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Poly[[aqua(μ-4,4′-bipyridine-κ²N:N′)-(μ₃-2-nitro-5-sulfonatobenzoato-κ³O¹:O¹′:O⁵)copper(II)] 4,4′-bipyridine hemisolvate]

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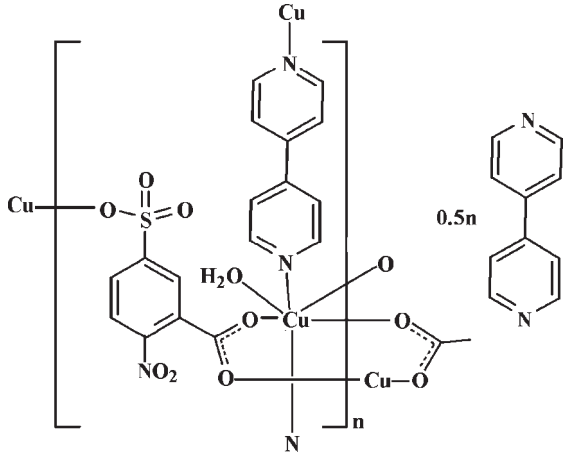
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.065; wR factor = 0.135; data-to-parameter ratio = 12.9.

In the title compound, $[Cu(C_7H_3NO_7S)(C_{10}H_8N_2)(H_2O)]\cdot 0.5C_{10}H_8N_2$, the Cu^{II} atom is six-coordinated by two N atoms from two different bipyridine (bipy) ligands, one sulfonate O atom and two carboxylate O atoms from three 2-nitro-5-sulfonatobenzoate ligands and one water O atom in a distorted octahedral geometry. The bipy solvent molecule lies on an inversion center. The Cu^{II} atoms are linked by the bipy ligands, forming one-dimensional chains, which are connected by the 2-nitro-5-sulfonatobenzoate ligands into a two-dimensional layer-like network. The two-dimensional structure is extended by O—H···O and O—H···N hydrogen bonds into a three-dimensional supramolecular network.

Related literature

For general background to copper(II) sulfonate complexes, see: Du *et al.* (2009); Li *et al.* (2009); Liu *et al.* (2009); Sonnauer & Stock (2008); Sonnauer *et al.* (2009). For related structures, see: Dong *et al.* (2009).



Experimental

Crystal data

$[Cu(C_7H_3NO_7S)(C_{10}H_8N_2)(H_2O)]\cdot 0.5C_{10}H_8N_2$
M_r = 561.00
Monoclinic, $P2_1/c$
a = 11.4549 (17) Å
b = 11.0447 (16) Å
c = 17.089 (3) Å
β = 92.738 (3)°
V = 2159.5 (5) Å³
Z = 4
Mo $K\alpha$ radiation
μ = 1.17 mm⁻¹
T = 293 K
0.23 × 0.17 × 0.14 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.767, T_{max} = 0.850
11892 measured reflections
4260 independent reflections
2560 reflections with $I > 2\sigma(I)$
R_{int} = 0.088

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.135
S = 1.00
4260 reflections
331 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.86 e Å⁻³
$\Delta\rho_{min}$ = −0.46 e Å⁻³

Table 1
Selected bond lengths (Å).

Cu1—N2	1.986 (4)	Cu1—O4	1.969 (3)
Cu1—N3^{i}	2.004 (4)	Cu1—O5^{iii}	2.299 (4)
Cu1—O2^{ii}	2.565 (4)	Cu1—O6	2.032 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H1A···O1^{ii}	0.83 (5)	1.94 (5)	2.758 (5)	171 (6)
O6—H1B···N4^{iv}	0.86 (5)	2.00 (5)	2.801 (6)	156 (5)

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

Baicheng Normal College is thanked for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2230).

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supplementary materials

Acta Cryst. (2009). E**65**, m1272-m1273 [**doi:10.1107/S1600536809039294**]

Poly[[aqua(μ-4,4'-bipyridine-κ^2N:N')(μ_3-2-nitro-5-sulfonatobenzoato-κ^3O^1:$O^{1'}$:O^5)copper(II)] 4,4'-bipyridine hemisolvate]

Z. Zhang

Comment

In recent years, the design and synthesis of copper(II) sulfonates have attracted great attention because of their flexible coordination modes, interesting inorganic-organic lamellar structures, selective and reversible guest inclusion properties, and their ability to intercalate guest molecules (Du *et al.*, 2009; Sonnauer *et al.*, 2009). It is noteworthy that some copper(II) sulfonate complexes with nitrogen-based secondary ligands, exhibiting different bonding modes dependent on the presence of secondary ligands, have been reported (Liu *et al.*, 2009; Sonnauer & Stock, 2008). It has also been demonstrated that the existence and changes of the secondary ligands can have a great effect on the structures of copper(II) sulfonates, often with surprising results (Li *et al.*, 2009). In this paper, we utilized 2-nitro-5-sulfobenzoic acid (H_2nsb) as an organic sulfonate ligand and 4,4'-bipyridine (bipy) as an N-donor ligand, providing a coordination compound, [Cu(nsb)(bipy)(H_2O)].0.5bipy, which is reported here.

In the title compound, the central Cu^{II} ion is six-coordinated by two N atoms from two different bipy ligands, one sulfonate O atom, two carboxylate O atoms from three nsb ligand and one water molecule in a distorted octahedral coordination geometry (Table 1). There are free bipy molecules in the structure, stabilized by hydrogen bonds (Fig. 1). The Cu—O distances are comparable to those found in other crystallographically characterized Cu^{II} complexes (Dong *et al.*, 2009). The Cu atoms are linked by the bipy ligands, forming an extended one-dimensional chain. These chains are further connected by the nsb ligands into a two-dimensional layer-like network. In addition, the existence of O—H···O and O—H···N hydrogen bonds (Table 2) extends the two-dimensional layer into a three-dimensional supramolecular architecture (Fig. 2).

Experimental

A mixture of $Cu(CH_3CO_2)_2.2H_2O$ (0.040 g, 0.2 mmol), 2-nitro-5-sulfobenzoic acid (0.049 g, 0.2 mmol), 4,4'-bipyridine (0.039 g, 0.2 mmol), and H_2O (15 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor, which was heated at 443 K for 72 h and then it was cooled to room temperature. Blue crystals of the title compound were collected.

Refinement

H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H= 0.93 Å and U_{iso}(H)= 1.2U_{eq}(C). The H atoms of the water molecule were located in a difference Fourier map and refined with a distance restraint of O—H = 0.85 (1) Å and with U_{iso}(H) = 1.5U_{eq}(O).

Figures

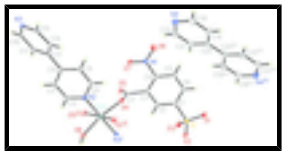

Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) x, 1+y, z; (ii) 1-x, -0.5+y, 1.5-z; (iii) 1-x, 1-y, 1-z; (iv) -x, 1-y, 2-z.]

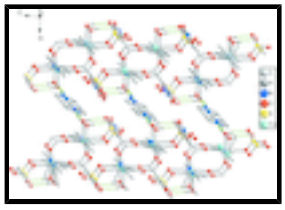

Fig. 2. View of the three-dimensional supramolecular network in the title compound. Dashed lines denote hydrogen bonds.

Poly[[aqua(μ-4,4'-bipyridine-κ^2*N*:*N*')(μ$_3$-2-nitro-5- sulfonatobenzoato-κ^3*O*^{1}:*O*$^{1'}$:*O*^{5})copper(II)] 4,4'-bipyridine hemisolvate]

Crystal data

$[Cu(C_7H_3NO_7S)(C_{10}H_8N_2)(H_2O)]\cdot 0.5C_{10}H_8N_2$	F_{000} = 1144
M_r = 561.00	D_x = 1.725 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 4260 reflections
a = 11.4549 (17) Å	θ = 1.8–26.0º
b = 11.0447 (16) Å	μ = 1.17 mm^{-1}
c = 17.089 (3) Å	T = 293 K
β = 92.738 (3)º	Block, blue
V = 2159.5 (5) Å^3	0.23 × 0.17 × 0.14 mm
Z = 4	

Data collection

Bruker SMART APEX CCD diffractometer	4260 independent reflections
Radiation source: fine-focus sealed tube	2560 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.088
T = 293 K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 1.8º
Absorption correction: multi-scan (SADABS; Bruker, 2001)	h = −14→14
T_{min} = 0.767, T_{max} = 0.850	k = −13→13
11892 measured reflections	l = −21→10

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.065$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.135$	$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
4260 reflections	$\Delta\rho_{max} = 0.86$ e Å^{-3}
331 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2223 (4)	0.7923 (4)	0.6944 (3)	0.0215 (13)
C2	0.2994 (4)	0.7254 (4)	0.6511 (3)	0.0198 (12)
H2	0.3565	0.7656	0.6243	0.024*
C3	0.2929 (4)	0.5989 (5)	0.6472 (3)	0.0195 (12)
C4	0.2051 (5)	0.5449 (4)	0.6866 (3)	0.0224 (13)
C5	0.1244 (5)	0.6090 (5)	0.7293 (4)	0.0321 (15)
H5	0.0649	0.5692	0.7542	0.039*
C6	0.1356 (5)	0.7338 (5)	0.7335 (4)	0.0313 (15)
H6	0.0846	0.7786	0.7627	0.038*
C7	0.3842 (5)	0.5338 (4)	0.6006 (3)	0.0177 (12)
C8	0.5609 (4)	0.2511 (4)	0.6504 (3)	0.0229 (13)
H8	0.5129	0.2936	0.6831	0.027*
C9	0.5560 (4)	0.1262 (4)	0.6501 (3)	0.0237 (13)
H9	0.5067	0.0860	0.6831	0.028*
C10	0.6248 (5)	0.0607 (4)	0.6005 (3)	0.0183 (13)
C11	0.6982 (4)	0.1266 (4)	0.5532 (3)	0.0205 (13)
H11	0.7454	0.0869	0.5186	0.025*
C12	0.6997 (4)	0.2501 (4)	0.5582 (3)	0.0208 (13)
H12	0.7504	0.2924	0.5273	0.025*
C13	0.6233 (4)	−0.0732 (4)	0.5994 (3)	0.0191 (13)
C14	0.6096 (4)	−0.1390 (4)	0.6673 (3)	0.0207 (13)
H14	0.5960	−0.0992	0.7140	0.025*
C15	0.6162 (5)	−0.2632 (4)	0.6656 (3)	0.0241 (13)
H15	0.6098	−0.3057	0.7122	0.029*
C16	0.6431 (5)	−0.2628 (4)	0.5338 (3)	0.0248 (13)
H16	0.6541	−0.3054	0.4878	0.030*
C17	0.6397 (5)	−0.1375 (4)	0.5304 (3)	0.0236 (13)
H17	0.6482	−0.0971	0.4833	0.028*
C18	0.0395 (6)	0.2255 (6)	1.0226 (4)	0.052 (2)
H18	0.0316	0.1641	1.0593	0.063*
C19	0.0134 (6)	0.3431 (6)	1.0445 (4)	0.0483 (19)
H19	−0.0057	0.3597	1.0957	0.058*
C20	0.0160 (5)	0.4360 (5)	0.9900 (4)	0.0353 (16)
C21	0.0488 (5)	0.4042 (6)	0.9165 (4)	0.0408 (17)
H21	0.0509	0.4629	0.8776	0.049*

C22	0.0790 (5)	0.2855 (6)	0.8995 (4)	0.0421 (17)
H22	0.1028	0.2677	0.8495	0.051*
N1	0.1916 (4)	0.4121 (4)	0.6833 (3)	0.0327 (13)
N2	0.6323 (4)	0.3136 (3)	0.6052 (3)	0.0212 (11)
N3	0.6313 (4)	−0.3253 (4)	0.5997 (3)	0.0194 (10)
N4	0.0754 (4)	0.1954 (5)	0.9520 (3)	0.0406 (14)
O1	0.1331 (3)	0.9957 (3)	0.7351 (2)	0.0321 (9)
O2	0.3416 (3)	0.9755 (3)	0.7461 (2)	0.0283 (10)
O3	0.2451 (4)	0.9910 (3)	0.6178 (2)	0.0373 (10)
O4	0.4740 (3)	0.5046 (3)	0.6409 (2)	0.0223 (8)
O5	0.3643 (3)	0.5231 (3)	0.5297 (2)	0.0277 (9)
O6	0.8116 (3)	0.4917 (4)	0.6061 (2)	0.0259 (9)
O7	0.2618 (3)	0.3519 (3)	0.6486 (3)	0.0376 (11)
O8	0.1112 (4)	0.3662 (4)	0.7165 (3)	0.0676 (17)
S1	0.23675 (13)	0.95326 (12)	0.69752 (9)	0.0243 (4)
Cu1	0.63413 (5)	0.49342 (5)	0.60435 (4)	0.0195 (2)
H1A	0.833 (5)	0.486 (5)	0.653 (3)	0.029*
H1B	0.843 (5)	0.543 (5)	0.576 (3)	0.029*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.025 (3)	0.019 (3)	0.021 (3)	0.002 (2)	−0.001 (3)	−0.003 (3)
C2	0.024 (3)	0.018 (3)	0.019 (3)	−0.002 (2)	0.004 (2)	0.001 (2)
C3	0.020 (3)	0.018 (3)	0.021 (3)	0.003 (2)	0.001 (3)	−0.002 (3)
C4	0.027 (3)	0.013 (3)	0.027 (4)	0.001 (2)	0.005 (3)	0.005 (2)
C5	0.027 (3)	0.029 (3)	0.042 (4)	−0.001 (3)	0.018 (3)	0.007 (3)
C6	0.032 (3)	0.026 (3)	0.037 (4)	0.009 (3)	0.013 (3)	0.001 (3)
C7	0.030 (3)	0.007 (3)	0.016 (3)	−0.005 (2)	0.006 (3)	0.001 (2)
C8	0.029 (3)	0.015 (3)	0.027 (3)	0.000 (2)	0.014 (3)	0.001 (3)
C9	0.030 (3)	0.014 (3)	0.028 (4)	−0.004 (2)	0.007 (3)	0.002 (3)
C10	0.029 (3)	0.005 (2)	0.020 (3)	0.002 (2)	−0.007 (3)	0.001 (2)
C11	0.028 (3)	0.011 (3)	0.024 (3)	−0.001 (2)	0.010 (3)	−0.004 (2)
C12	0.026 (3)	0.011 (3)	0.027 (3)	−0.001 (2)	0.007 (3)	0.004 (2)
C13	0.024 (3)	0.009 (3)	0.025 (4)	0.000 (2)	0.005 (3)	−0.002 (3)
C14	0.030 (3)	0.013 (3)	0.021 (3)	0.002 (2)	0.010 (3)	0.000 (2)
C15	0.032 (3)	0.016 (3)	0.025 (4)	−0.001 (2)	0.008 (3)	0.005 (3)
C16	0.040 (3)	0.014 (3)	0.022 (3)	0.003 (3)	0.011 (3)	−0.006 (3)
C17	0.035 (3)	0.015 (3)	0.021 (3)	−0.001 (3)	0.006 (3)	0.006 (3)
C18	0.068 (5)	0.043 (4)	0.048 (5)	0.014 (4)	0.020 (4)	0.011 (4)
C19	0.066 (5)	0.034 (4)	0.045 (5)	0.019 (4)	0.013 (4)	−0.004 (4)
C20	0.030 (4)	0.039 (4)	0.038 (4)	0.007 (3)	0.004 (3)	−0.004 (3)
C21	0.049 (4)	0.037 (4)	0.037 (4)	0.010 (3)	0.003 (4)	0.000 (3)
C22	0.047 (4)	0.043 (4)	0.037 (4)	0.007 (3)	0.004 (3)	−0.013 (4)
N1	0.033 (3)	0.025 (3)	0.041 (4)	−0.006 (2)	0.006 (3)	0.001 (3)
N2	0.029 (3)	0.011 (2)	0.024 (3)	0.002 (2)	0.005 (2)	−0.003 (2)
N3	0.022 (2)	0.011 (2)	0.026 (3)	−0.0013 (19)	0.005 (2)	0.001 (2)
N4	0.038 (3)	0.036 (3)	0.048 (4)	0.002 (2)	0.000 (3)	−0.003 (3)

O1	0.031 (2)	0.026 (2)	0.039 (2)	0.0052 (19)	0.0013 (19)	−0.006 (2)
O2	0.029 (2)	0.020 (2)	0.036 (3)	−0.0042 (16)	0.0006 (19)	−0.0048 (19)
O3	0.065 (3)	0.023 (2)	0.025 (2)	0.002 (2)	0.002 (2)	0.001 (2)
O4	0.0249 (19)	0.0142 (18)	0.028 (2)	0.0021 (17)	0.0053 (17)	0.0024 (19)
O5	0.045 (2)	0.017 (2)	0.021 (2)	0.0056 (17)	0.0079 (19)	−0.0030 (18)
O6	0.030 (2)	0.021 (2)	0.027 (2)	−0.0013 (18)	0.0064 (19)	0.006 (2)
O7	0.046 (3)	0.019 (2)	0.049 (3)	−0.005 (2)	0.019 (2)	−0.007 (2)
O8	0.066 (3)	0.035 (3)	0.106 (5)	−0.012 (2)	0.056 (3)	0.005 (3)
S1	0.0298 (8)	0.0166 (7)	0.0269 (9)	0.0041 (6)	0.0063 (7)	−0.0020 (6)
Cu1	0.0252 (3)	0.0066 (3)	0.0273 (4)	0.0008 (3)	0.0082 (3)	−0.0005 (3)

Geometric parameters (Å, °)

C1—C6	1.382 (7)	C15—H15	0.9300
C1—C2	1.391 (7)	C16—N3	1.334 (6)
C1—S1	1.787 (5)	C16—C17	1.385 (7)
C2—C3	1.401 (6)	C16—H16	0.9300
C2—H2	0.9300	C17—H17	0.9300
C3—C4	1.373 (7)	C18—N4	1.335 (8)
C3—C7	1.525 (7)	C18—C19	1.389 (9)
C4—C5	1.398 (7)	C18—H18	0.9300
C4—N1	1.475 (7)	C19—C20	1.386 (9)
C5—C6	1.386 (7)	C19—H19	0.9300
C5—H5	0.9300	C20—C21	1.375 (8)
C6—H6	0.9300	C20—C20^{i}	1.505 (11)
C7—O5	1.227 (6)	C21—C22	1.390 (8)
C7—O4	1.254 (6)	C21—H21	0.9300
C8—N2	1.341 (6)	C22—N4	1.342 (8)
C8—C9	1.381 (7)	C22—H22	0.9300
C8—H8	0.9300	N1—O8	1.216 (6)
C9—C10	1.388 (7)	N1—O7	1.219 (6)
C9—H9	0.9300	O1—S1	1.454 (4)
C10—C11	1.398 (7)	O2—S1	1.448 (4)
C10—C13	1.479 (6)	O3—S1	1.432 (4)
C11—C12	1.366 (6)	O6—H1A	0.83 (5)
C11—H11	0.9300	O6—H1B	0.86 (5)
C12—N2	1.339 (6)	Cu1—N2	1.986 (4)
C12—H12	0.9300	Cu1—N3^{ii}	2.004 (4)
C13—C14	1.384 (7)	Cu1—O2^{iii}	2.565 (4)
C13—C17	1.397 (7)	Cu1—O4	1.969 (3)
C14—C15	1.374 (6)	Cu1—O5^{iv}	2.299 (4)
C14—H14	0.9300	Cu1—O6	2.032 (4)
C15—N3	1.337 (6)		
C6—C1—C2	119.9 (5)	N4—C18—C19	123.8 (7)
C6—C1—S1	121.2 (4)	N4—C18—H18	118.1
C2—C1—S1	118.9 (4)	C19—C18—H18	118.1
C1—C2—C3	121.4 (5)	C20—C19—C18	119.9 (7)
C1—C2—H2	119.3	C20—C19—H19	120.0

C3—C2—H2	119.3	C18—C19—H19	120.0
C4—C3—C2	116.7 (5)	C21—C20—C19	116.2 (6)
C4—C3—C7	126.0 (5)	C21—C20—C20^{i}	121.8 (8)
C2—C3—C7	117.3 (5)	C19—C20—C20^{i}	122.0 (8)
C3—C4—C5	123.6 (5)	C20—C21—C22	120.9 (6)
C3—C4—N1	119.4 (5)	C20—C21—H21	119.5
C5—C4—N1	116.9 (5)	C22—C21—H21	119.5
C6—C5—C4	117.9 (5)	N4—C22—C21	122.9 (6)
C6—C5—H5	121.0	N4—C22—H22	118.6
C4—C5—H5	121.0	C21—C22—H22	118.6
C1—C6—C5	120.5 (5)	O8—N1—O7	122.2 (5)
C1—C6—H6	119.8	O8—N1—C4	118.4 (5)
C5—C6—H6	119.8	O7—N1—C4	119.4 (5)
O5—C7—O4	128.8 (5)	C12—N2—C8	117.4 (4)
O5—C7—C3	117.5 (5)	C12—N2—Cu1	120.8 (4)
O4—C7—C3	113.6 (5)	C8—N2—Cu1	121.7 (4)
N2—C8—C9	122.5 (5)	C16—N3—C15	117.9 (4)
N2—C8—H8	118.7	C16—N3—Cu1^{v}	123.2 (4)
C9—C8—H8	118.7	C15—N3—Cu1^{v}	118.8 (4)
C8—C9—C10	119.9 (5)	C18—N4—C22	116.2 (6)
C8—C9—H9	120.0	C7—O4—Cu1	126.4 (3)
C10—C9—H9	120.0	C7—O5—Cu1^{iv}	168.9 (4)
C9—C10—C11	117.2 (4)	Cu1—O6—H1A	105 (4)
C9—C10—C13	121.5 (5)	Cu1—O6—H1B	115 (4)
C11—C10—C13	121.4 (5)	H1A—O6—H1B	122 (5)
C12—C11—C10	119.3 (5)	O3—S1—O2	113.9 (2)
C12—C11—H11	120.4	O3—S1—O1	114.8 (2)
C10—C11—H11	120.4	O2—S1—O1	111.4 (2)
N2—C12—C11	123.7 (5)	O3—S1—C1	105.8 (3)
N2—C12—H12	118.1	O2—S1—C1	105.0 (2)
C11—C12—H12	118.1	O1—S1—C1	104.9 (2)
C14—C13—C17	117.7 (5)	O4—Cu1—N2	92.84 (16)
C14—C13—C10	121.1 (5)	O4—Cu1—N3^{ii}	86.36 (16)
C17—C13—C10	121.1 (5)	N2—Cu1—N3^{ii}	177.66 (18)
C15—C14—C13	119.9 (5)	O4—Cu1—O6	160.42 (16)
C15—C14—H14	120.1	N2—Cu1—O6	90.09 (17)
C13—C14—H14	120.1	N3^{ii}—Cu1—O6	91.39 (17)
N3—C15—C14	122.6 (5)	O4—Cu1—O5^{iv}	111.89 (14)
N3—C15—H15	118.7	N2—Cu1—O5^{iv}	85.92 (16)
C14—C15—H15	118.7	N3^{ii}—Cu1—O5^{iv}	92.34 (16)
N3—C16—C17	123.2 (5)	O6—Cu1—O5^{iv}	87.62 (15)
N3—C16—H16	118.4	O2^{iii}—Cu1—N2	85.20 (17)
C17—C16—H16	118.4	O2^{iii}—Cu1—N3^{ii}	96.74 (17)
C16—C17—C13	118.5 (5)	O2^{iii}—Cu1—O4	75.35 (13)
C16—C17—H17	120.7	O2^{iii}—Cu1—O5^{iv}	168.81 (12)

C13—C17—H17	120.7	O2^{iii}—Cu1—O6	85.63 (13)
C6—C1—C2—C3	−1.2 (8)	C20^{i}—C20—C21—C22	179.5 (7)
S1—C1—C2—C3	179.4 (4)	C20—C21—C22—N4	1.7 (10)
C1—C2—C3—C4	1.4 (8)	C3—C4—N1—O8	−177.7 (6)
C1—C2—C3—C7	−177.9 (5)	C5—C4—N1—O8	0.9 (8)
C2—C3—C4—C5	0.1 (9)	C3—C4—N1—O7	3.5 (8)
C7—C3—C4—C5	179.2 (5)	C5—C4—N1—O7	−178.0 (5)
C2—C3—C4—N1	178.5 (5)	C11—C12—N2—C8	1.0 (8)
C7—C3—C4—N1	−2.3 (9)	C11—C12—N2—Cu1	−176.6 (4)
C3—C4—C5—C6	−1.7 (9)	C9—C8—N2—C12	0.5 (8)
N1—C4—C5—C6	179.8 (5)	C9—C8—N2—Cu1	178.1 (4)
C2—C1—C6—C5	−0.5 (9)	C17—C16—N3—C15	−0.4 (8)
S1—C1—C6—C5	178.9 (5)	C17—C16—N3—Cu1^{v}	179.2 (4)
C4—C5—C6—C1	1.9 (9)	C14—C15—N3—C16	1.6 (8)
C4—C3—C7—O5	95.3 (7)	C14—C15—N3—Cu1^{v}	−178.0 (4)
C2—C3—C7—O5	−85.6 (6)	C19—C18—N4—C22	−3.8 (10)
C4—C3—C7—O4	−88.7 (7)	C21—C22—N4—C18	0.7 (9)
C2—C3—C7—O4	90.4 (6)	O5—C7—O4—Cu1	26.7 (7)
N2—C8—C9—C10	−1.5 (9)	C3—C7—O4—Cu1	−148.7 (3)
C8—C9—C10—C11	0.9 (8)	O4—C7—O5—Cu1^{iv}	−29 (2)
C8—C9—C10—C13	179.0 (5)	C3—C7—O5—Cu1^{iv}	146.5 (15)
C9—C10—C11—C12	0.6 (8)	C6—C1—S1—O3	−130.7 (5)
C13—C10—C11—C12	−177.6 (5)	C2—C1—S1—O3	48.7 (5)
C10—C11—C12—N2	−1.6 (8)	C6—C1—S1—O2	108.6 (5)
C9—C10—C13—C14	−35.0 (8)	C2—C1—S1—O2	−72.0 (5)
C11—C10—C13—C14	143.0 (5)	C6—C1—S1—O1	−9.0 (5)
C9—C10—C13—C17	147.2 (5)	C2—C1—S1—O1	170.5 (4)
C11—C10—C13—C17	−34.7 (8)	C7—O4—Cu1—N2	−106.1 (4)
C17—C13—C14—C15	2.0 (8)	C7—O4—Cu1—N3^{ii}	71.7 (4)
C10—C13—C14—C15	−175.8 (5)	C7—O4—Cu1—O6	155.6 (5)
C13—C14—C15—N3	−2.5 (8)	C7—O4—Cu1—O5^{iv}	−19.4 (4)
N3—C16—C17—C13	0.1 (8)	C12—N2—Cu1—O4	153.9 (4)
C14—C13—C17—C16	−0.9 (8)	C8—N2—Cu1—O4	−23.6 (4)
C10—C13—C17—C16	176.9 (5)	C12—N2—Cu1—O6	−45.4 (4)
N4—C18—C19—C20	4.6 (11)	C8—N2—Cu1—O6	137.1 (4)
C18—C19—C20—C21	−2.0 (10)	C12—N2—Cu1—O5^{iv}	42.2 (4)
C18—C19—C20—C20^{i}	177.6 (7)	C8—N2—Cu1—O5^{iv}	−135.3 (4)
C19—C20—C21—C22	−0.9 (10)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H1A···O1^{iii}	0.83 (5)	1.94 (5)	2.758 (5)	171 (6)
O6—H1B···N4^{vi}	0.86 (5)	2.00 (5)	2.801 (6)	156 (5)

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

Fig. 1

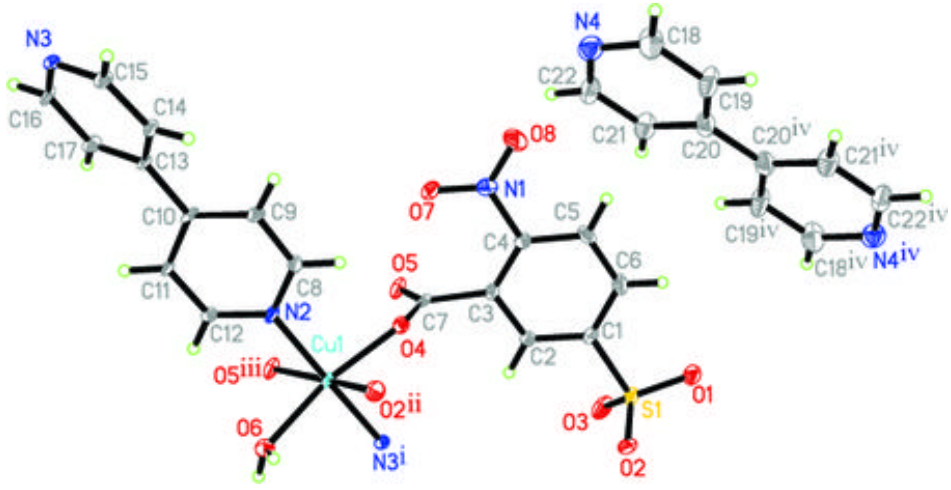
N3
C15
C14
C16
C17
C13
C10
C9
C11
C8
N2
C12
Cu1
O5iii
O2ii
O6
N3i
O5
C7
O4
C3
C4
C5
C6
C1
C2
O8
N1
O7
S1
O1
O3
O2
N4
C18
C22
C19
C21
C20
C20iv
C21iv
C19iv
C22iv
C18iv
N4iv

Fig. 2