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Dimethylammonium tetraaqua-(hydrogensulfato)sulfatocuprate(II)

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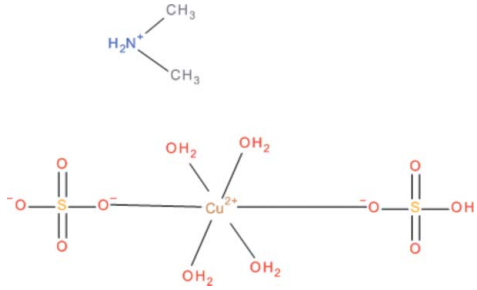
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(N–C) = 0.005 Å; R factor = 0.032; wR factor = 0.092; data-to-parameter ratio = 19.4.

In the title salt, $[(CH_3)_2NH_2][Cu(HSO_4)(SO_4)(H_2O)_4]$, one type of cation and anion is present in the asymmetric unit. The Cu^{II} atom in the complex anion, $[Cu(HSO_4)(SO_4)(H_2O)_4]^-$, has a tetragonal bipyramidal [4 + 2] coordination caused by a Jahn–Teller distortion, with the aqua ligands in equatorial and two O atoms of tetrahedral HSO_4 and SO_4 units in apical positions. Both types of ions form sheets parallel to (010). The interconnection within and between the sheets is reinforced by O—H···O and N—H···O hydrogen bonds, respectively, involving the water molecules, the two types of sulfate anions and the ammonium groups.

Related literature

For related structures, see: Montgomery & Lingafelter (1966); Montgomery *et al.* (1967); Held (2003, 2014). For bond-valence parameters, see: Brown & Altermatt (1985).



Experimental

Crystal data

$(C_2H_8N)[Cu(HSO_4)(SO_4)(H_2O)_4]$
M_r = 374.8
Orthorhombic, *Pbca*
a = 7.1825 (9) Å
b = 17.9973 (15) Å
c = 19.410 (3) Å
V = 2509.0 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 2.13 mm^{-1}
T = 295 K
0.29 × 0.27 × 0.25 mm

Data collection

Nonius MACH3 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.960, T_{max} = 0.999
7482 measured reflections
3801 independent reflections
2231 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
3 standard reflections every 100 reflections
intensity decay: −1.4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.092
S = 0.97
3801 reflections
196 parameters
8 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···O13^{i}	0.90	2.22	2.932 (4)	136
N3—H3A···O11^{ii}	0.90	2.00	2.871 (3)	164
O1—H1D···O12^{iii}	0.84 (2)	1.82 (2)	2.656 (3)	175 (4)
O1—H1E···O12^{iv}	0.85 (2)	1.85 (2)	2.687 (3)	171 (4)
O2—H2D···O24^{v}	0.85 (2)	1.90 (2)	2.745 (3)	174 (3)
O2—H2E···O24^{vi}	0.84 (2)	1.94 (2)	2.777 (3)	174 (4)
O3—H3D···O23^{vii}	0.86 (2)	1.87 (2)	2.722 (3)	173 (4)
O3—H3E···O14^{iv}	0.85 (2)	1.82 (2)	2.661 (3)	167 (4)
O4—H4D···O23^{vi}	0.84 (2)	1.91 (2)	2.753 (3)	175 (4)
O4—H4E···O14^{viii}	0.87 (2)	1.76 (2)	2.627 (3)	171 (5)
O21—H21···O13^{ix}	0.82	1.71	2.484 (3)	156

Symmetry codes: (i) $-x-\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (iv) $x+1, y, z$; (v) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (vi) $x-1, y, z$; (vii) $-x+2, -y, -z$; (viii) $-x+1, -y, -z$; (ix) $-x+\frac{3}{2}, y-\frac{1}{2}, z$.

Data collection: *CAD-4* (Enraf–Nonius, 1989); cell refinement: *CAD-4*; data reduction: *WinGX* (Farrugia, 2012); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2002) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5006).

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supplementary materials

Acta Cryst. (2014). E**70**, m119 [doi:10.1107/S1600536814004486]

Dimethylammonium tetraaqua(hydrogensulfato)sulfatocuprate(II)

Peter Held

1. Comment

In the course of a systematic search for new "double salts" of simple secondary amines and monovalent cations of various inorganic acids, the structures of the new compounds $(C_2N_2H_{10})Li_2(SO_4)_2$ and $[NH_2(CH_2CH_3)_2][H_2PO_4]$ have been described (Held, 2003, 2014). In continuation of these studies, ethylenediamine and lithium were replaced with dimethylamine and divalent copper, respectively, yielding crystals of the title compound with composition $[(CH_3)_2NH_2][Cu(HSO_4)(SO_4)(H_2O)_4]$.

The structure of the title compound consists of SO_4^{2-} and HSO_4^- anions, $NH_2(CH_3)_2^+$ and Cu^{2+} cations as well as water molecules as basic structure units. All atoms are located on general Wykoff position 8*c*. The Cu^{2+} cation is surrounded by six O atoms of four equatorially placed water molecules (averaged distance = 1.952 (17) Å) and of two apical sulfate groups (averaged distance = 2.45 (6) Å), forming a distorted tetragonal bipyramid, $[Cu(H_2O)_4(SO_4)(HSO_4)]$, which is markedly elongated to both apices due to the Jahn-Teller-effect of the Cu^{2+} cation, leading to a pronounced [4 + 2] coordination (Fig. 1) and an overall bond valence sum (Brown & Altermatt, 1985) of 2.17 valence units. Caused by the dissimilar coordination partners, the Cu—O distances vary widely in comparison with more uniform O environments, *e.g.* in the Tutton's salt $(NH_4)_2Cu(SO_4)_2(H_2O)_6$ with a hexa-coordination of Cu^{2+} by water molecules (Montgomery & Lingafelter (1966); Montgomery *et al.*(1967)). As expected, the S—O distance of the OH-function (1.545 (2) Å) is considerably longer than the other S—O distances (average distance 1.459 (11) Å).

In the title compound, the $[Cu(H_2O)_4Cu(SO_4)_2]^{2-}$ anions form sheets parallel to (010), hold apart from each other by dimethylammonium groups (Fig. 2). Hydrogen bonds of medium strength involving water molecules as donor groups and O atoms of the sulfate anions as acceptor groups interconnect neighbouring $[Cu(H_2O)_4(SO_4)(HSO_4)]^{2-}$ units. Together with N—H···O hydrogen bonds of the ammonium hydrogen atoms, a three-dimensional framework (Fig. 3) is formed.

2. Experimental

The title compound was obtained by reaction of aqueous solution of copper(II) sulfate with dimethylamine and sulfuric acid in the stoichiometric ratio 1:1:1. The solution was kept at room temperature by cooling. The title compound crystallized by slow evaporation of the solvent at room temperature in form of optical clear, light-blue crystals with dimensions up to 5 mm within a few weeks.

3. Refinement

The H atoms were clearly discernible from difference Fourier maps. However, to all hydrogen atoms riding model contraints were applied in the least squares refinement, with C—H = 0.96 Å for methyl H atoms (U_{iso}(H) = 1.5U_{eq}(C)), with N—H = 0.90 Å (U_{iso}(H) = 1.2U_{eq}(N)) and with O—H = 0.82 Å (U_{iso}(H) = 1.2U_{eq}(O)) for the H atom of the HSO_4^- anion . All H atoms of the water molecules were refined with a distance restraint of O—H ≃ 0.87 Å.

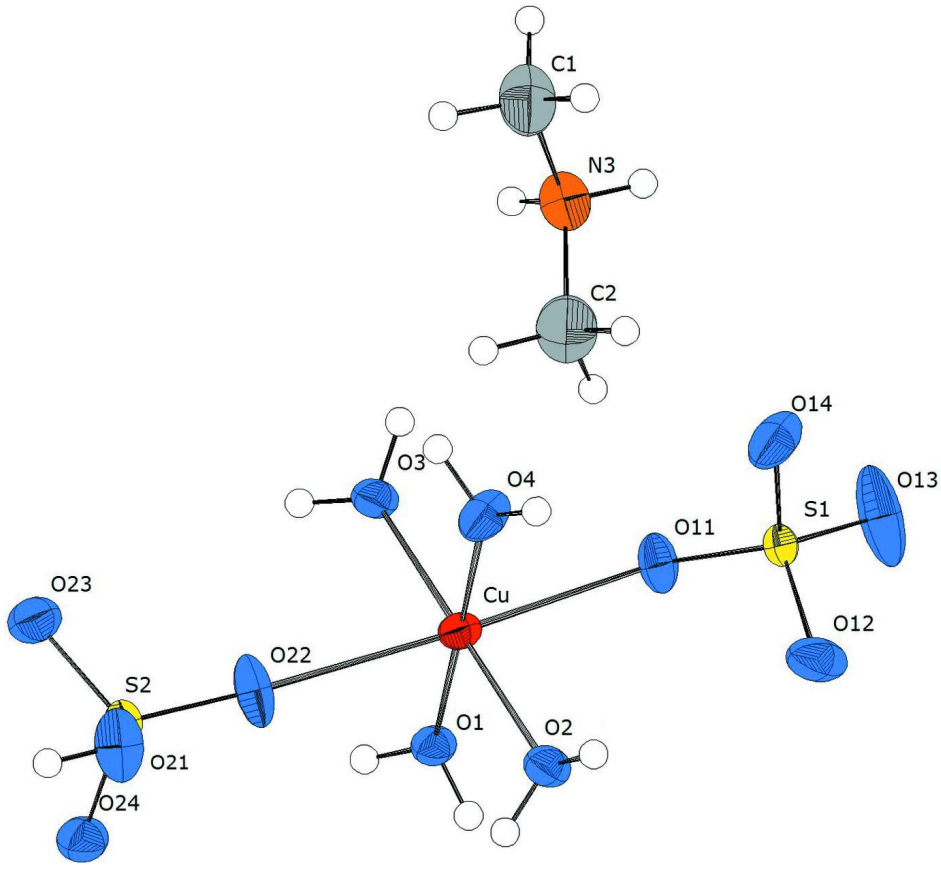

Figure 1

The molecular entities in the structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

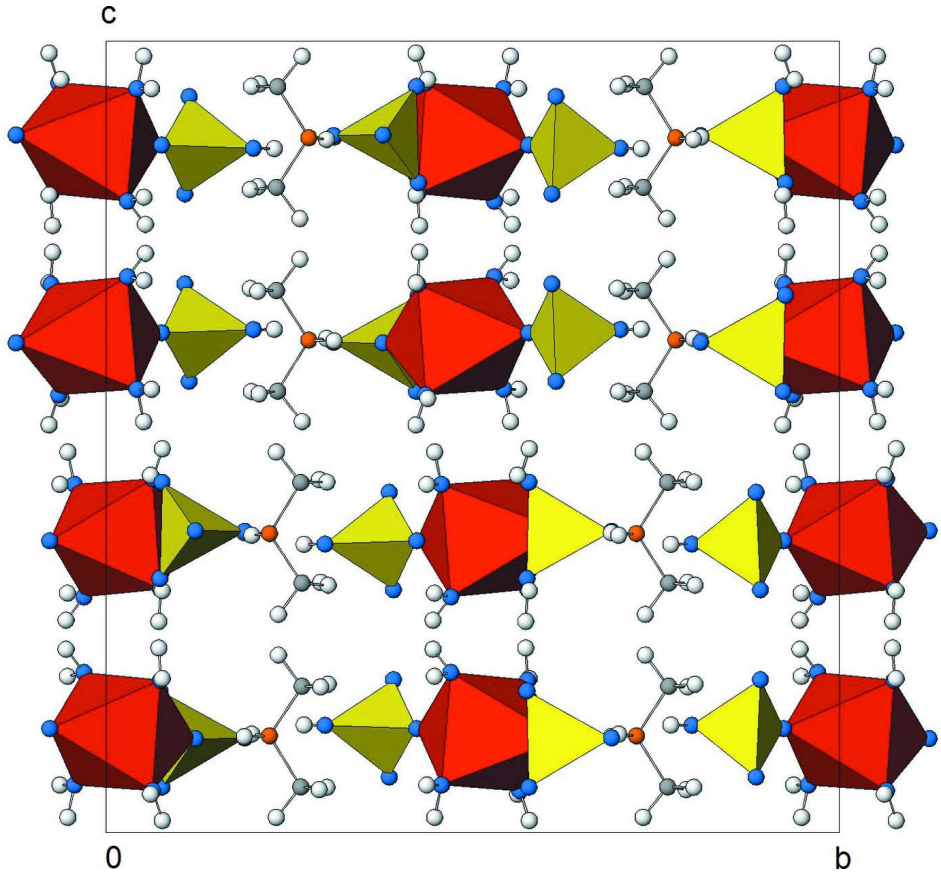

Figure 2

(100)-projection of the crystal structure of the title compound. Colour scheme: $[Cu(H_2O)_4(SO_4)(HSO_4)]$ bipyramids (red), (SO_4) tetrahedra (yellow), N (orange), C (grey) and H (white).

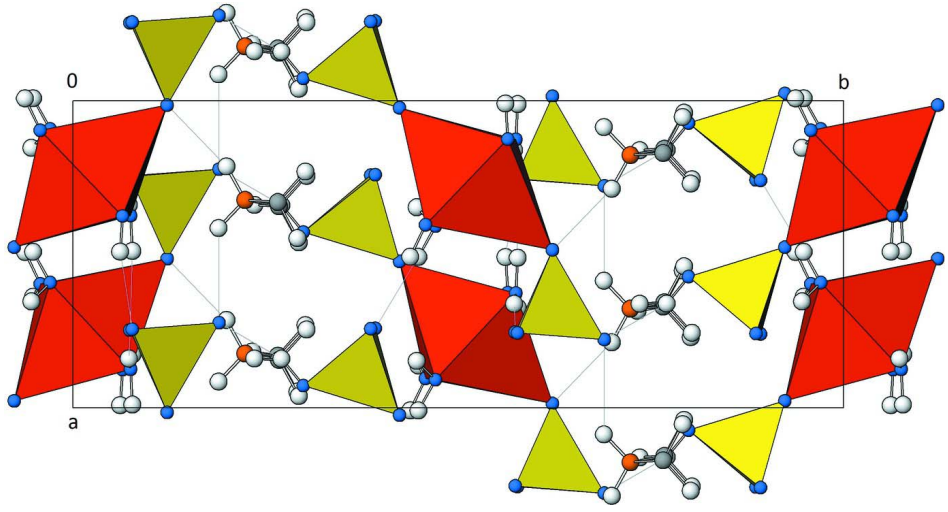

Figure 3

(001)-projection of the crystal structure of the title compound. Colour scheme as in Fig. 2. Hydrogen bonding is indicated by small grey lines.

Dimethylammonium tetraaqua(hydrogensulfato)sulfatocuprate(II)

Crystal data

$(C_2H_8N)[Cu(HSO_4)(SO_4)(H_2O)_4]$
M_r = 374.8
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 7.1825 (9) Å
b = 17.9973 (15) Å
c = 19.410 (3) Å
V = 2509.0 (6) Å^3
Z = 8
$F(000)$ = 1544
D_x = 1.985 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 21.0–26.0°
μ = 2.13 mm^{-1}
T = 295 K
Parallelepiped, light blue
0.29 × 0.27 × 0.25 mm

Data collection

Nonius MACH3 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.960, T_{max} = 0.999
7482 measured reflections
3801 independent reflections
2231 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 30.4°, θ_{min} = 2.3°
h = −10→0
k = −25→0
l = −27→27
3 standard reflections every 100 reflections
intensity decay: −1.4%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.092
S = 0.97
3801 reflections
196 parameters
8 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.4413P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0081 (3)

Special details

Experimental. A suitable single-crystal was carefully selected under a polarizing microscope and mounted in a glass capillary.

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}
Cu	0.73284 (4)	0.015242 (18)	0.126573 (17)	0.01956 (10)

O1	0.8740 (3)	0.07478 (12)	0.19257 (11)	0.0228 (4)
O2	0.5919 (3)	−0.02976 (12)	0.20235 (11)	0.0253 (5)
O3	0.8752 (3)	0.06422 (15)	0.05293 (11)	0.0293 (5)
O4	0.5959 (3)	−0.04258 (14)	0.06014 (12)	0.0312 (5)
S1	0.31024 (8)	0.11572 (4)	0.11869 (4)	0.01745 (14)
O11	0.5141 (3)	0.12213 (11)	0.11860 (11)	0.0278 (5)
O12	0.2463 (3)	0.07405 (15)	0.17900 (12)	0.0422 (6)
O13	0.2226 (3)	0.18941 (12)	0.11961 (17)	0.0566 (9)
O14	0.2441 (3)	0.07687 (16)	0.05733 (11)	0.0425 (7)
S2	1.14451 (9)	−0.12021 (4)	0.13213 (4)	0.01923 (15)
O21	1.0717 (3)	−0.20091 (11)	0.13532 (13)	0.0376 (6)
H21	1.1602	−0.2297	0.1359	0.056*
O22	0.9771 (3)	−0.07646 (12)	0.13129 (14)	0.0397 (6)
O23	1.2575 (3)	−0.11363 (13)	0.07020 (10)	0.0326 (5)
O24	1.2594 (3)	−0.10790 (13)	0.19321 (10)	0.0305 (5)
N3	−0.3234 (4)	−0.27683 (14)	0.12215 (14)	0.0310 (6)
H3A	−0.2138	−0.3010	0.1241	0.037*
H3B	−0.4141	−0.3113	0.1212	0.037*
C1	−0.3443 (6)	−0.2325 (2)	0.1854 (2)	0.0477 (10)
H1A	−0.3395	−0.2647	0.2248	0.072*
H1B	−0.4617	−0.2070	0.1845	0.072*
H1C	−0.2452	−0.1968	0.1881	0.072*
C2	−0.3304 (6)	−0.2343 (2)	0.0576 (2)	0.0465 (10)
H2A	−0.3167	−0.2676	0.0192	0.070*
H2B	−0.2312	−0.1986	0.0570	0.070*
H2C	−0.4478	−0.2091	0.0543	0.070*
H1D	0.841 (5)	0.0743 (19)	0.2340 (11)	0.044 (12)*
H1E	0.992 (3)	0.075 (2)	0.193 (2)	0.052 (14)*
H2D	0.651 (4)	−0.0538 (16)	0.2328 (13)	0.026 (9)*
H2E	0.489 (4)	−0.051 (2)	0.198 (2)	0.053 (13)*
H3D	0.827 (5)	0.077 (2)	0.0141 (13)	0.056 (13)*
H3E	0.994 (3)	0.063 (2)	0.050 (2)	0.040 (11)*
H4D	0.490 (3)	−0.062 (2)	0.062 (2)	0.058 (14)*
H4E	0.637 (6)	−0.054 (2)	0.0194 (13)	0.072 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.01968 (17)	0.02313 (17)	0.01587 (14)	−0.00449 (13)	0.00006 (14)	0.00032 (16)
O1	0.0208 (11)	0.0291 (11)	0.0184 (10)	−0.0035 (9)	−0.0013 (8)	−0.0016 (9)
O2	0.0204 (11)	0.0325 (13)	0.0230 (10)	−0.0041 (10)	−0.0013 (8)	0.0079 (9)
O3	0.0179 (11)	0.0488 (15)	0.0212 (10)	−0.0047 (11)	−0.0006 (9)	0.0110 (10)
O4	0.0244 (12)	0.0445 (14)	0.0247 (11)	−0.0111 (11)	0.0019 (9)	−0.0131 (10)
S1	0.0138 (3)	0.0171 (3)	0.0214 (3)	0.0002 (2)	−0.0004 (2)	−0.0004 (3)
O11	0.0145 (8)	0.0256 (10)	0.0433 (13)	−0.0021 (7)	−0.0001 (9)	0.0009 (10)
O12	0.0254 (12)	0.0729 (19)	0.0283 (11)	−0.0128 (13)	−0.0034 (10)	0.0189 (12)
O13	0.0242 (11)	0.0190 (10)	0.127 (3)	0.0033 (9)	−0.0063 (16)	−0.0017 (15)
O14	0.0236 (11)	0.0750 (19)	0.0288 (11)	−0.0113 (13)	0.0038 (10)	−0.0206 (12)
S2	0.0168 (3)	0.0172 (3)	0.0237 (3)	0.0008 (2)	−0.0003 (3)	−0.0003 (3)
O21	0.0240 (10)	0.0198 (10)	0.0689 (16)	−0.0024 (8)	0.0041 (11)	−0.0010 (11)

O22	0.0227 (10)	0.0305 (12)	0.0658 (16)	0.0115 (9)	−0.0030 (12)	−0.0021 (13)
O23	0.0296 (11)	0.0438 (13)	0.0244 (10)	−0.0043 (12)	0.0014 (9)	0.0018 (9)
O24	0.0281 (11)	0.0400 (12)	0.0233 (10)	−0.0026 (11)	−0.0024 (9)	−0.0032 (9)
N3	0.0294 (12)	0.0226 (11)	0.0411 (15)	0.0025 (10)	0.0030 (12)	−0.0047 (12)
C1	0.037 (2)	0.053 (2)	0.053 (2)	−0.0009 (19)	0.0071 (18)	−0.023 (2)
C2	0.046 (3)	0.039 (2)	0.055 (2)	−0.0008 (19)	−0.0074 (19)	0.0110 (19)

Geometric parameters (Å, º)

Cu—O4	1.927 (2)	S1—O11	1.4689 (19)
Cu—O1	1.954 (2)	S2—O22	1.438 (2)
Cu—O2	1.961 (2)	S2—O23	1.455 (2)
Cu—O3	1.966 (2)	S2—O24	1.461 (2)
Cu—O22	2.410 (2)	S2—O21	1.545 (2)
Cu—O11	2.489 (2)	O21—H21	0.8200
O1—H1D	0.838 (18)	N3—C2	1.470 (5)
O1—H1E	0.846 (18)	N3—C1	1.471 (4)
O2—H2D	0.848 (18)	N3—H3A	0.9000
O2—H2E	0.837 (19)	N3—H3B	0.9000
O3—H3D	0.857 (18)	C1—H1A	0.9600
O3—H3E	0.852 (18)	C1—H1B	0.9600
O4—H4D	0.843 (18)	C1—H1C	0.9600
O4—H4E	0.869 (19)	C2—H2A	0.9600
S1—O14	1.461 (2)	C2—H2B	0.9600
S1—O12	1.464 (2)	C2—H2C	0.9600
S1—O13	1.468 (2)		

O4—Cu—O1	178.97 (10)	O14—S1—O11	111.16 (14)
O4—Cu—O2	90.88 (10)	O12—S1—O11	110.73 (14)
O1—Cu—O2	90.15 (9)	O13—S1—O11	110.88 (13)
O4—Cu—O3	91.21 (11)	S1—O11—Cu	124.65 (12)
O1—Cu—O3	87.76 (9)	O22—S2—O23	114.37 (15)
O2—Cu—O3	177.57 (10)	O22—S2—O24	113.48 (15)
O4—Cu—O22	91.55 (10)	O23—S2—O24	110.06 (12)
O1—Cu—O22	88.45 (9)	O22—S2—O21	103.44 (13)
O2—Cu—O22	93.69 (9)	O23—S2—O21	107.35 (14)
O3—Cu—O22	87.49 (10)	O24—S2—O21	107.53 (14)
O4—Cu—O11	93.07 (9)	S2—O21—H21	109.5
O1—Cu—O11	86.81 (8)	S2—O22—Cu	169.84 (15)
O2—Cu—O11	92.29 (8)	C2—N3—C1	115.2 (3)
O3—Cu—O11	86.36 (9)	C2—N3—H3A	108.5
O22—Cu—O11	172.37 (7)	C1—N3—H3A	108.5
Cu—O1—H1D	118 (3)	C2—N3—H3B	108.5
Cu—O1—H1E	122 (3)	C1—N3—H3B	108.5
H1D—O1—H1E	106 (4)	H3A—N3—H3B	107.5
Cu—O2—H2D	118 (2)	N3—C1—H1A	109.5
Cu—O2—H2E	125 (3)	N3—C1—H1B	109.5
H2D—O2—H2E	106 (4)	H1A—C1—H1B	109.5
Cu—O3—H3D	123 (3)	N3—C1—H1C	109.5
Cu—O3—H3E	123 (3)	H1A—C1—H1C	109.5

H3D—O3—H3E	111 (4)	H1B—C1—H1C	109.5
Cu—O4—H4D	132 (3)	N3—C2—H2A	109.5
Cu—O4—H4E	124 (3)	N3—C2—H2B	109.5
H4D—O4—H4E	104 (4)	H2A—C2—H2B	109.5
O14—S1—O12	107.74 (15)	N3—C2—H2C	109.5
O14—S1—O13	107.63 (17)	H2A—C2—H2C	109.5
O12—S1—O13	108.58 (17)	H2B—C2—H2C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*B*···O13^{i}	0.90	2.22	2.932 (4)	136
N3—H3*A*···O11^{ii}	0.90	2.00	2.871 (3)	164
O1—H1*D*···O12^{iii}	0.84 (2)	1.82 (2)	2.656 (3)	175 (4)
O1—H1*E*···O12^{iv}	0.85 (2)	1.85 (2)	2.687 (3)	171 (4)
O2—H2*D*···O24^{v}	0.85 (2)	1.90 (2)	2.745 (3)	174 (3)
O2—H2*E*···O24^{vi}	0.84 (2)	1.94 (2)	2.777 (3)	174 (4)
O3—H3*D*···O23^{vii}	0.86 (2)	1.87 (2)	2.722 (3)	173 (4)
O3—H3*E*···O14^{iv}	0.85 (2)	1.82 (2)	2.661 (3)	167 (4)
O4—H4*D*···O23^{vi}	0.84 (2)	1.91 (2)	2.753 (3)	175 (4)
O4—H4*E*···O14^{viii}	0.87 (2)	1.76 (2)	2.627 (3)	171 (5)
O21—H21···O13^{ix}	0.82	1.71	2.484 (3)	156

Symmetry codes: (i) −*x*−1/2, *y*−1/2, *z*; (ii) −*x*+1/2, *y*−1/2, *z*; (iii) *x*+1/2, *y*, −*z*+1/2; (iv) *x*+1, *y*, *z*; (v) *x*−1/2, *y*, −*z*+1/2; (vi) *x*−1, *y*, *z*; (vii) −*x*+2, −*y*, −*z*; (viii) −*x*+1, −*y*, −*z*; (ix) −*x*+3/2, *y*−1/2, *z*.