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Crystal structure of bis{(*Z*)-(benzylamino)[(5*Z*)-2-(benzylimino-κ*N*)-5-(2-methoxy-2-oxoethylidene)-4-oxothiolan-3-ylidene]methanethiolato-κ*S*}copper(II)

Konstantin Obydennov,[a]* Liliya Khamidullina,[a] Pavel Slepukhin[b] and Yury Morzherin[a]

[a]Ural Federal University, Mira 19 Ekaterinburg 620002, Russian Federation, and [b]I. Postovsky Institute of Organic Synthesis, Kovalevskoy 22 Ekaterinburg 620090, Russian Federation. *Correspondence e-mail: k.l.obydennov@urfu.ru

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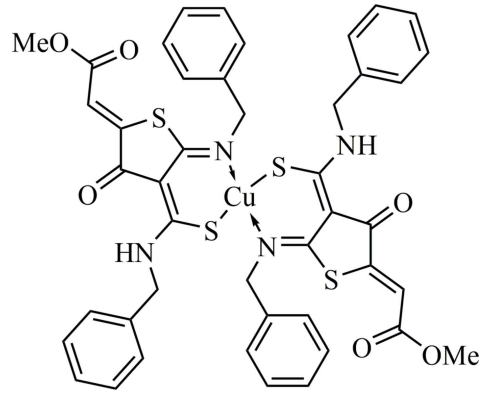
The title complex, $[Cu(C_{22}H_{19}N_2O_3S_2)_2]$, was obtained from the reaction between (*Z*)-methyl 2-(5-benzylimino-4-benzylcarbamothioyl-3-oxothiolan-2-ylidene)acetate and $Cu(NO_3)_2$. The Cu^{II} atom is tetracoordinated by two *N*,*S*-bidentate ligands, forming a highly distorted tetrahedral environment. The structure displays two intramolecular N—H···O hydrogen bonds.

Keywords: crystal structure; copper(II) complex; thioamide.

CCDC reference: 1039799

1. Related literature

For synthesis and applications of thioamide complexes, see: Jiang *et al.* (2013); Zieliński & Jurczak (2005); Arena *et al.* (2001); Shamkhy *et al.* (2013). For the importance of copper in biological systems, see: Siegel (1973); Mohan *et al.* (1998). For the synthesis of the title compound, see: Obydennov *et al.* (2013).



2. Experimental

2.1. Crystal data

$[Cu(C_{22}H_{19}N_2O_3S_2)_2]$
M_r = 910.56
Triclinic, $P\overline{1}$
a = 10.7595 (6) Å
b = 11.6318 (5) Å
c = 18.8162 (8) Å
α = 104.846 (4)°
β = 91.038 (4)°
γ = 109.119 (4)°
V = 2137.25 (18) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.76 mm^{-1}
T = 295 K
0.28 × 0.11 × 0.03 mm

2.2. Data collection

Agilent Xcalibur Eos diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.769, T_{max} = 1.000
20682 measured reflections
11592 independent reflections
5788 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.162
S = 1.01
11592 reflections
534 parameters
18 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—S1	2.2387 (10)	Cu1—N2	1.976 (3)
Cu1—S2	2.2341 (8)	Cu1—N3	1.969 (3)
S2—Cu1—S1	91.69 (3)	N3—Cu1—S1	144.11 (9)
N2—Cu1—S1	96.02 (8)	N3—Cu1—S2	97.17 (7)
N2—Cu1—S2	144.94 (9)	N3—Cu1—N2	96.32 (12)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.87	2.604 (4)	142
N4—H4···O4	0.86	1.88	2.612 (3)	141

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007);

program(s) used to refine structure: *SHELXS97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: LR2133).

References

Agilent (2011). *CrysAlis PRO*. Agilent Technologies, Yarnton, Oxfordshire, England.
Arena, G., Contino, A., Longo, E., Sciotto, D. & Spoto, G. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 2287–2291.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Jiang, Q., He, L.-T., Luo, S.-Z., Yang, Y.-Q., Yang, L., Feng, W. & Yuan, L.-H. (2013). *Chin. Chem. Lett.* **24**, 881–884.
Mohan, A., Radha, K. & Srinivas Mohan, M. (1998). *Asian J. Chem.* **10**, 50–55.
Obydennov, K. L., Klimareva, E. L., Kosterina, M. F., Slepukhin, P. A. & Morzherin, Yu. Yu. (2013). *Tetrahedron Lett.* **54**, 4876–4879.
Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.
Shamkhy, E. T., Al-Karkhi, I. H. T. & Jaffar Al-Mulla, E. A. (2013). *Res. Chem. Intermed*. **39**, 2463–2471.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siegel, H. (1973). *Metal Ions in Biological Systems*, Vol. 2, ch. 2. New York: Marcel Dekker.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zieliński, T. & Jurczak, J. (2005). *Tetrahedron*, **61**, 4081–4089. .

supporting information

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Crystal structure of bis{(*Z*)-(benzylamino)[(5*Z*)-2-(benzylimino-κ*N*)-5-(2-methoxy-2-oxoethylidene)-4-oxothiolan-3-ylidene]methanethiolato-κ*S*}copper(II)

Konstantin Obydennov, Liliya Khamidullina, Pavel Slepukhin and Yury Morzherin

S1. Structural commentary

The structure of the title complex, (I), $C_{44}H_{38}CuN_4O_6S_4$, has triclinic ($P\bar{1}$) symmetry. The ligands form two six-membered cycles with the including in the coordination of the N-atoms of the benzylamino-groups and S-atoms of the thioamide moiety (Fig.1). Metallocycles are non-planar, been in the "pseudo-cover" conformation in which Cu-atoms are deviated from the least-squared planes of the atoms S1N2C6C5C7 and C15C23C27N3S2 on the distances 0.697 and 0.548 Å accordingly. The nearest coordination of the central ion is the distorted tetrahedron (Table 2). Deviations from the ideal in the tetrahedron geometry are very serious, so the coordination of the Cu^{2+}-ion is may regard also as distorted squared. In this case S-atoms with interatomic angle S1Cu1S2 91.7° occupy the cis-positions toward Cu-atom. Due to strong π-conjugation in the metallocycle, the bonds lengths of the 2p-atoms in the metallocycles have the medium magnitude between the thioenamine and mercaptoenimine configurations, and we can`t make conclusion about dominated form of the ligand in the complex. Most principal elements of the structure which together the central ion ordered the conformation of the ligands are intramolecular H-bond NH···O between NH-group of the thioamide moiety and CO-group in the thiophene moiety, and also polar S···O contact between the S-atom in the thiophene ring and CO-group of the COOMe-substituent which. This contact fixed COOMe-substituent in the plane of the thiophene moietiy. No any shortened intermolecular contacts in the crystal presented.

S2. Synthesis and crystallization

The title complex was synthesized by the addition of $Cu(NO_3)_2$ (1 mmol) to an ethanol - chloroform solution of (Z)-methyl 2-(5-(benzylamino)-4-(benzylcarbamothioyl)-3-oxothien-2(3H)-ylidene)acetate (2 mmol) (Obydennov *et al.*, 2013). The mixture was stirred for 5 hr. The resulting deep green solution was filtered and left to evaporate at room temperature. The crystalline complex, which deposited upon standing for several days, and dark green prismatic crystals were isolated. M.p. 175-177 °C.

S3. Refinement

The non-hydrogen atoms were refined in the anisotropic approximation, hydrogen atoms were included in the refinement isotropically in the "riding" model with C—H = 0.93 Å for aryl, 0.96 Å for methine and 0.96 Å for methyl H atoms, respectively. U_{iso}(H) = 1.2Ueq(C) for aryl and methine, and 1.5Ueq(C) for methyl H atoms. Final results of the refinement: R_1 = 0.0577, wR_2 = 0.1280 [I>=2σ (I)], R_1 = 0.1278, wR_2 = 0.1623 (all data), GooF= 1.005, $\Delta\rho_{\bar{e}}$= 0.55/-0.26 $\bar{e}$/Å^3.

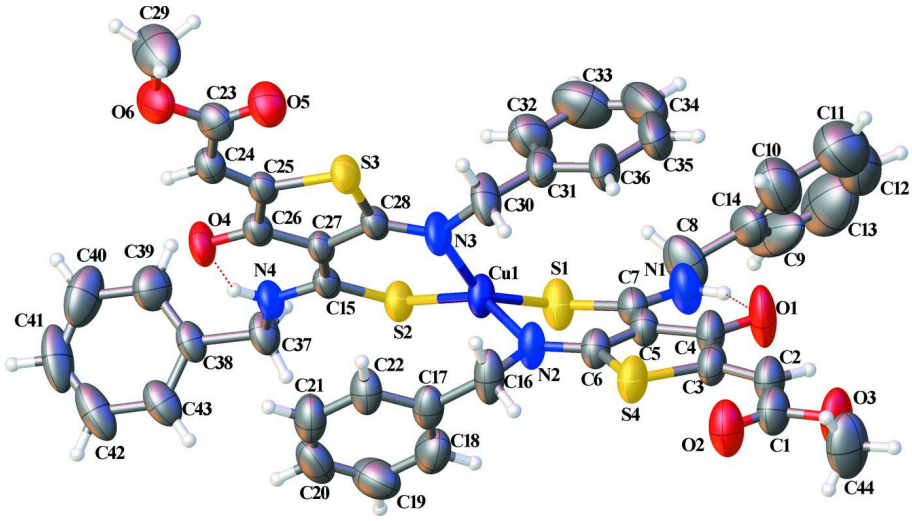

Figure 1

The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

Bis{(*Z*)-(benzylamino)[(5*Z*)-2-(benzylimino-κ*N*)-5-(2-methoxy-2-oxoethylidene)-4-oxothiolan-3-ylidene]methanethiolato-κ*S*}copper(II)

Crystal data

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$b = 11.6318$ (5) Å
$c = 18.8162$ (8) Å
$\alpha = 104.846$ (4)°
$\beta = 91.038$ (4)°
$\gamma = 109.119$ (4)°
$V = 2137.25$ (18) Å^3
$Z = 2$
$F(000) = 942$
$D_x = 1.415$ Mg m^{-3}
Melting point = 448–450 K
Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
Cell parameters from 4392 reflections
$\theta = 2.2$–28.9°
$\mu = 0.76$ mm^{-1}
$T = 295$ K
Plate, brown–green
0.28 × 0.11 × 0.03 mm

Data collection

Agilent Xcalibur Eos diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 15.9555 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.769$, $T_{max} = 1.000$
20682 measured reflections
11592 independent reflections
5788 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 30.8°$, $\theta_{min} = 1.9°$
$h = -9 \rightarrow 15$
$k = -16 \rightarrow 16$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.162$
$S = 1.01$
11592 reflections
534 parameters
18 restraints
Primary atom site location: iterative
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.020P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.40787 (4)	0.74099 (3)	0.72941 (2)	0.05996 (16)
S1	0.51282 (11)	0.79437 (8)	0.84313 (6)	0.0751 (3)
S2	0.38829 (9)	0.53810 (6)	0.71147 (5)	0.0575 (2)
S3	0.40369 (9)	0.68404 (6)	0.47870 (5)	0.0562 (2)
S4	0.27743 (11)	1.08801 (7)	0.80003 (5)	0.0688 (3)
O1	0.5766 (3)	1.2189 (2)	0.94766 (17)	0.1086 (11)
O2	0.1979 (3)	1.3090 (2)	0.83944 (17)	0.0977 (10)
O3	0.3119 (3)	1.4830 (2)	0.92986 (17)	0.1020 (10)
O4	0.2511 (3)	0.32945 (17)	0.46259 (12)	0.0670 (7)
O5	0.3904 (3)	0.6636 (2)	0.32537 (14)	0.0771 (8)
O6	0.3091 (3)	0.4783 (2)	0.23764 (14)	0.0789 (8)
N1	0.6358 (3)	1.0149 (3)	0.93368 (19)	0.0833 (10)
H1	0.6444	1.0925	0.9547	0.100*
N2	0.3141 (3)	0.8641 (2)	0.75264 (15)	0.0634 (8)
N3	0.4323 (3)	0.7478 (2)	0.62691 (15)	0.0619 (8)
N4	0.2820 (3)	0.33696 (19)	0.60191 (15)	0.0540 (7)
H4	0.2546	0.2986	0.5560	0.065*
C1	0.2875 (5)	1.3650 (3)	0.8881 (2)	0.0803 (12)
C11	1.0348 (8)	1.2765 (7)	1.0241 (5)	0.167 (3)
H11	1.0853	1.3488	1.0116	0.201*
C2	0.3841 (4)	1.3137 (3)	0.9089 (2)	0.0759 (11)
H2	0.4481	1.3637	0.9485	0.091*
C3	0.3868 (4)	1.1983 (3)	0.87429 (19)	0.0652 (10)
C4	0.4870 (4)	1.1502 (3)	0.8979 (2)	0.0709 (11)
C5	0.4632 (3)	1.0215 (3)	0.85765 (18)	0.0579 (9)
C6	0.3552 (4)	0.9737 (3)	0.80132 (18)	0.0560 (8)
C7	0.5387 (4)	0.9518 (3)	0.87919 (19)	0.0616 (9)
C8	0.7285 (4)	0.9667 (4)	0.9613 (3)	0.0999 (15)
H8A	0.7535	0.9121	0.9202	0.120*
H8B	0.6867	0.9165	0.9939	0.120*

C9	0.8502 (4)	1.0727 (4)	1.0027 (2)	0.0849 (12)
C12	1.0621 (7)	1.2424 (7)	1.0856 (5)	0.146 (3)
H12	1.1302	1.3058	1.1188	0.176*
C14	0.9028 (6)	1.0608 (7)	1.0646 (3)	0.143 (3)
H14	0.8572	0.9890	1.0791	0.172*
C15	0.3333 (3)	0.4624 (2)	0.62032 (17)	0.0461 (7)
C13	1.0132 (8)	1.1404 (9)	1.1077 (4)	0.172 (3)
H13	1.0502	1.1253	1.1479	0.206*
C10	0.9071 (6)	1.1758 (5)	0.9789 (4)	0.140 (2)
H10	0.8706	1.1858	0.9367	0.169*
C16	0.1912 (4)	0.8263 (3)	0.7030 (2)	0.0810 (13)
H16A	0.2130	0.8451	0.6564	0.097*
H16B	0.1367	0.8746	0.7253	0.097*
C17	0.1150 (4)	0.6869 (3)	0.6886 (2)	0.0626 (9)
C18	0.0831 (4)	0.6326 (4)	0.7450 (2)	0.0837 (12)
H18	0.1079	0.6826	0.7937	0.100*
C19	0.0137 (5)	0.5034 (5)	0.7308 (3)	0.0981 (14)
H19	−0.0076	0.4675	0.7698	0.118*
C20	−0.0225 (4)	0.4300 (4)	0.6599 (3)	0.0880 (13)
H20	−0.0679	0.3435	0.6501	0.106*
C21	0.0076 (4)	0.4832 (3)	0.6037 (2)	0.0821 (12)
H21	−0.0180	0.4329	0.5552	0.099*
C22	0.0758 (4)	0.6110 (3)	0.6174 (2)	0.0696 (10)
H22	0.0955	0.6462	0.5780	0.083*
C23	0.3386 (3)	0.5502 (3)	0.3077 (2)	0.0616 (9)
C24	0.3035 (3)	0.4749 (3)	0.35970 (18)	0.0539 (8)
H24	0.2595	0.3881	0.3413	0.065*
C25	0.3315 (3)	0.5246 (2)	0.43259 (18)	0.0468 (7)
C26	0.3026 (3)	0.4466 (2)	0.48604 (17)	0.0491 (8)
C27	0.3422 (3)	0.5206 (2)	0.56072 (16)	0.0440 (7)
C28	0.3958 (3)	0.6539 (2)	0.56731 (18)	0.0496 (8)
C29	0.3578 (6)	0.5428 (5)	0.1827 (3)	0.124 (2)
H29A	0.3697	0.4837	0.1397	0.185*
H29B	0.4410	0.6090	0.2023	0.185*
H29C	0.2952	0.5787	0.1695	0.185*
C44	0.2253 (6)	1.5477 (4)	0.9119 (3)	0.123 (2)
H44A	0.2314	1.5521	0.8617	0.185*
H44B	0.2519	1.6319	0.9447	0.185*
H44C	0.1356	1.5018	0.9174	0.185*
C30	0.4953 (4)	0.8788 (3)	0.6213 (2)	0.0805 (13)
H30A	0.4336	0.9242	0.6326	0.097*
H30B	0.5149	0.8756	0.5708	0.097*
C31	0.6208 (4)	0.9498 (3)	0.67281 (19)	0.0654 (10)
C32	0.7061 (5)	0.8926 (4)	0.6841 (3)	0.0973 (14)
H32	0.6863	0.8067	0.6613	0.117*
C33	0.8238 (6)	0.9612 (7)	0.7295 (4)	0.132 (2)
H33	0.8830	0.9213	0.7369	0.159*
C34	0.8531 (7)	1.0867 (7)	0.7634 (4)	0.143 (3)

H34	0.9319	1.1326	0.7941	0.171*
C35	0.7679 (7)	1.1433 (5)	0.7522 (3)	0.127 (2)
H35	0.7879	1.2291	0.7752	0.152*
C36	0.6503 (5)	1.0765 (3)	0.7069 (2)	0.0904 (14)
H36	0.5915	1.1170	0.6995	0.108*
C37	0.2678 (4)	0.2582 (2)	0.65237 (19)	0.0633 (10)
H37A	0.2112	0.2787	0.6895	0.076*
H37B	0.3537	0.2731	0.6773	0.076*
C38	0.2073 (4)	0.1210 (2)	0.60763 (19)	0.0555 (9)
C39	0.2769 (5)	0.0647 (3)	0.5591 (2)	0.0826 (12)
H39	0.3645	0.1094	0.5552	0.099*
C40	0.2169 (7)	−0.0599 (4)	0.5151 (3)	0.1066 (18)
H40	0.2631	−0.0979	0.4810	0.128*
C41	0.0899 (7)	−0.1246 (4)	0.5230 (3)	0.108 (2)
H41	0.0495	−0.2074	0.4939	0.129*
C42	0.0218 (5)	−0.0716 (4)	0.5718 (3)	0.0971 (16)
H42	−0.0643	−0.1179	0.5773	0.117*
C43	0.0803 (4)	0.0518 (3)	0.6137 (2)	0.0744 (11)
H43	0.0322	0.0889	0.6470	0.089*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0769 (3)	0.03305 (19)	0.0597 (3)	0.01695 (19)	−0.0049 (2)	−0.00118 (16)
S1	0.0958 (8)	0.0461 (4)	0.0716 (6)	0.0212 (5)	−0.0190 (5)	0.0024 (4)
S2	0.0704 (6)	0.0339 (4)	0.0607 (5)	0.0152 (4)	0.0009 (4)	0.0046 (3)
S3	0.0655 (6)	0.0324 (3)	0.0623 (5)	0.0100 (3)	0.0039 (4)	0.0079 (3)
S4	0.0893 (8)	0.0414 (4)	0.0684 (6)	0.0259 (4)	−0.0060 (5)	−0.0005 (4)
O1	0.110 (3)	0.0588 (15)	0.116 (2)	0.0235 (15)	−0.044 (2)	−0.0350 (15)
O2	0.112 (3)	0.0607 (15)	0.101 (2)	0.0280 (16)	−0.0212 (19)	−0.0062 (15)
O3	0.126 (3)	0.0490 (13)	0.114 (2)	0.0398 (16)	−0.0192 (19)	−0.0171 (14)
O4	0.0852 (18)	0.0291 (10)	0.0644 (15)	0.0005 (10)	−0.0023 (12)	0.0010 (9)
O5	0.090 (2)	0.0573 (14)	0.0767 (18)	0.0144 (13)	0.0028 (14)	0.0200 (12)
O6	0.0743 (19)	0.0867 (17)	0.0542 (16)	0.0073 (14)	−0.0073 (13)	0.0105 (13)
N1	0.079 (2)	0.0547 (16)	0.094 (3)	0.0169 (16)	−0.0216 (19)	−0.0076 (16)
N2	0.076 (2)	0.0408 (13)	0.0623 (18)	0.0227 (13)	−0.0179 (15)	−0.0069 (12)
N3	0.083 (2)	0.0261 (11)	0.0617 (17)	0.0068 (12)	−0.0001 (15)	0.0037 (11)
N4	0.0609 (18)	0.0276 (11)	0.0609 (17)	0.0046 (11)	0.0007 (13)	0.0054 (10)
C1	0.099 (4)	0.0474 (19)	0.083 (3)	0.023 (2)	0.002 (3)	0.0006 (19)
C11	0.151 (6)	0.125 (5)	0.201 (7)	0.028 (4)	0.042 (5)	0.027 (5)
C2	0.091 (3)	0.0440 (18)	0.077 (3)	0.0186 (19)	−0.003 (2)	−0.0031 (16)
C3	0.081 (3)	0.0397 (16)	0.062 (2)	0.0153 (17)	0.0063 (19)	−0.0011 (14)
C4	0.083 (3)	0.0433 (17)	0.068 (2)	0.0154 (18)	−0.006 (2)	−0.0075 (16)
C5	0.059 (2)	0.0421 (16)	0.059 (2)	0.0117 (15)	0.0011 (17)	−0.0008 (14)
C6	0.069 (2)	0.0382 (15)	0.054 (2)	0.0169 (15)	0.0003 (17)	0.0045 (13)
C7	0.062 (2)	0.0500 (17)	0.057 (2)	0.0094 (16)	0.0015 (17)	0.0006 (15)
C8	0.078 (3)	0.083 (3)	0.126 (4)	0.019 (2)	−0.031 (3)	0.022 (3)
C9	0.061 (3)	0.093 (3)	0.074 (3)	0.014 (2)	−0.003 (2)	−0.004 (2)

C12	0.123 (5)	0.113 (4)	0.153 (6)	0.017 (4)	0.019 (4)	−0.018 (4)
C14	0.085 (4)	0.257 (8)	0.058 (3)	0.053 (4)	−0.004 (3)	0.003 (4)
C15	0.0424 (18)	0.0281 (13)	0.0605 (19)	0.0082 (12)	0.0069 (14)	0.0048 (12)
C13	0.153 (6)	0.226 (7)	0.114 (5)	0.077 (5)	−0.017 (4)	−0.003 (5)
C10	0.116 (5)	0.095 (4)	0.175 (6)	0.017 (4)	0.004 (4)	0.004 (4)
C16	0.095 (3)	0.0490 (18)	0.085 (3)	0.0317 (19)	−0.029 (2)	−0.0108 (17)
C17	0.061 (2)	0.0516 (18)	0.069 (2)	0.0272 (16)	−0.0134 (18)	−0.0030 (16)
C18	0.082 (3)	0.084 (3)	0.068 (3)	0.026 (2)	−0.003 (2)	−0.005 (2)
C19	0.075 (3)	0.104 (4)	0.102 (4)	0.008 (3)	0.013 (3)	0.036 (3)
C20	0.057 (3)	0.062 (2)	0.122 (4)	0.0059 (19)	−0.004 (3)	0.005 (3)
C21	0.086 (3)	0.062 (2)	0.078 (3)	0.021 (2)	−0.013 (2)	−0.008 (2)
C22	0.078 (3)	0.0512 (19)	0.067 (2)	0.0195 (18)	−0.013 (2)	0.0004 (16)
C23	0.051 (2)	0.062 (2)	0.066 (2)	0.0148 (17)	−0.0035 (17)	0.0150 (17)
C24	0.050 (2)	0.0418 (15)	0.062 (2)	0.0105 (14)	0.0005 (16)	0.0084 (14)
C25	0.0395 (18)	0.0347 (14)	0.061 (2)	0.0113 (12)	0.0046 (15)	0.0066 (13)
C26	0.0425 (19)	0.0360 (14)	0.063 (2)	0.0111 (13)	0.0051 (15)	0.0063 (13)
C27	0.0422 (18)	0.0273 (12)	0.0555 (18)	0.0083 (12)	0.0035 (14)	0.0043 (12)
C28	0.046 (2)	0.0313 (13)	0.062 (2)	0.0078 (13)	0.0047 (15)	0.0050 (13)
C29	0.139 (5)	0.128 (4)	0.070 (3)	0.000 (4)	0.002 (3)	0.031 (3)
C44	0.148 (5)	0.069 (3)	0.150 (5)	0.059 (3)	−0.024 (4)	−0.003 (3)
C30	0.117 (4)	0.0311 (15)	0.073 (3)	0.0042 (18)	−0.011 (2)	0.0094 (15)
C31	0.086 (3)	0.0375 (16)	0.060 (2)	0.0082 (17)	0.0143 (19)	0.0073 (14)
C32	0.084 (4)	0.069 (3)	0.128 (4)	0.019 (3)	0.017 (3)	0.019 (3)
C33	0.079 (4)	0.151 (5)	0.165 (6)	0.032 (4)	0.014 (4)	0.050 (5)
C34	0.089 (5)	0.151 (6)	0.113 (5)	−0.026 (4)	0.009 (4)	−0.004 (4)
C35	0.119 (5)	0.069 (3)	0.125 (5)	−0.022 (3)	0.027 (4)	−0.019 (3)
C36	0.108 (4)	0.0363 (18)	0.096 (3)	0.001 (2)	0.015 (3)	−0.0032 (18)
C37	0.077 (3)	0.0331 (15)	0.068 (2)	0.0060 (15)	−0.0014 (18)	0.0117 (14)
C38	0.063 (2)	0.0306 (14)	0.064 (2)	0.0051 (15)	−0.0056 (17)	0.0134 (14)
C39	0.095 (3)	0.053 (2)	0.097 (3)	0.024 (2)	0.015 (3)	0.017 (2)
C40	0.181 (6)	0.061 (3)	0.087 (3)	0.061 (3)	0.009 (3)	0.011 (2)
C41	0.169 (6)	0.031 (2)	0.097 (4)	0.007 (3)	−0.041 (4)	0.012 (2)
C42	0.097 (4)	0.055 (2)	0.113 (4)	−0.013 (2)	−0.037 (3)	0.034 (2)
C43	0.071 (3)	0.0506 (19)	0.091 (3)	0.0036 (18)	−0.009 (2)	0.0266 (19)

Geometric parameters (Å, º)

Cu1—S1	2.2387 (10)	C5—C7	1.439 (5)
Cu1—S2	2.2341 (8)	C8—C9	1.502 (5)
Cu1—N2	1.976 (3)	C9—C14	1.344 (7)
Cu1—N3	1.969 (3)	C9—C10	1.348 (7)
S1—C7	1.707 (3)	C12—C13	1.308 (10)
S2—C15	1.707 (3)	C14—C13	1.336 (8)
S3—C25	1.732 (3)	C15—C27	1.441 (4)
S3—C28	1.788 (3)	C16—C17	1.508 (5)
S4—C3	1.737 (4)	C17—C18	1.363 (5)
S4—C6	1.792 (3)	C17—C22	1.372 (5)
O1—C4	1.234 (4)	C18—C19	1.393 (6)

O2—C1	1.201 (5)	C19—C20	1.356 (6)
O3—C1	1.332 (4)	C20—C21	1.350 (6)
O3—C44	1.459 (5)	C21—C22	1.377 (5)
O4—C26	1.244 (3)	C23—C24	1.450 (5)
O5—C23	1.203 (4)	C24—C25	1.331 (4)
O6—C23	1.335 (4)	C25—C26	1.492 (4)
O6—C29	1.437 (5)	C26—C27	1.419 (4)
N1—C7	1.325 (4)	C27—C28	1.437 (4)
N1—C8	1.441 (5)	C30—C31	1.502 (5)
N2—C6	1.295 (4)	C31—C32	1.340 (6)
N2—C16	1.476 (4)	C31—C36	1.373 (4)
N3—C28	1.297 (4)	C32—C33	1.385 (7)
N3—C30	1.484 (4)	C33—C34	1.361 (8)
N4—C15	1.326 (3)	C34—C35	1.334 (8)
N4—C37	1.457 (4)	C35—C36	1.382 (8)
C1—C2	1.449 (6)	C37—C38	1.514 (4)
C11—C12	1.371 (9)	C38—C39	1.365 (5)
C11—C10	1.541 (9)	C38—C43	1.364 (5)
C2—C3	1.343 (4)	C39—C40	1.399 (6)
C3—C4	1.475 (5)	C40—C41	1.358 (8)
C4—C5	1.429 (4)	C41—C42	1.338 (7)
C5—C6	1.419 (5)	C42—C43	1.374 (5)

S2—Cu1—S1	91.69 (3)	N4—C15—C27	116.5 (3)
N2—Cu1—S1	96.02 (8)	C27—C15—S2	126.54 (19)
N2—Cu1—S2	144.94 (9)	C12—C13—C14	110.7 (8)
N3—Cu1—S1	144.11 (9)	C9—C10—C11	117.7 (7)
N3—Cu1—S2	97.17 (7)	N2—C16—C17	110.8 (3)
N3—Cu1—N2	96.32 (12)	C18—C17—C16	121.7 (3)
C7—S1—Cu1	105.69 (13)	C18—C17—C22	118.3 (3)
C15—S2—Cu1	107.41 (10)	C22—C17—C16	120.1 (4)
C25—S3—C28	92.49 (14)	C17—C18—C19	120.9 (4)
C3—S4—C6	91.48 (16)	C20—C19—C18	119.8 (4)
C1—O3—C44	116.2 (3)	C21—C20—C19	119.7 (4)
C23—O6—C29	115.6 (3)	C20—C21—C22	120.9 (4)
C7—N1—C8	126.5 (3)	C17—C22—C21	120.5 (4)
C6—N2—Cu1	126.7 (2)	O5—C23—O6	123.9 (3)
C6—N2—C16	119.7 (3)	O5—C23—C24	124.1 (3)
C16—N2—Cu1	113.34 (19)	O6—C23—C24	111.9 (3)
C28—N3—Cu1	127.4 (2)	C25—C24—C23	122.9 (3)
C28—N3—C30	119.7 (3)	C24—C25—S3	126.2 (2)
C30—N3—Cu1	112.9 (2)	C24—C25—C26	123.0 (3)
C15—N4—C37	126.0 (3)	C26—C25—S3	110.8 (2)
O2—C1—O3	124.4 (4)	O4—C26—C25	119.7 (3)
O2—C1—C2	124.7 (3)	O4—C26—C27	127.6 (3)
O3—C1—C2	110.9 (4)	C27—C26—C25	112.8 (2)
C12—C11—C10	109.2 (7)	C26—C27—C15	121.4 (2)
C3—C2—C1	123.9 (4)	C26—C27—C28	112.3 (3)

C2—C3—S4	126.4 (3)	C28—C27—C15	126.3 (3)
C2—C3—C4	121.8 (3)	N3—C28—S3	119.8 (2)
C4—C3—S4	111.8 (2)	N3—C28—C27	128.6 (3)
O1—C4—C3	120.3 (3)	C27—C28—S3	111.6 (2)
O1—C4—C5	127.8 (4)	N3—C30—C31	112.4 (3)
C5—C4—C3	111.9 (3)	C32—C31—C30	121.1 (3)
C4—C5—C7	120.4 (3)	C32—C31—C36	119.7 (4)
C6—C5—C4	112.6 (3)	C36—C31—C30	119.2 (4)
C6—C5—C7	126.8 (3)	C31—C32—C33	120.1 (5)
N2—C6—S4	120.3 (3)	C34—C33—C32	120.4 (6)
N2—C6—C5	127.7 (3)	C35—C34—C33	119.4 (6)
C5—C6—S4	112.0 (2)	C34—C35—C36	121.1 (5)
N1—C7—S1	116.6 (3)	C31—C36—C35	119.4 (5)
N1—C7—C5	117.0 (3)	N4—C37—C38	108.1 (3)
C5—C7—S1	126.4 (3)	C39—C38—C37	121.0 (3)
N1—C8—C9	111.1 (4)	C43—C38—C37	120.4 (3)
C14—C9—C8	117.5 (5)	C43—C38—C39	118.6 (3)
C14—C9—C10	120.4 (5)	C38—C39—C40	120.2 (4)
C10—C9—C8	122.0 (5)	C41—C40—C39	118.9 (5)
C13—C12—C11	134.0 (8)	C42—C41—C40	121.5 (4)
C13—C14—C9	127.4 (8)	C41—C42—C43	119.4 (5)
N4—C15—S2	116.9 (2)	C38—C43—C42	121.4 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.87	2.604 (4)	142
N4—H4···O4	0.86	1.88	2.612 (3)	141