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(Acetamide-κO){2,2′,2″-boranetriyltris[6-*tert*-butyl-4-methylpyridazine-3(2*H*)-thione]-$\kappa^4 B,S,S',S''$}-copper(I) trifluoromethanesulfonate chloroform disolvate

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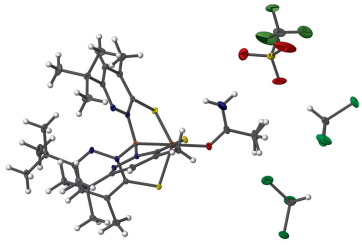
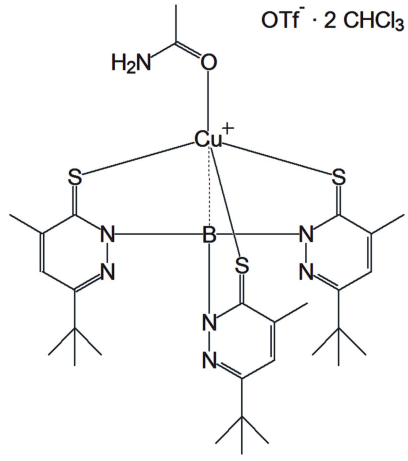
Structural data: full structural data are available from iucrdata.iucr.org

In the title solvated complex salt, $[Cu(C_{27}H_{39}BN_6S_3)(C_2H_5NO)](CF_3O_3S)\cdot 2CHCl_3$, the Cu^I atom is coordinated by the three S atoms of the pyridazine-3-thione rings in the equatorial plane [Cu—S = 2.3072 (4)–2.3280 (4) Å] and the B atom of the scorpionate ligand and the O atom of an acetamide ligand as the apices of a trigonal bipyramid [Cu—B = 2.0456 (16) Å and Cu—O = 1.9957 (11) Å]. The amide group of the latter ligand is involved in a bifurcated hydrogen bond to the trifluoromethanesulfonate anion.

3D view



Chemical scheme



Structure description

Since the first description of a metallaboratrane complex (Hill *et al.*, 1999), this class of compounds has been used extensively in coordination chemistry (Amgoune & Bourissou, 2011; Bouhadir & Bourissou, 2016). Their *Z*-type coordination mode provides an entry into electronically interesting metal atoms, which recently were successfully used in catalytic dinitrogen reduction (Anderson *et al.*, 2013). Our group is focusing on thiopyridazine-based soft scorpionates and their related metallaboratrane complexes (Nuss *et al.*, 2011*a*,*b*; Holler *et al.*, 2016, 2017). In an attempted synthesis of the boratrane complex {2,2′,2″-boranetriyltris[6-*tert*-butyl-4-methylpyridazine-3(2*H*)-thione]}(trifluoromethanesulfonato)copper(I) (= $[Cu\{B(Pn^{Me,tBu})_3\}(OTf)]$), described in the literature by our group (Holler *et al.*, 2016), the title compound formed serendipitously by reaction with residual acetamide from the acetonitrile solvent.

As in the boratrane complexes $[Cu\{B(Pn^{Me,tBu})_3\}X]$ (X = Cl, OTf, N_3, NCS) the Cu^I atom in the title compound (Fig. 1) has a slightly distorted trigonal–bipyramidal environment (Table 1) with a rather short Cu—B distance comparable to 2.0432 (14) Å

Table 1
Selected bond lengths (Å).

Cu1—O1	1.9957 (11)	B1—N32	1.537 (2)
Cu1—B1	2.0456 (16)	S1—C13	1.7102 (15)
Cu1—S1	2.3072 (4)	S2—C23	1.7069 (15)
Cu1—S2	2.3280 (4)	S3—C33	1.7129 (15)
Cu1—S3	2.3245 (4)	O1—C1	1.2531 (19)
B1—N12	1.530 (2)	N1—C1	1.330 (2)
B1—N22	1.536 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O42	0.88	2.48 (1)	3.196 (3)	140 (1)
N1—H1···O43	0.88	2.47 (1)	3.282 (2)	154 (2)
C5—H5···O43	1.00	2.21	3.171 (2)	160

observed in the trifluoromethanesulfonate complex (Holler *et al.*, 2016). Not the trifluoromethanesulfonate anion but the neutral acetamide molecule [Cu1—O1 1.9957 (11) Å] occupies the axial position opposite to the B atom. In the other boratrane complexes [Cu{B(Pn^{Me,tBu})$_3$}*X*] with more polarizing ligands, the Cu—B distance is distinctly longer [*e.g.* 2.065 (2) Å for *X* = Cl, 2.068 (4) Å for *X* = N$_3$, 2.0667 (13) Å for *X* = NCS]. One H atom of the NH$_2$ group shows a bifurcated hydrogen bond (Table 2) to the trifluoromethanesulfonate anion (Fig. 1), the other one is not able to build a hydrogen bond. A non-classical hydrogen-bonding interaction can be assumed between C5 of a chloroform solvent molecule and the trifluoromethanesulfonate anion (Table 2).

Synthesis and crystallization

During an attempted synthesis of [Cu{B(Pn^{Me,tBu})$_3$}(OTf)] (Holler *et al.*, 2016), the title compound crystallized due to residual acetamide in the used acetonitrile solvent. AgOTf (21.4 mg, 0.083 mmol) and [Cu{B(Pn^{Me,tBu})$_3$}Cl] (54.4 mg, 0.083 mmol) were suspended in anhydrous acetonitrile (4 ml). The reaction mixture was stirred at room temperature for 90 min, the resulting suspension was centrifuged and filtered. The solvent was removed *in vacuo* to obtain an orange solid. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a CDCl$_3$ solution.

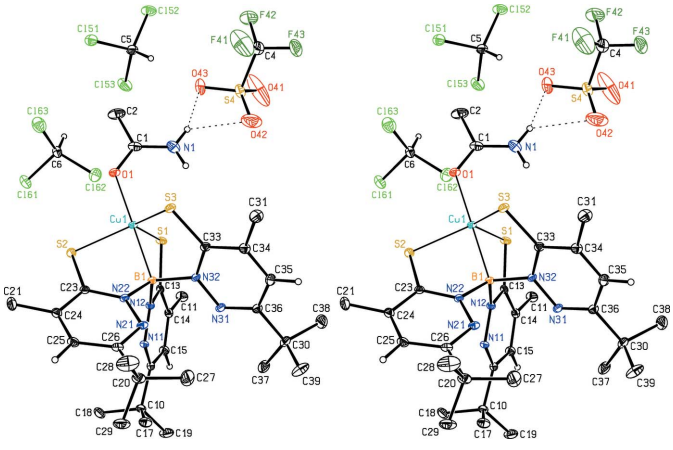


Figure 1
Stereoscopic plot of the molecular structure of the title compound, with the atom labelling and displacement ellipsoids drawn at the 50% probability level. The H atoms of the methyl groups were omitted for clarity and hydrogen bonds are indicated by dotted lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Cu(C$_{27}$H$_{39}$BN$_6$S$_3$)(C$_2$H$_5$NO)]·(CF$_3$O$_3$S)·2CHCl$_3$
M_r	1065.05
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, *b*, *c* (Å)	9.7516 (5), 14.0606 (7), 17.5108 (8)
α, β, γ (°)	77.6301 (12), 88.5283 (12), 84.3407 (13)
V (Å^3)	2333.8 (2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	1.05
Crystal size (mm)	0.30 × 0.30 × 0.25
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.781, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	67349, 13577, 11705
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.078, 1.04
No. of reflections	13577
No. of parameters	559
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.92, −0.84

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and modified *ORTEP* (Johnson, 1965).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Acknowledgements

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full crystallographic data

IUCrData (2018). **3**, x180037 [https://doi.org/10.1107/S2414314618000378]

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Crystal data

$[Cu(C_{27}H_{39}BN_6S_3)(C_2H_5NO)](CF_3O_3S)\cdot 2CHCl_3$
$M_r = 1065.05$
Triclinic, $P\overline{1}$
$a = 9.7516$ (5) Å
$b = 14.0606$ (7) Å
$c = 17.5108$ (8) Å
$\alpha = 77.6301$ (12)°
$\beta = 88.5283$ (12)°
$\gamma = 84.3407$ (13)°
$V = 2333.8$ (2) Å^3
$Z = 2$
$F(000) = 1092$
$D_x = 1.516$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9907 reflections
$\theta = 2.4$–$30.9°$
$\mu = 1.05$ mm^{-1}
$T = 100$ K
Needle, orange
0.30 × 0.30 × 0.25 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: Incoatec microfocus sealed tube
Multilayer monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
$T_{min} = 0.781$, $T_{max} = 1.000$
67349 measured reflections
13577 independent reflections
11705 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.4°$
$h = -13\rightarrow 11$
$k = -19\rightarrow 19$
$l = -24\rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.078$
$S = 1.04$
13577 reflections
559 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 2.2891P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ 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.
The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints.
The positions of the H atoms of the NH_2 group were taken from a difference Fourier map, the N-H distances were fixed to 0.88 Å, and the H atoms were refined with common isotropic displacement parameters without any constraints to the bond angles (DFIX of SHELXL).
The H atoms of the tertiary C-H groups were refined with individual isotropic displacement parameter and all Cl-C-H angles equal at a C-H distance of 1.00 Å (AFIX 13 of SHELXL).
The H atoms of the pyridazine rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group (AFIX 43 of SHELXL).
The H atoms of the methyl group C2 are disordered over two orientations and were refined with site occupation factors of 0.5 at two positions rotated from each other by 60 ° with common isotropic displacement parameters for the H atoms and idealized geometry with tetrahedral angles, enabling rotation around the C-C bond, and C-H distances of 0.98 Å (AFIX 127 of SHELXL).
The H atoms of the other methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C-C bond, and C-H distances of 0.98 Å (AFIX 137 of SHELXL).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.60968 (2)	0.20838 (2)	0.38078 (2)	0.00951 (4)	
B1	0.71205 (17)	0.29107 (12)	0.29100 (9)	0.0088 (3)	
S1	0.57399 (4)	0.35515 (3)	0.42048 (2)	0.01168 (7)	
N11	0.65149 (13)	0.44467 (9)	0.19758 (7)	0.0095 (2)	
N12	0.64043 (13)	0.39511 (9)	0.27274 (7)	0.0087 (2)	
C13	0.59286 (15)	0.43478 (11)	0.33301 (8)	0.0093 (3)	
C14	0.56363 (16)	0.53826 (11)	0.31957 (9)	0.0104 (3)	
C15	0.57755 (16)	0.58927 (11)	0.24415 (9)	0.0117 (3)	
H15	0.5597	0.6585	0.2324	0.013 (3)*	
C16	0.61860 (15)	0.53951 (11)	0.18313 (8)	0.0095 (3)	
C11	0.52055 (18)	0.58650 (12)	0.38631 (9)	0.0156 (3)	
H111	0.5129	0.6577	0.3678	0.030 (4)*	
H112	0.5895	0.5673	0.4279	0.030 (4)*	
H113	0.4312	0.5660	0.4067	0.030 (4)*	
C10	0.62200 (16)	0.59086 (11)	0.09690 (8)	0.0112 (3)	
C17	0.72883 (18)	0.53512 (13)	0.05234 (9)	0.0158 (3)	
H171	0.7275	0.5671	−0.0032	0.024 (3)*	
H172	0.7062	0.4675	0.0582	0.024 (3)*	
H173	0.8208	0.5352	0.0736	0.024 (3)*	
C18	0.47721 (18)	0.59089 (13)	0.06413 (9)	0.0170 (3)	
H181	0.4100	0.6276	0.0921	0.022 (3)*	
H182	0.4536	0.5234	0.0711	0.022 (3)*	

H183	0.4758	0.6217	0.0083	0.022 (3)*
C19	0.6576 (2)	0.69636 (13)	0.08720 (10)	0.0203 (4)
H191	0.7467	0.6967	0.1117	0.026 (3)*
H192	0.5861	0.7334	0.1123	0.026 (3)*
H193	0.6627	0.7265	0.0314	0.026 (3)*
S2	0.47375 (4)	0.18882 (3)	0.27889 (2)	0.01202 (7)
N21	0.81967 (13)	0.25598 (10)	0.17063 (7)	0.0104 (2)
N22	0.70889 (13)	0.24464 (9)	0.21931 (7)	0.0086 (2)
C23	0.59319 (15)	0.20611 (11)	0.20547 (8)	0.0095 (3)
C24	0.58048 (16)	0.18098 (11)	0.13119 (9)	0.0118 (3)
C25	0.68960 (17)	0.19529 (11)	0.08072 (9)	0.0125 (3)
H25	0.6844	0.1812	0.0302	0.013 (3)*
C26	0.81106 (16)	0.23107 (11)	0.10295 (8)	0.0107 (3)
C21	0.45413 (18)	0.13648 (14)	0.11430 (10)	0.0192 (3)
H211	0.4612	0.1230	0.0616	0.030 (4)*
H212	0.3725	0.1820	0.1176	0.030 (4)*
H213	0.4461	0.0753	0.1526	0.030 (4)*
C20	0.93890 (17)	0.23879 (13)	0.05078 (9)	0.0149 (3)
C27	1.0515 (2)	0.28196 (18)	0.08835 (11)	0.0293 (5)
H271	1.0171	0.3471	0.0961	0.035 (4)*
H272	1.1327	0.2871	0.0540	0.035 (4)*
H273	1.0769	0.2393	0.1390	0.035 (4)*
C28	0.9908 (2)	0.13528 (15)	0.04119 (12)	0.0295 (4)
H281	1.0096	0.0930	0.0928	0.038 (4)*
H282	1.0756	0.1378	0.0098	0.038 (4)*
H283	0.9204	0.1090	0.0148	0.038 (4)*
C29	0.90288 (19)	0.30397 (14)	−0.02973 (10)	0.0219 (4)
H291	0.8292	0.2774	−0.0533	0.031 (4)*
H292	0.9846	0.3057	−0.0636	0.031 (4)*
H293	0.8718	0.3704	−0.0237	0.031 (4)*
S3	0.82167 (4)	0.11527 (3)	0.39188 (2)	0.01176 (7)
N31	0.92069 (14)	0.37649 (9)	0.29250 (7)	0.0106 (2)
N32	0.86078 (13)	0.29183 (9)	0.31774 (7)	0.0088 (2)
C33	0.92504 (16)	0.20649 (11)	0.35591 (8)	0.0101 (3)
C34	1.07121 (16)	0.19957 (12)	0.36420 (9)	0.0123 (3)
C35	1.13219 (16)	0.28460 (12)	0.34005 (9)	0.0136 (3)
H35	1.2287	0.2844	0.3466	0.013 (3)*
C36	1.05351 (16)	0.37346 (11)	0.30531 (9)	0.0112 (3)
C31	1.15042 (17)	0.10264 (12)	0.39708 (10)	0.0179 (3)
H311	1.1505	0.0603	0.3593	0.033 (4)*
H312	1.1068	0.0715	0.4459	0.033 (4)*
H313	1.2455	0.1130	0.4075	0.033 (4)*
C30	1.11954 (17)	0.46933 (12)	0.27993 (9)	0.0142 (3)
C37	1.01312 (19)	0.55349 (13)	0.24390 (11)	0.0223 (4)
H371	0.9716	0.5382	0.1981	0.029 (4)*
H372	1.0585	0.6138	0.2279	0.029 (4)*
H373	0.9412	0.5623	0.2826	0.029 (4)*
C38	1.1822 (2)	0.49394 (14)	0.35226 (11)	0.0226 (4)

H381	1.1103	0.4978	0.3919	0.028 (3)*	
H382	1.2212	0.5570	0.3373	0.028 (3)*	
H383	1.2551	0.4428	0.3737	0.028 (3)*	
C39	1.2336 (2)	0.45756 (15)	0.21951 (12)	0.0266 (4)	
H391	1.3034	0.4050	0.2428	0.034 (4)*	
H392	1.2766	0.5189	0.2035	0.034 (4)*	
H393	1.1937	0.4412	0.1737	0.034 (4)*	
O1	0.50619 (12)	0.13097 (9)	0.46848 (6)	0.0141 (2)	
N1	0.63787 (18)	0.15133 (13)	0.56714 (8)	0.0269 (4)	
H1	0.6497 (17)	0.1481 (11)	0.61732 (17)	0.051 (6)*	
H2	0.7028 (4)	0.1743 (7)	0.5345 (3)	0.051 (6)*	
C1	0.52584 (18)	0.12306 (12)	0.54010 (9)	0.0156 (3)	
C2	0.4219 (2)	0.08140 (15)	0.59873 (11)	0.0253 (4)	
H21	0.4449	0.0918	0.6503	0.030 (5)*	0.5
H22	0.4224	0.0111	0.6009	0.030 (5)*	0.5
H23	0.3301	0.1140	0.5835	0.030 (5)*	0.5
H26	0.3534	0.0528	0.5728	0.030 (5)*	0.5
H27	0.3759	0.1334	0.6222	0.030 (5)*	0.5
H28	0.4681	0.0306	0.6396	0.030 (5)*	0.5
S4	0.69763 (4)	0.19514 (3)	0.76954 (2)	0.01869 (9)	
O41	0.6850 (2)	0.26256 (18)	0.81963 (14)	0.0783 (9)	
O42	0.78492 (18)	0.22124 (16)	0.70386 (10)	0.0559 (6)	
O43	0.57126 (17)	0.16211 (15)	0.74994 (10)	0.0497 (5)	
C4	0.7908 (2)	0.08710 (15)	0.82866 (13)	0.0307 (5)	
F41	0.8094 (2)	0.01563 (11)	0.79042 (13)	0.0813 (7)	
F42	0.7206 (2)	0.05371 (16)	0.89335 (10)	0.0805 (7)	
F43	0.91260 (13)	0.10607 (10)	0.85081 (8)	0.0353 (3)	
C5	0.27392 (19)	0.09671 (13)	0.79934 (10)	0.0181 (3)	
H5	0.3718	0.1010	0.7815	0.018 (5)*	
Cl51	0.20528 (5)	0.00752 (3)	0.75860 (2)	0.01963 (8)	
Cl52	0.27224 (5)	0.06392 (3)	0.90262 (2)	0.02408 (9)	
Cl53	0.18189 (7)	0.21172 (3)	0.76548 (3)	0.03567 (13)	
C6	0.00360 (19)	0.27671 (14)	0.58025 (10)	0.0211 (4)	
H6	−0.0290	0.2856	0.6331	0.016 (5)*	
Cl61	−0.12433 (5)	0.33344 (3)	0.51087 (3)	0.02413 (9)	
Cl62	0.15851 (6)	0.33209 (5)	0.55838 (3)	0.04365 (15)	
Cl63	0.02976 (5)	0.15066 (4)	0.58212 (3)	0.03120 (11)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01068 (9)	0.01070 (9)	0.00664 (8)	−0.00324 (7)	0.00189 (6)	0.00010 (6)
B1	0.0098 (7)	0.0090 (7)	0.0072 (7)	−0.0021 (6)	0.0010 (5)	−0.0006 (6)
S1	0.01605 (18)	0.01208 (17)	0.00631 (15)	−0.00111 (14)	0.00136 (13)	−0.00095 (13)
N11	0.0104 (6)	0.0114 (6)	0.0060 (5)	−0.0025 (5)	0.0000 (4)	0.0003 (4)
N12	0.0091 (6)	0.0096 (6)	0.0068 (5)	−0.0011 (5)	0.0004 (4)	−0.0006 (4)
C13	0.0075 (6)	0.0126 (7)	0.0076 (6)	−0.0014 (5)	−0.0010 (5)	−0.0017 (5)
C14	0.0099 (7)	0.0119 (7)	0.0100 (6)	−0.0011 (5)	−0.0005 (5)	−0.0037 (5)

C15	0.0136 (7)	0.0096 (7)	0.0117 (7)	−0.0003 (5)	−0.0004 (5)	−0.0018 (5)
C16	0.0085 (6)	0.0110 (7)	0.0088 (6)	−0.0021 (5)	−0.0009 (5)	−0.0011 (5)
C11	0.0219 (8)	0.0147 (8)	0.0114 (7)	−0.0011 (6)	0.0020 (6)	−0.0058 (6)
C10	0.0144 (7)	0.0113 (7)	0.0074 (6)	−0.0022 (6)	0.0001 (5)	−0.0006 (5)
C17	0.0181 (8)	0.0180 (8)	0.0104 (7)	−0.0009 (6)	0.0029 (6)	−0.0019 (6)
C18	0.0166 (8)	0.0225 (9)	0.0107 (7)	−0.0007 (6)	−0.0035 (6)	−0.0014 (6)
C19	0.0331 (10)	0.0139 (8)	0.0138 (7)	−0.0082 (7)	0.0039 (7)	−0.0008 (6)
S2	0.00963 (17)	0.01723 (19)	0.00919 (16)	−0.00386 (14)	0.00166 (12)	−0.00178 (13)
N21	0.0100 (6)	0.0108 (6)	0.0091 (5)	−0.0009 (5)	0.0034 (4)	−0.0001 (5)
N22	0.0097 (6)	0.0086 (6)	0.0073 (5)	−0.0020 (5)	0.0018 (4)	−0.0010 (4)
C23	0.0104 (7)	0.0082 (7)	0.0088 (6)	−0.0007 (5)	−0.0003 (5)	0.0004 (5)
C24	0.0141 (7)	0.0105 (7)	0.0104 (6)	−0.0013 (6)	−0.0021 (5)	−0.0010 (5)
C25	0.0171 (8)	0.0122 (7)	0.0082 (6)	−0.0011 (6)	0.0004 (5)	−0.0025 (5)
C26	0.0123 (7)	0.0098 (7)	0.0088 (6)	0.0001 (5)	0.0017 (5)	0.0003 (5)
C21	0.0180 (8)	0.0275 (9)	0.0142 (7)	−0.0092 (7)	−0.0024 (6)	−0.0060 (7)
C20	0.0135 (7)	0.0198 (8)	0.0100 (7)	−0.0002 (6)	0.0039 (5)	−0.0013 (6)
C27	0.0162 (9)	0.0540 (14)	0.0196 (9)	−0.0135 (9)	0.0071 (7)	−0.0085 (9)
C28	0.0294 (11)	0.0261 (10)	0.0289 (10)	0.0072 (8)	0.0147 (8)	−0.0028 (8)
C29	0.0217 (9)	0.0276 (10)	0.0125 (7)	−0.0012 (7)	0.0051 (6)	0.0037 (7)
S3	0.01200 (17)	0.00877 (17)	0.01345 (17)	−0.00237 (13)	0.00103 (13)	0.00051 (13)
N31	0.0127 (6)	0.0099 (6)	0.0094 (6)	−0.0043 (5)	0.0018 (5)	−0.0015 (5)
N32	0.0093 (6)	0.0088 (6)	0.0083 (5)	−0.0028 (5)	0.0016 (4)	−0.0012 (4)
C33	0.0117 (7)	0.0106 (7)	0.0082 (6)	−0.0020 (5)	0.0018 (5)	−0.0021 (5)
C34	0.0116 (7)	0.0124 (7)	0.0120 (7)	0.0003 (6)	0.0006 (5)	−0.0015 (5)
C35	0.0092 (7)	0.0159 (8)	0.0152 (7)	−0.0012 (6)	0.0006 (5)	−0.0025 (6)
C36	0.0116 (7)	0.0119 (7)	0.0100 (6)	−0.0032 (6)	0.0014 (5)	−0.0015 (5)
C31	0.0132 (8)	0.0141 (8)	0.0238 (8)	0.0022 (6)	0.0003 (6)	0.0003 (6)
C30	0.0132 (7)	0.0126 (7)	0.0165 (7)	−0.0055 (6)	0.0004 (6)	−0.0004 (6)
C37	0.0193 (9)	0.0136 (8)	0.0307 (9)	−0.0064 (7)	−0.0058 (7)	0.0054 (7)
C38	0.0253 (9)	0.0180 (8)	0.0254 (9)	−0.0082 (7)	−0.0079 (7)	−0.0026 (7)
C39	0.0251 (10)	0.0245 (10)	0.0295 (10)	−0.0109 (8)	0.0135 (8)	−0.0019 (8)
O1	0.0168 (6)	0.0157 (6)	0.0094 (5)	−0.0055 (4)	0.0024 (4)	0.0000 (4)
N1	0.0345 (9)	0.0319 (9)	0.0142 (7)	−0.0096 (7)	−0.0064 (6)	−0.0008 (6)
C1	0.0220 (8)	0.0126 (7)	0.0107 (7)	0.0007 (6)	0.0025 (6)	−0.0005 (6)
C2	0.0342 (11)	0.0234 (9)	0.0161 (8)	−0.0046 (8)	0.0118 (7)	−0.0003 (7)
S4	0.01392 (19)	0.0259 (2)	0.01742 (19)	0.00031 (16)	−0.00234 (15)	−0.00779 (16)
O41	0.0784 (15)	0.0889 (16)	0.0795 (15)	0.0601 (13)	−0.0531 (13)	−0.0693 (14)
O42	0.0315 (9)	0.0828 (15)	0.0354 (9)	−0.0050 (9)	0.0045 (7)	0.0264 (9)
O43	0.0292 (9)	0.0682 (13)	0.0457 (10)	−0.0266 (8)	−0.0211 (7)	0.0134 (9)
C4	0.0354 (11)	0.0243 (10)	0.0314 (10)	−0.0098 (9)	−0.0130 (9)	0.0011 (8)
F41	0.1206 (17)	0.0260 (8)	0.1020 (15)	0.0210 (9)	−0.0678 (13)	−0.0290 (9)
F42	0.0704 (12)	0.1111 (16)	0.0433 (9)	−0.0553 (12)	−0.0201 (8)	0.0445 (10)
F43	0.0242 (6)	0.0349 (7)	0.0446 (7)	0.0012 (5)	−0.0162 (5)	−0.0035 (6)
C5	0.0244 (9)	0.0165 (8)	0.0129 (7)	−0.0054 (7)	−0.0006 (6)	−0.0004 (6)
Cl51	0.0286 (2)	0.01408 (18)	0.01680 (18)	−0.00217 (16)	−0.00037 (15)	−0.00460 (14)
Cl52	0.0418 (3)	0.0175 (2)	0.01294 (18)	−0.00320 (18)	0.00092 (17)	−0.00309 (15)
Cl53	0.0603 (4)	0.0128 (2)	0.0336 (3)	−0.0020 (2)	−0.0247 (2)	−0.00196 (18)
C6	0.0194 (8)	0.0268 (9)	0.0172 (8)	−0.0071 (7)	−0.0055 (6)	−0.0021 (7)

Cl61	0.0251 (2)	0.0273 (2)	0.02019 (19)	0.00107 (17)	−0.00861 (16)	−0.00619 (17)
Cl62	0.0293 (3)	0.0593 (4)	0.0372 (3)	−0.0246 (3)	−0.0087 (2)	0.0117 (3)
Cl63	0.0311 (3)	0.0285 (2)	0.0338 (3)	0.0043 (2)	−0.0091 (2)	−0.0082 (2)

Geometric parameters (Å, º)

Cu1—O1	1.9957 (11)	C29—H291	0.98
Cu1—B1	2.0456 (16)	C29—H292	0.98
Cu1—S1	2.3072 (4)	C29—H293	0.98
Cu1—S2	2.3280 (4)	S3—C33	1.7129 (15)
Cu1—S3	2.3245 (4)	N31—C36	1.315 (2)
B1—N12	1.530 (2)	N31—N32	1.3609 (17)
B1—N22	1.536 (2)	N32—C33	1.3450 (19)
B1—N32	1.537 (2)	C33—C34	1.428 (2)
S1—C13	1.7102 (15)	C34—C35	1.368 (2)
N11—C16	1.312 (2)	C34—C31	1.505 (2)
N11—N12	1.3580 (17)	C35—C36	1.424 (2)
N12—C13	1.3476 (19)	C35—H35	0.95
C13—C14	1.424 (2)	C36—C30	1.526 (2)
C14—C15	1.371 (2)	C31—H311	0.98
C14—C11	1.503 (2)	C31—H312	0.98
C15—C16	1.427 (2)	C31—H313	0.98
C15—H15	0.95	C30—C37	1.532 (2)
C16—C10	1.529 (2)	C30—C39	1.537 (2)
C11—H111	0.98	C30—C38	1.538 (2)
C11—H112	0.98	C37—H371	0.98
C11—H113	0.98	C37—H372	0.98
C10—C19	1.530 (2)	C37—H373	0.98
C10—C18	1.538 (2)	C38—H381	0.98
C10—C17	1.539 (2)	C38—H382	0.98
C17—H171	0.98	C38—H383	0.98
C17—H172	0.98	C39—H391	0.98
C17—H173	0.98	C39—H392	0.98
C18—H181	0.98	C39—H393	0.98
C18—H182	0.98	O1—C1	1.2531 (19)
C18—H183	0.98	N1—C1	1.330 (2)
C19—H191	0.98	N1—H1	0.88
C19—H192	0.98	N1—H2	0.88
C19—H193	0.98	C1—C2	1.494 (2)
S2—C23	1.7069 (15)	C2—H21	0.98
N21—C26	1.3128 (19)	C2—H22	0.98
N21—N22	1.3592 (17)	C2—H23	0.98
N22—C23	1.3476 (19)	C2—H26	0.98
C23—C24	1.430 (2)	C2—H27	0.98
C24—C25	1.368 (2)	C2—H28	0.98
C24—C21	1.499 (2)	S4—O41	1.4180 (18)
C25—C26	1.426 (2)	S4—O42	1.4186 (17)
C25—H25	0.95	S4—O43	1.4335 (15)

C26—C20	1.525 (2)	S4—C4	1.819 (2)
C21—H211	0.98	C4—F41	1.318 (3)
C21—H212	0.98	C4—F43	1.328 (2)
C21—H213	0.98	C4—F42	1.330 (3)
C20—C27	1.532 (3)	C5—Cl53	1.7613 (19)
C20—C28	1.535 (3)	C5—Cl51	1.7616 (17)
C20—C29	1.536 (2)	C5—Cl52	1.7681 (17)
C27—H271	0.98	C5—H5	1.00
C27—H272	0.98	C6—Cl63	1.759 (2)
C27—H273	0.98	C6—Cl62	1.7634 (19)
C28—H281	0.98	C6—Cl61	1.7706 (18)
C28—H282	0.98	C6—H6	1.00
C28—H283	0.98		

O1—Cu1—B1	178.41 (6)	H281—C28—H282	109.5
O1—Cu1—S1	96.36 (4)	C20—C28—H283	109.5
O1—Cu1—S2	97.59 (3)	H281—C28—H283	109.5
O1—Cu1—S3	100.60 (4)	H282—C28—H283	109.5
B1—Cu1—S1	82.30 (5)	C20—C29—H291	109.5
B1—Cu1—S2	82.29 (5)	C20—C29—H292	109.5
B1—Cu1—S3	80.87 (5)	H291—C29—H292	109.5
S1—Cu1—S2	117.067 (16)	C20—C29—H293	109.5
S1—Cu1—S3	122.661 (16)	H291—C29—H293	109.5
S2—Cu1—S3	114.275 (16)	H292—C29—H293	109.5
N12—B1—N22	110.36 (12)	C33—S3—Cu1	98.89 (5)
N12—B1—N32	110.22 (12)	C36—N31—N32	116.77 (13)
N22—B1—N32	111.05 (12)	C33—N32—N31	125.63 (13)
N12—B1—Cu1	108.99 (10)	C33—N32—B1	117.40 (12)
N22—B1—Cu1	108.41 (10)	N31—N32—B1	116.49 (12)
N32—B1—Cu1	107.74 (10)	N32—C33—C34	118.20 (14)
C13—S1—Cu1	100.03 (5)	N32—C33—S3	116.16 (11)
C16—N11—N12	117.27 (12)	C34—C33—S3	125.63 (12)
C13—N12—N11	125.30 (13)	C35—C34—C33	116.28 (14)
C13—N12—B1	118.21 (12)	C35—C34—C31	123.32 (15)
N11—N12—B1	115.52 (12)	C33—C34—C31	120.40 (14)
N12—C13—C14	118.27 (13)	C34—C35—C36	121.12 (14)
N12—C13—S1	116.41 (11)	C34—C35—H35	119.4
C14—C13—S1	125.32 (11)	C36—C35—H35	119.4
C15—C14—C13	116.65 (13)	N31—C36—C35	121.54 (14)
C15—C14—C11	123.18 (14)	N31—C36—C30	116.77 (14)
C13—C14—C11	120.17 (13)	C35—C36—C30	121.69 (14)
C14—C15—C16	120.70 (14)	C34—C31—H311	109.5
C14—C15—H15	119.6	C34—C31—H312	109.5
C16—C15—H15	119.6	H311—C31—H312	109.5
N11—C16—C15	121.49 (13)	C34—C31—H313	109.5
N11—C16—C10	115.32 (13)	H311—C31—H313	109.5
C15—C16—C10	123.14 (13)	H312—C31—H313	109.5
C14—C11—H111	109.5	C36—C30—C37	111.35 (13)

C14—C11—H112	109.5	C36—C30—C39	109.45 (14)
H111—C11—H112	109.5	C37—C30—C39	109.13 (15)
C14—C11—H113	109.5	C36—C30—C38	108.56 (13)
H111—C11—H113	109.5	C37—C30—C38	108.75 (15)
H112—C11—H113	109.5	C39—C30—C38	109.59 (15)
C16—C10—C19	111.28 (12)	C30—C37—H371	109.5
C16—C10—C18	106.94 (12)	C30—C37—H372	109.5
C19—C10—C18	109.35 (14)	H371—C37—H372	109.5
C16—C10—C17	110.15 (13)	C30—C37—H373	109.5
C19—C10—C17	109.19 (14)	H371—C37—H373	109.5
C18—C10—C17	109.90 (13)	H372—C37—H373	109.5
C10—C17—H171	109.5	C30—C38—H381	109.5
C10—C17—H172	109.5	C30—C38—H382	109.5
H171—C17—H172	109.5	H381—C38—H382	109.5
C10—C17—H173	109.5	C30—C38—H383	109.5
H171—C17—H173	109.5	H381—C38—H383	109.5
H172—C17—H173	109.5	H382—C38—H383	109.5
C10—C18—H181	109.5	C30—C39—H391	109.5
C10—C18—H182	109.5	C30—C39—H392	109.5
H181—C18—H182	109.5	H391—C39—H392	109.5
C10—C18—H183	109.5	C30—C39—H393	109.5
H181—C18—H183	109.5	H391—C39—H393	109.5
H182—C18—H183	109.5	H392—C39—H393	109.5
C10—C19—H191	109.5	C1—O1—Cu1	126.57 (11)
C10—C19—H192	109.5	C1—N1—H1	122.0 (10)
H191—C19—H192	109.5	C1—N1—H2	120.0 (5)
C10—C19—H193	109.5	H1—N1—H2	118.0 (11)
H191—C19—H193	109.5	O1—C1—N1	122.19 (15)
H192—C19—H193	109.5	O1—C1—C2	120.47 (16)
C23—S2—Cu1	98.58 (5)	N1—C1—C2	117.35 (15)
C26—N21—N22	117.27 (13)	C1—C2—H21	109.5
C23—N22—N21	125.56 (12)	C1—C2—H22	109.5
C23—N22—B1	118.35 (12)	H21—C2—H22	109.5
N21—N22—B1	115.68 (12)	C1—C2—H23	109.5
N22—C23—C24	117.84 (13)	H21—C2—H23	109.5
N22—C23—S2	117.35 (11)	H22—C2—H23	109.5
C24—C23—S2	124.79 (12)	C1—C2—H26	109.5
C25—C24—C23	116.89 (14)	C1—C2—H27	109.5
C25—C24—C21	123.78 (14)	H26—C2—H27	109.5
C23—C24—C21	119.26 (14)	C1—C2—H28	109.5
C24—C25—C26	120.82 (14)	H26—C2—H28	109.5
C24—C25—H25	119.6	H27—C2—H28	109.5
C26—C25—H25	119.6	O41—S4—O42	114.45 (17)
N21—C26—C25	121.43 (14)	O41—S4—O43	115.73 (14)
N21—C26—C20	116.74 (14)	O42—S4—O43	112.91 (12)
C25—C26—C20	121.79 (13)	O41—S4—C4	103.43 (11)
C24—C21—H211	109.5	O42—S4—C4	103.86 (11)
C24—C21—H212	109.5	O43—S4—C4	104.62 (10)

H211—C21—H212	109.5	F41—C4—F43	108.8 (2)
C24—C21—H213	109.5	F41—C4—F42	107.0 (2)
H211—C21—H213	109.5	F43—C4—F42	107.10 (17)
H212—C21—H213	109.5	F41—C4—S4	111.16 (15)
C26—C20—C27	110.35 (13)	F43—C4—S4	111.75 (14)
C26—C20—C28	107.82 (14)	F42—C4—S4	110.83 (18)
C27—C20—C28	109.58 (16)	Cl53—C5—Cl51	110.00 (9)
C26—C20—C29	110.21 (14)	Cl53—C5—Cl52	111.11 (10)
C27—C20—C29	109.32 (15)	Cl51—C5—Cl52	110.97 (9)
C28—C20—C29	109.54 (15)	Cl53—C5—H5	108.2
C20—C27—H271	109.5	Cl51—C5—H5	108.2
C20—C27—H272	109.5	Cl52—C5—H5	108.2
H271—C27—H272	109.5	Cl63—C6—Cl62	110.81 (11)
C20—C27—H273	109.5	Cl63—C6—Cl61	110.20 (9)
H271—C27—H273	109.5	Cl62—C6—Cl61	110.20 (10)
H272—C27—H273	109.5	Cl63—C6—H6	108.5
C20—C28—H281	109.5	Cl62—C6—H6	108.5
C20—C28—H282	109.5	Cl61—C6—H6	108.5

C16—N11—N12—C13	3.0 (2)	N22—N21—C26—C20	−176.71 (13)
C16—N11—N12—B1	−165.51 (13)	C24—C25—C26—N21	−3.4 (2)
N22—B1—N12—C13	158.33 (12)	C24—C25—C26—C20	174.30 (15)
N32—B1—N12—C13	−78.65 (16)	N21—C26—C20—C27	−3.7 (2)
Cu1—B1—N12—C13	39.39 (15)	C25—C26—C20—C27	178.49 (16)
N22—B1—N12—N11	−32.30 (17)	N21—C26—C20—C28	115.97 (17)
N32—B1—N12—N11	90.72 (14)	C25—C26—C20—C28	−61.9 (2)
Cu1—B1—N12—N11	−151.23 (10)	N21—C26—C20—C29	−124.51 (16)
N11—N12—C13—C14	−6.4 (2)	C25—C26—C20—C29	57.7 (2)
B1—N12—C13—C14	161.87 (13)	C36—N31—N32—C33	1.5 (2)
N11—N12—C13—S1	174.17 (11)	C36—N31—N32—B1	−170.30 (13)
B1—N12—C13—S1	−17.60 (17)	N12—B1—N32—C33	162.22 (12)
Cu1—S1—C13—N12	−9.41 (12)	N22—B1—N32—C33	−75.16 (16)
Cu1—S1—C13—C14	171.16 (12)	Cu1—B1—N32—C33	43.41 (15)
N12—C13—C14—C15	4.3 (2)	N12—B1—N32—N31	−25.27 (17)
S1—C13—C14—C15	−176.24 (12)	N22—B1—N32—N31	97.35 (15)
N12—C13—C14—C11	−175.42 (14)	Cu1—B1—N32—N31	−144.07 (10)
S1—C13—C14—C11	4.0 (2)	N31—N32—C33—C34	−6.9 (2)
C13—C14—C15—C16	0.3 (2)	B1—N32—C33—C34	164.80 (13)
C11—C14—C15—C16	−179.91 (14)	N31—N32—C33—S3	172.11 (11)
N12—N11—C16—C15	2.2 (2)	B1—N32—C33—S3	−16.14 (17)
N12—N11—C16—C10	−175.47 (12)	Cu1—S3—C33—N32	−14.42 (12)
C14—C15—C16—N11	−3.8 (2)	Cu1—S3—C33—C34	164.56 (13)
C14—C15—C16—C10	173.68 (14)	N32—C33—C34—C35	7.2 (2)
N11—C16—C10—C19	−150.24 (14)	S3—C33—C34—C35	−171.76 (12)
C15—C16—C10—C19	32.2 (2)	N32—C33—C34—C31	−172.15 (14)
N11—C16—C10—C18	90.39 (16)	S3—C33—C34—C31	8.9 (2)
C15—C16—C10—C18	−87.21 (17)	C33—C34—C35—C36	−2.8 (2)
N11—C16—C10—C17	−29.00 (18)	C31—C34—C35—C36	176.48 (15)

C15—C16—C10—C17	153.41 (14)	N32—N31—C36—C35	3.3 (2)
C26—N21—N22—C23	3.0 (2)	N32—N31—C36—C30	−177.65 (13)
C26—N21—N22—B1	−169.56 (13)	C34—C35—C36—N31	−2.5 (2)
N12—B1—N22—C23	−81.11 (16)	C34—C35—C36—C30	178.49 (15)
N32—B1—N22—C23	156.35 (13)	N31—C36—C30—C37	0.6 (2)
Cu1—B1—N22—C23	38.18 (16)	C35—C36—C30—C37	179.61 (15)
N12—B1—N22—N21	92.02 (15)	N31—C36—C30—C39	−120.15 (16)
N32—B1—N22—N21	−30.51 (17)	C35—C36—C30—C39	58.9 (2)
Cu1—B1—N22—N21	−148.69 (10)	N31—C36—C30—C38	120.28 (16)
N21—N22—C23—C24	−4.6 (2)	C35—C36—C30—C38	−60.7 (2)
B1—N22—C23—C24	167.75 (13)	Cu1—O1—C1—N1	−13.2 (2)
N21—N22—C23—S2	174.18 (11)	Cu1—O1—C1—C2	166.38 (12)
B1—N22—C23—S2	−13.43 (18)	O41—S4—C4—F41	179.0 (2)
Cu1—S2—C23—N22	−13.88 (12)	O42—S4—C4—F41	−61.2 (2)
Cu1—S2—C23—C24	164.85 (12)	O43—S4—C4—F41	57.4 (2)
N22—C23—C24—C25	2.1 (2)	O41—S4—C4—F43	−59.2 (2)
S2—C23—C24—C25	−176.67 (12)	O42—S4—C4—F43	60.60 (19)
N22—C23—C24—C21	179.03 (14)	O43—S4—C4—F43	179.21 (17)
S2—C23—C24—C21	0.3 (2)	O41—S4—C4—F42	60.2 (2)
C23—C24—C25—C26	1.7 (2)	O42—S4—C4—F42	179.97 (17)
C21—C24—C25—C26	−175.14 (15)	O43—S4—C4—F42	−61.42 (18)
N22—N21—C26—C25	1.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O42	0.88	2.48 (1)	3.196 (3)	140 (1)
N1—H1···O43	0.88	2.47 (1)	3.282 (2)	154 (2)
C5—H5···O43	1.00	2.21	3.171 (2)	160