2	−0.0272	0.2050	−0.1579	0.066*
C3	0.0052 (5)	0.0986 (2)	−0.1506 (3)	0.0541 (10)
H3	−0.0761	0.0883	−0.2088	0.065*
C4	0.0969 (4)	0.04186 (19)	−0.0944 (2)	0.0423 (8)
C5	0.2197 (4)	0.06290 (17)	−0.0093 (2)	0.0353 (7)
C6	0.3202 (4)	0.00945 (16)	0.0501 (2)	0.0352 (7)
C7	0.3036 (4)	−0.06449 (17)	0.0284 (3)	0.0427 (8)
C8	0.1765 (5)	−0.0840 (2)	−0.0580 (3)	0.0532 (10)
H8	0.1609	−0.1326	−0.0749	0.064*
C9	0.0787 (5)	−0.0343 (2)	−0.1156 (3)	0.0532 (10)
H9	−0.0036	−0.0495	−0.1710	0.064*
C10	0.4149 (5)	−0.11097 (18)	0.0962 (3)	0.0506 (9)
H10	0.4066	−0.1607	0.0860	0.061*

C11	0.5327 (5)	−0.08488 (17)	0.1751 (3)	0.0475 (9)
H11	0.6048	−0.1159	0.2189	0.057*
C12	0.5431 (4)	−0.00930 (16)	0.1890 (2)	0.0362 (7)
C13	0.7915 (4)	0.00404 (19)	0.3364 (3)	0.0481 (9)
H13	0.8215	−0.0438	0.3523	0.058*
C14	0.8710 (5)	0.0619 (2)	0.3822 (3)	0.0493 (9)
H14	0.9655	0.0622	0.4364	0.059*
C15	0.7838 (4)	0.12364 (18)	0.3324 (2)	0.0385 (7)
C31	0.1612 (7)	0.4606 (4)	0.1058 (4)	0.111 (2)
H31A	0.2316	0.4733	0.1694	0.166*
H31B	0.0442	0.4747	0.1012	0.166*
H31C	0.2027	0.4852	0.0563	0.166*
Cu1	0.44408 (4)	0.138051 (18)	0.15183 (3)	0.03011 (13)
N1	0.2516 (3)	0.13245 (13)	0.02083 (18)	0.0343 (6)
N2	0.4373 (3)	0.03481 (13)	0.12916 (18)	0.0334 (6)
N3	0.6532 (3)	0.10168 (13)	0.25914 (18)	0.0347 (6)
N4	0.6587 (3)	0.02680 (13)	0.26229 (19)	0.0370 (6)
N5	0.8209 (4)	0.19272 (15)	0.3524 (2)	0.0529 (8)
H5A	0.7596	0.2259	0.3174	0.063*
H5B	0.9063	0.2044	0.4004	0.063*
O1	0.4992 (3)	0.35921 (11)	0.0990 (2)	0.0515 (6)
O2	0.6055 (3)	0.25862 (13)	0.02490 (17)	0.0525 (6)
O3	0.4648 (3)	0.24075 (11)	0.15597 (17)	0.0434 (6)
O4	0.7439 (3)	0.29447 (14)	0.18900 (18)	0.0538 (7)
O5	0.2591 (3)	0.13987 (12)	0.24556 (18)	0.0480 (6)
H4	0.1973	0.1805	0.2347	0.072*
H5	0.3107	0.1423	0.3096	0.072*
O6	0.1687 (4)	0.3845 (2)	0.0919 (3)	0.0984 (12)
H12	0.2611	0.3620	0.0915	0.148*
O7	0.0713 (4)	0.2581 (2)	0.1844 (3)	0.1175 (16)
H6	0.1204	0.2972	0.1766	0.176*
H7	−0.0386	0.2670	0.1828	0.176*
O8	0.3587 (5)	0.1592 (2)	0.4472 (3)	0.1121 (14)
H17	0.4504	0.1598	0.4992	0.168*
H18	0.2726	0.1752	0.4720	0.168*
S1	0.58095 (10)	0.28883 (4)	0.11578 (6)	0.03254 (19)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.046 (2)	0.046 (2)	0.0389 (18)	−0.0066 (15)	0.0051 (15)	0.0077 (15)
C2	0.046 (2)	0.077 (3)	0.0372 (19)	−0.0089 (19)	−0.0022 (16)	0.0165 (19)
C3	0.0403 (19)	0.086 (3)	0.0324 (18)	−0.0197 (19)	0.0020 (15)	−0.0022 (19)
C4	0.0389 (18)	0.061 (2)	0.0299 (16)	−0.0185 (16)	0.0142 (14)	−0.0122 (15)
C5	0.0363 (17)	0.0417 (17)	0.0304 (15)	−0.0119 (14)	0.0127 (13)	−0.0075 (13)
C6	0.0352 (16)	0.0366 (16)	0.0381 (17)	−0.0090 (13)	0.0175 (14)	−0.0069 (14)
C7	0.0465 (19)	0.0374 (17)	0.053 (2)	−0.0135 (15)	0.0298 (16)	−0.0170 (16)
C8	0.057 (2)	0.048 (2)	0.064 (3)	−0.0223 (18)	0.032 (2)	−0.0255 (19)

C9	0.050 (2)	0.070 (3)	0.044 (2)	−0.0303 (19)	0.0202 (17)	−0.0283 (19)
C10	0.061 (2)	0.0277 (16)	0.075 (3)	−0.0035 (16)	0.039 (2)	−0.0118 (18)
C11	0.053 (2)	0.0319 (17)	0.064 (2)	0.0059 (15)	0.0256 (18)	0.0052 (16)
C12	0.0389 (17)	0.0307 (15)	0.0439 (18)	0.0049 (13)	0.0199 (15)	0.0023 (14)
C13	0.053 (2)	0.048 (2)	0.043 (2)	0.0213 (17)	0.0115 (17)	0.0141 (17)
C14	0.049 (2)	0.055 (2)	0.0372 (18)	0.0147 (17)	−0.0026 (16)	0.0036 (16)
C15	0.0375 (17)	0.0467 (19)	0.0293 (16)	0.0077 (14)	0.0048 (14)	0.0000 (14)
C31	0.090 (4)	0.147 (6)	0.096 (4)	0.053 (4)	0.026 (3)	0.035 (4)
Cu1	0.0322 (2)	0.0259 (2)	0.0296 (2)	−0.00044 (14)	0.00279 (15)	−0.00061 (14)
N1	0.0318 (13)	0.0393 (14)	0.0302 (13)	−0.0064 (11)	0.0049 (11)	0.0000 (11)
N2	0.0378 (14)	0.0286 (13)	0.0354 (14)	−0.0010 (10)	0.0123 (12)	−0.0030 (11)
N3	0.0386 (15)	0.0293 (13)	0.0341 (14)	0.0055 (11)	0.0049 (11)	0.0012 (11)
N4	0.0407 (15)	0.0326 (14)	0.0376 (14)	0.0116 (11)	0.0095 (12)	0.0035 (11)
N5	0.0575 (19)	0.0450 (17)	0.0422 (17)	0.0028 (14)	−0.0134 (15)	−0.0033 (14)
O1	0.0539 (15)	0.0301 (12)	0.0713 (18)	0.0039 (10)	0.0170 (13)	0.0049 (11)
O2	0.0635 (16)	0.0543 (15)	0.0387 (13)	−0.0005 (12)	0.0110 (12)	−0.0137 (11)
O3	0.0458 (13)	0.0280 (11)	0.0564 (15)	−0.0053 (9)	0.0129 (11)	−0.0011 (10)
O4	0.0359 (13)	0.0714 (17)	0.0474 (15)	−0.0082 (12)	−0.0021 (11)	−0.0075 (12)
O5	0.0465 (14)	0.0536 (15)	0.0445 (14)	0.0042 (11)	0.0128 (11)	−0.0029 (11)
O6	0.054 (2)	0.094 (3)	0.153 (4)	0.0053 (18)	0.037 (2)	0.015 (2)
O7	0.077 (2)	0.103 (3)	0.195 (4)	0.046 (2)	0.075 (3)	0.068 (3)
O8	0.097 (3)	0.176 (4)	0.057 (2)	0.041 (3)	0.0068 (19)	−0.019 (2)
S1	0.0335 (4)	0.0271 (4)	0.0331 (4)	−0.0026 (3)	0.0009 (3)	−0.0041 (3)

Geometric parameters (Å, º)

C1—N1	1.318 (4)	C14—C15	1.427 (4)
C1—C2	1.408 (5)	C14—H14	0.9300
C1—H1	0.9300	C15—N5	1.325 (4)
C2—C3	1.349 (6)	C15—N3	1.336 (4)
C2—H2	0.9300	C31—O6	1.424 (6)
C3—C4	1.404 (5)	C31—H31A	0.9600
C3—H3	0.9300	C31—H31B	0.9600
C4—C5	1.402 (4)	C31—H31C	0.9600
C4—C9	1.439 (5)	Cu1—O3	1.906 (2)
C5—N1	1.358 (4)	Cu1—N2	1.934 (2)
C5—C6	1.410 (4)	Cu1—N3	2.068 (2)
C6—N2	1.348 (4)	Cu1—N1	2.090 (2)
C6—C7	1.400 (4)	Cu1—O5	2.220 (2)
C7—C10	1.421 (5)	N3—N4	1.386 (3)
C7—C8	1.424 (5)	N5—H5A	0.8600
C8—C9	1.342 (5)	N5—H5B	0.8600
C8—H8	0.9300	O1—S1	1.450 (2)
C9—H9	0.9300	O2—S1	1.455 (2)
C10—C11	1.354 (5)	O3—S1	1.498 (2)
C10—H10	0.9300	O4—S1	1.451 (2)
C11—C12	1.411 (4)	O5—H4	0.8913
C11—H11	0.9300	O5—H5	0.8938

C12—N2	1.317 (4)	O6—H12	0.8515
C12—N4	1.375 (4)	O7—H6	0.8442
C13—C14	1.328 (5)	O7—H7	0.8906
C13—N4	1.357 (4)	O8—H17	0.8981
C13—H13	0.9300	O8—H18	0.8983

N1—C1—C2	121.9 (3)	O6—C31—H31A	109.5
N1—C1—H1	119.1	O6—C31—H31B	109.5
C2—C1—H1	119.1	H31A—C31—H31B	109.5
C3—C2—C1	120.0 (4)	O6—C31—H31C	109.5
C3—C2—H2	120.0	H31A—C31—H31C	109.5
C1—C2—H2	120.0	H31B—C31—H31C	109.5
C2—C3—C4	120.4 (3)	O3—Cu1—N2	170.82 (10)
C2—C3—H3	119.8	O3—Cu1—N3	104.67 (10)
C4—C3—H3	119.8	N2—Cu1—N3	77.52 (10)
C5—C4—C3	115.5 (3)	O3—Cu1—N1	96.64 (10)
C5—C4—C9	117.5 (3)	N2—Cu1—N1	79.71 (10)
C3—C4—C9	127.0 (3)	N3—Cu1—N1	155.91 (10)
N1—C5—C4	124.5 (3)	O3—Cu1—O5	91.88 (9)
N1—C5—C6	116.3 (3)	N2—Cu1—O5	96.76 (9)
C4—C5—C6	119.2 (3)	N3—Cu1—O5	96.34 (10)
N2—C6—C7	121.9 (3)	N1—Cu1—O5	94.02 (10)
N2—C6—C5	115.0 (3)	C1—N1—C5	117.6 (3)
C7—C6—C5	123.1 (3)	C1—N1—Cu1	131.1 (2)
C6—C7—C10	115.8 (3)	C5—N1—Cu1	111.23 (19)
C6—C7—C8	116.3 (3)	C12—N2—C6	121.1 (3)
C10—C7—C8	127.9 (3)	C12—N2—Cu1	121.2 (2)
C9—C8—C7	121.8 (3)	C6—N2—Cu1	117.7 (2)
C9—C8—H8	119.1	C15—N3—N4	105.4 (2)
C7—C8—H8	119.1	C15—N3—Cu1	143.2 (2)
C8—C9—C4	122.1 (3)	N4—N3—Cu1	111.22 (18)
C8—C9—H9	118.9	C13—N4—C12	132.7 (3)
C4—C9—H9	118.9	C13—N4—N3	110.3 (3)
C11—C10—C7	121.8 (3)	C12—N4—N3	116.8 (2)
C11—C10—H10	119.1	C15—N5—H5A	120.0
C7—C10—H10	119.1	C15—N5—H5B	120.0
C10—C11—C12	118.1 (3)	H5A—N5—H5B	120.0
C10—C11—H11	120.9	S1—O3—Cu1	129.60 (14)
C12—C11—H11	120.9	Cu1—O5—H4	109.7
N2—C12—N4	112.6 (3)	Cu1—O5—H5	113.0
N2—C12—C11	121.2 (3)	H4—O5—H5	103.1
N4—C12—C11	126.2 (3)	C31—O6—H12	123.5
C14—C13—N4	108.2 (3)	H6—O7—H7	109.3
C14—C13—H13	125.9	H17—O8—H18	103.3
N4—C13—H13	125.9	O1—S1—O4	109.94 (15)
C13—C14—C15	106.8 (3)	O1—S1—O2	110.92 (15)
C13—C14—H14	126.6	O4—S1—O2	110.86 (15)
C15—C14—H14	126.6	O1—S1—O3	107.19 (14)

N5—C15—N3	123.2 (3)	O4—S1—O3	107.99 (14)
N5—C15—C14	127.6 (3)	O2—S1—O3	109.84 (14)
N3—C15—C14	109.2 (3)		

N1—C1—C2—C3	1.8 (6)	N4—C12—N2—C6	176.8 (3)
C1—C2—C3—C4	0.4 (6)	C11—C12—N2—C6	−2.9 (4)
C2—C3—C4—C5	−1.7 (5)	N4—C12—N2—Cu1	−3.3 (4)
C2—C3—C4—C9	179.0 (3)	C11—C12—N2—Cu1	177.0 (2)
C3—C4—C5—N1	0.9 (5)	C7—C6—N2—C12	0.9 (4)
C9—C4—C5—N1	−179.7 (3)	C5—C6—N2—C12	−177.8 (3)
C3—C4—C5—C6	−178.5 (3)	C7—C6—N2—Cu1	−179.0 (2)
C9—C4—C5—C6	0.9 (4)	C5—C6—N2—Cu1	2.3 (3)
N1—C5—C6—N2	−0.8 (4)	N3—Cu1—N2—C12	5.9 (2)
C4—C5—C6—N2	178.7 (3)	N1—Cu1—N2—C12	178.0 (2)
N1—C5—C6—C7	−179.5 (3)	O5—Cu1—N2—C12	−89.1 (2)
C4—C5—C6—C7	−0.1 (5)	N3—Cu1—N2—C6	−174.2 (2)
N2—C6—C7—C10	1.4 (4)	N1—Cu1—N2—C6	−2.1 (2)
C5—C6—C7—C10	−179.9 (3)	O5—Cu1—N2—C6	90.8 (2)
N2—C6—C7—C8	−179.2 (3)	N5—C15—N3—N4	179.5 (3)
C5—C6—C7—C8	−0.5 (5)	C14—C15—N3—N4	−0.4 (3)
C6—C7—C8—C9	0.3 (5)	N5—C15—N3—Cu1	−5.7 (6)
C10—C7—C8—C9	179.6 (3)	C14—C15—N3—Cu1	174.4 (3)
C7—C8—C9—C4	0.6 (5)	O3—Cu1—N3—C15	7.6 (4)
C5—C4—C9—C8	−1.2 (5)	N2—Cu1—N3—C15	178.4 (4)
C3—C4—C9—C8	178.2 (3)	N1—Cu1—N3—C15	159.1 (3)
C6—C7—C10—C11	−1.8 (5)	O5—Cu1—N3—C15	−86.0 (4)
C8—C7—C10—C11	178.9 (3)	O3—Cu1—N3—N4	−177.80 (18)
C7—C10—C11—C12	0.0 (5)	N2—Cu1—N3—N4	−6.98 (18)
C10—C11—C12—N2	2.5 (5)	N1—Cu1—N3—N4	−26.3 (4)
C10—C11—C12—N4	−177.3 (3)	O5—Cu1—N3—N4	88.58 (19)
N4—C13—C14—C15	−1.0 (4)	C14—C13—N4—C12	175.1 (3)
C13—C14—C15—N5	−179.0 (3)	C14—C13—N4—N3	0.8 (4)
C13—C14—C15—N3	0.8 (4)	N2—C12—N4—C13	−177.5 (3)
C2—C1—N1—C5	−2.6 (5)	C11—C12—N4—C13	2.2 (6)
C2—C1—N1—Cu1	179.4 (3)	N2—C12—N4—N3	−3.4 (4)
C4—C5—N1—C1	1.2 (5)	C11—C12—N4—N3	176.3 (3)
C6—C5—N1—C1	−179.3 (3)	C15—N3—N4—C13	−0.2 (3)
C4—C5—N1—Cu1	179.7 (2)	Cu1—N3—N4—C13	−176.9 (2)
C6—C5—N1—Cu1	−0.9 (3)	C15—N3—N4—C12	−175.6 (3)
O3—Cu1—N1—C1	−8.8 (3)	Cu1—N3—N4—C12	7.8 (3)
N2—Cu1—N1—C1	179.8 (3)	N3—Cu1—O3—S1	77.66 (19)
N3—Cu1—N1—C1	−161.0 (3)	N1—Cu1—O3—S1	−91.02 (19)
O5—Cu1—N1—C1	83.6 (3)	O5—Cu1—O3—S1	174.72 (18)
O3—Cu1—N1—C5	173.1 (2)	Cu1—O3—S1—O1	155.30 (18)
N2—Cu1—N1—C5	1.6 (2)	Cu1—O3—S1—O4	−86.3 (2)
N3—Cu1—N1—C5	20.8 (4)	Cu1—O3—S1—O2	34.7 (2)
O5—Cu1—N1—C5	−94.6 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H4···O7	0.89	1.79	2.671 (4)	167
O5—H5···O8	0.89	1.90	2.774 (4)	164
O6—H12···O1	0.85	1.89	2.668 (4)	152
O7—H6···O6	0.84	2.10	2.878 (5)	153
O7—H7···O4^{i}	0.89	1.84	2.726 (4)	173
O8—H17···O6^{ii}	0.90	2.07	2.906 (5)	154
O8—H18···O2^{iii}	0.90	2.09	2.957 (4)	163
N5—H5*A*···O4	0.86	2.19	2.916 (4)	143
N5—H5*B*···O2^{ii}	0.86	2.17	3.022 (4)	175

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