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cis-Bis[1,1-dibenzyl-3-(furan-2-ylcarbonyl)thioureato-κ^2O,S]copper(II)

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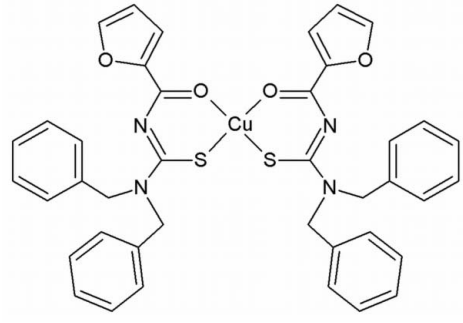
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.122; data-to-parameter ratio = 16.1.

In the title compound, $[Cu(C_{20}H_{17}N_2O_2S)_2]$, the Cu^{II} atom is coordinated by the S and O atoms of two 1,1-dibenzyl-3-(furan-2-ylcarbonyl)thioureate ligands in a distorted square-planar geometry. The two O and two S atoms are mutually *cis* to each other. The Cu—S and Cu—O bond lengths lie within the ranges of those found in related structures. The dihedral angle between the planes of the two chelating rings is 26.15 (6)°.

Related literature

For general background, see: Arslan *et al.* (2003). For synthesis details, see: Nagasawa & Mitsunobu (1981). For related structures, see: Binzet *et al.* (2006); Gomes *et al.* (2007); Pérez *et al.* (2011).



Experimental

Crystal data

$[Cu(C_{20}H_{17}N_2O_2S)_2]$
M_r = 762.37
Monoclinic, $P2_1/n$
a = 18.8390 (3) Å
b = 10.8730 (2) Å
c = 19.6200 (3) Å
β = 114.748 (1)°
V = 3649.79 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.76 mm^{-1}
T = 293 K
0.49 × 0.44 × 0.39 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: gaussian (Coppens *et al.*, 1965)
T_{min} = 0.779, T_{max} = 0.886
21982 measured reflections
7413 independent reflections
6761 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.122
S = 1.07
7413 reflections
460 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Data collection: *COLLECT* (Enraf–Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997), *SCALEPACK* and *SORTAV* (Blessing, 1987, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5517).

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supporting information

Acta Cryst. (2011). E**67**, m621 [doi:10.1107/S160053681101422X]

cis-Bis[1,1-dibenzyl-3-(furan-2-ylcarbonyl)thioureato-κ^2O,S]copper(II)

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S1. Comment

N-acyl-*N*′,*N*′-disubstituted thioureas have attracted the attention of researches over the last three decades with regard to coordination behaviour towards transition metals (Arslan *et al.*, 2003). During complex formation, the ligand is deprotonated, which results in a neutral complex with a six-membered ring chelating the metal ion.

In the crystal structure of the title complex, the two furoylthiourea molecules adopt a *cis* conformation, bonded to the central Cu^{II} ion as shown in Fig. 1. The complex coordination geometry is a distorted square-plane as reflected by angles O1—Cu—S2 [166.02 (6)°] and O2—Cu—S1 [163.52 (7)°]. The distance of Cu atom from the best plane through the coordination sphere is 0.2486 (1) Å. The chelate ring systems, Cu–O1–C1–N1–C2–S1 and Cu–O2–C21–N3–C22–S2, are nearly planar with the largest deviations from the best plane being -0.118 (1) Å for C2 and 0.114 (2) Å for C22, respectively. The dihedral angle of 26.15 (6)° between these chelate planes indicates a strong distortion from square planar towards tetrahedral geometry. By comparison, the corresponding O—Ni—S angles and dihedral angle for the Ni^{II} analog (Pérez *et al.*, 2011) are 169.66 (5)°, 170.09 (6)° and 20.33 (6)°, respectively. As a result, the square-planar coordination geometry of the title molecule is more distorted. The Cu—S and Cu—O bond lengths lie within the range of those found in the related structures (Gomes *et al.*, 2007, Binzet *et al.*, 2006). The bond lengths of the thiocarbonyl and carbonyl bonds are longer than the average for C═S (1.68 Å) and C═O (1.20 Å) in thioureas, while the C—N bonds in the chelate rings are all shorter than the average for C—N single bond of about 1.48 Å. This indicates extensive electronic delocalization within the complex rings. Fig. 2 shows the arrangement of the complex molecules in the unit cell.

S2. Experimental

The 1,1-dibenzyl-3-[(furan-2-yl)-carbonyl]thiourea ligand was prepared using the standard procedure previously reported in the literature (Nagasawa & Mitsunobu, 1981) by the reaction of furoyl chloride with KSCN in anhydrous acetone, and then condensation with dibenzylamine. To an ethanol solution (30 ml) containing the ligand (0.70 g, 2 mmol) was added an ethanol solution of $Cu(CH_3COO)_2.H_2O$ (0.20 g, 1 mmol). The solution was stirred at room temperature for 2 h, and at once a solution of NaOH (1 N) was added to adjust pH to the neutral value. The mixture was filtered and the filtrate was evaporated under reduced pressure to give a green solid, which was washed with acetone. Single crystals were obtained by slow evaporation of a chloroform/dichloromethane solution (1:1, *v*/*v*) of the complex.

S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic, and C—H = 0.97 Å and 1.5U_{eq}(C) for methylene.

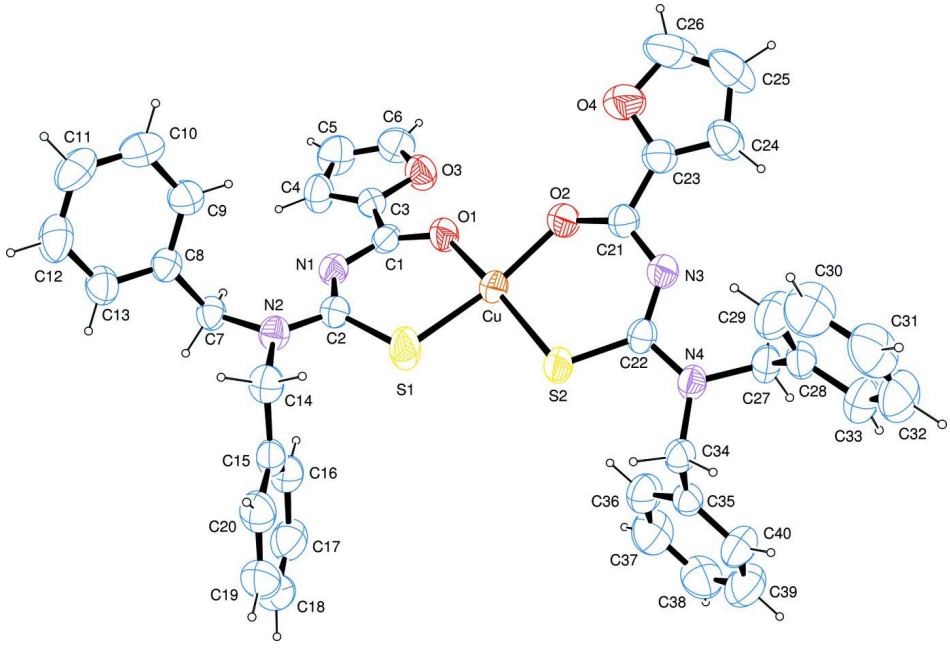

Figure 1

The molecular structure of title compound. Displacement ellipsoids are drawn at the 50% probability level.

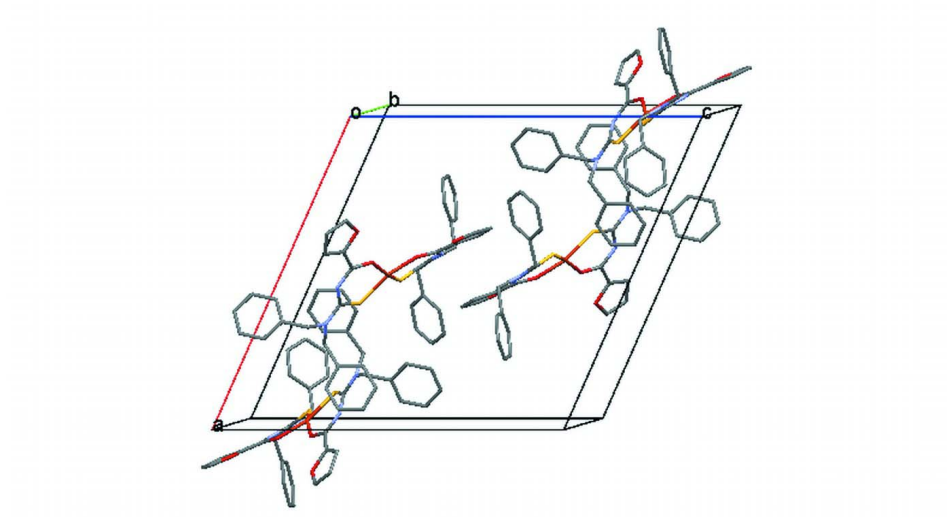

Figure 2

Crystal packing of title complex, viewed along [010]. H atoms have been omitted for clarity.

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c = 19.6200 (3) Å
β = 114.748 (1)°
V = 3649.79 (10) Å^3
Z = 4
$F(000)$ = 1580
D_x = 1.387 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 22283 reflections
θ = 2.9–26.7°
μ = 0.76 mm^{-1}
T = 293 K
Prism, blue
0.49 × 0.44 × 0.39 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Enraf–Nonius FR590
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
CCD rotation images, thick slices scans
Absorption correction: gaussian (Coppens *et al.*, 1965)
T_{min} = 0.779, T_{max} = 0.886
21982 measured reflections
7413 independent reflections
6761 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 26.7°, θ_{min} = 3.0°
h = −23→23
k = −13→13
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.122
S = 1.07
7413 reflections
460 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
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 1.1325P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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	0.508045 (16)	0.07839 (3)	0.297423 (16)	0.04477 (11)
S2	0.59888 (4)	0.07792 (6)	0.25262 (4)	0.05644 (19)
S1	0.53343 (5)	0.27665 (7)	0.32023 (5)	0.0707 (2)
O1	0.45058 (10)	0.06749 (15)	0.35857 (10)	0.0493 (4)
O2	0.46288 (11)	−0.07565 (18)	0.25155 (12)	0.0641 (5)
O3	0.39877 (11)	−0.02783 (16)	0.45314 (11)	0.0570 (4)
O4	0.35836 (12)	−0.2514 (2)	0.18813 (13)	0.0763 (6)
N1	0.44597 (11)	0.26752 (17)	0.40284 (11)	0.0424 (4)
N2	0.47257 (11)	0.45499 (18)	0.36697 (11)	0.0429 (4)
N3	0.53966 (11)	−0.14815 (18)	0.19153 (11)	0.0447 (4)
N4	0.65912 (11)	−0.09441 (17)	0.19891 (11)	0.0425 (4)
C1	0.43832 (12)	0.1451 (2)	0.39995 (12)	0.0395 (5)

C2	0.47889 (13)	0.3315 (2)	0.36579 (13)	0.0420 (5)
C3	0.40694 (13)	0.0971 (2)	0.45135 (13)	0.0415 (5)
C4	0.38350 (16)	0.1503 (3)	0.50008 (15)	0.0574 (7)
H4	0.3837	0.234	0.51	0.069*
C5	0.35819 (19)	0.0537 (3)	0.53378 (17)	0.0668 (8)
H5	0.338	0.0618	0.5695	0.08*
C6	0.36918 (17)	−0.0499 (3)	0.50399 (17)	0.0626 (7)
H6	0.358	−0.1279	0.5165	0.075*
C7	0.43616 (13)	0.5172 (2)	0.41091 (12)	0.0422 (5)
H7A	0.4716	0.58	0.4417	0.051*
H7B	0.4291	0.4577	0.4444	0.051*
C8	0.35843 (13)	0.5760 (2)	0.36437 (12)	0.0414 (5)
C9	0.29283 (14)	0.5045 (3)	0.32657 (14)	0.0545 (6)
H9	0.2976	0.4193	0.3272	0.065*
C10	0.22047 (16)	0.5575 (3)	0.28797 (17)	0.0673 (8)
H10	0.1768	0.5086	0.2627	0.081*
C11	0.21354 (17)	0.6836 (3)	0.28721 (16)	0.0685 (8)
H11	0.1648	0.72	0.2616	0.082*
C12	0.27814 (18)	0.7558 (3)	0.32403 (17)	0.0681 (8)
H12	0.2732	0.8409	0.3231	0.082*
C13	0.35041 (16)	0.7019 (2)	0.36246 (15)	0.0540 (6)
H13	0.3941	0.7512	0.3873	0.065*
C14	0.50761 (15)	0.5373 (2)	0.33057 (14)	0.0495 (6)
H14A	0.4777	0.6131	0.3175	0.059*
H14B	0.5031	0.4993	0.2842	0.059*
C15	0.59256 (15)	0.5687 (2)	0.37715 (14)	0.0465 (5)
C16	0.63705 (15)	0.5165 (2)	0.44601 (14)	0.0533 (6)
H16	0.615	0.4577	0.4658	0.064*
C17	0.71447 (18)	0.5511 (3)	0.48607 (18)	0.0709 (8)
H17	0.7439	0.516	0.5327	0.085*
C18	0.7477 (2)	0.6370 (4)	0.4571 (2)	0.0827 (10)
H18	0.7994	0.6608	0.4842	0.099*
C19	0.7043 (2)	0.6874 (3)	0.3881 (2)	0.0791 (10)
H19	0.727	0.7445	0.368	0.095*
C20	0.62787 (18)	0.6542 (3)	0.34867 (18)	0.0621 (7)
H20	0.599	0.6895	0.302	0.075*
C21	0.47872 (13)	−0.1453 (2)	0.20874 (13)	0.0441 (5)
C22	0.59750 (13)	−0.0648 (2)	0.21315 (12)	0.0405 (5)
C23	0.42344 (14)	−0.2456 (2)	0.17448 (13)	0.0491 (6)
C24	0.42619 (19)	−0.3425 (3)	0.13331 (16)	0.0645 (7)
H24	0.4649	−0.3597	0.1169	0.077*
C25	0.3587 (2)	−0.4131 (3)	0.1198 (2)	0.0890 (11)
H25	0.3443	−0.4861	0.0927	0.107*
C26	0.3200 (2)	−0.3554 (4)	0.1530 (2)	0.0917 (12)
H26	0.2728	−0.3822	0.1524	0.11*
C27	0.66466 (15)	−0.2122 (2)	0.16429 (13)	0.0476 (6)
H27A	0.628	−0.2702	0.1693	0.057*
H27B	0.7168	−0.2456	0.191	0.057*

C28	0.64762 (15)	−0.1988 (2)	0.08239 (14)	0.0484 (6)
C29	0.57841 (18)	−0.1499 (3)	0.03292 (17)	0.0744 (9)
H29	0.5418	−0.1239	0.0501	0.089*
C30	0.5620 (2)	−0.1384 (4)	−0.04314 (18)	0.0916 (11)
H30	0.5149	−0.104	−0.0762	0.11*
C31	0.6151 (2)	−0.1776 (4)	−0.06883 (19)	0.0873 (11)
H31	0.6042	−0.1704	−0.1195	0.105*
C32	0.6840 (2)	−0.2271 (3)	−0.02047 (19)	0.0816 (10)
H32	0.7201	−0.2543	−0.0381	0.098*
C33	0.70071 (19)	−0.2372 (3)	0.05522 (17)	0.0648 (7)
H33	0.7483	−0.2703	0.0881	0.078*
C34	0.72555 (14)	−0.0120 (2)	0.21270 (13)	0.0453 (5)
H34A	0.7097	0.0719	0.2159	0.054*
H34B	0.7394	−0.0166	0.1704	0.054*
C35	0.79670 (14)	−0.0422 (2)	0.28359 (14)	0.0452 (5)
C36	0.79724 (17)	−0.0283 (3)	0.35352 (16)	0.0621 (7)
H36	0.7525	−0.0007	0.3577	0.074*
C37	0.8635 (2)	−0.0550 (3)	0.41754 (18)	0.0785 (9)
H37	0.8628	−0.0459	0.4644	0.094*
C38	0.9302 (2)	−0.0947 (3)	0.4126 (2)	0.0787 (9)
H38	0.9748	−0.1119	0.4558	0.094*
C39	0.93044 (19)	−0.1087 (4)	0.3436 (2)	0.0822 (10)
H39	0.9754	−0.136	0.3397	0.099*
C40	0.86415 (17)	−0.0825 (3)	0.27935 (18)	0.0648 (8)
H40	0.865	−0.0922	0.2326	0.078*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.04319 (18)	0.04824 (19)	0.04929 (19)	0.00021 (12)	0.02570 (14)	−0.01030 (13)
S2	0.0615 (4)	0.0452 (4)	0.0818 (5)	−0.0050 (3)	0.0489 (4)	−0.0158 (3)
S1	0.0980 (6)	0.0474 (4)	0.1073 (6)	−0.0094 (4)	0.0828 (5)	−0.0144 (4)
O1	0.0552 (10)	0.0469 (9)	0.0563 (10)	−0.0054 (7)	0.0336 (8)	−0.0133 (8)
O2	0.0590 (11)	0.0696 (13)	0.0804 (13)	−0.0178 (9)	0.0454 (10)	−0.0342 (10)
O3	0.0683 (11)	0.0439 (9)	0.0703 (12)	−0.0069 (8)	0.0403 (10)	−0.0053 (9)
O4	0.0626 (12)	0.0881 (16)	0.0874 (15)	−0.0211 (11)	0.0405 (11)	−0.0213 (12)
N1	0.0440 (10)	0.0412 (10)	0.0481 (10)	0.0014 (8)	0.0252 (9)	−0.0018 (9)
N2	0.0474 (11)	0.0409 (10)	0.0433 (10)	0.0041 (8)	0.0218 (9)	0.0028 (8)
N3	0.0473 (11)	0.0462 (11)	0.0446 (10)	−0.0001 (9)	0.0233 (9)	−0.0041 (9)
N4	0.0487 (11)	0.0396 (10)	0.0472 (11)	0.0025 (8)	0.0279 (9)	−0.0029 (8)
C1	0.0328 (11)	0.0457 (13)	0.0402 (11)	0.0035 (9)	0.0154 (9)	−0.0033 (10)
C2	0.0432 (12)	0.0420 (12)	0.0429 (12)	0.0009 (9)	0.0202 (10)	−0.0027 (10)
C3	0.0412 (12)	0.0375 (12)	0.0477 (12)	−0.0010 (9)	0.0204 (10)	−0.0025 (10)
C4	0.0742 (18)	0.0493 (14)	0.0653 (16)	0.0050 (13)	0.0456 (15)	−0.0022 (13)
C5	0.080 (2)	0.073 (2)	0.0662 (18)	0.0004 (15)	0.0490 (16)	0.0085 (15)
C6	0.0674 (18)	0.0558 (16)	0.0739 (19)	−0.0076 (13)	0.0389 (15)	0.0094 (14)
C7	0.0445 (12)	0.0419 (12)	0.0371 (11)	0.0055 (10)	0.0140 (10)	−0.0031 (10)
C8	0.0432 (12)	0.0443 (13)	0.0358 (11)	0.0047 (10)	0.0157 (10)	−0.0013 (9)

C9	0.0476 (14)	0.0512 (15)	0.0579 (15)	0.0003 (11)	0.0153 (12)	−0.0010 (12)
C10	0.0427 (14)	0.083 (2)	0.0657 (18)	−0.0004 (14)	0.0126 (13)	0.0011 (16)
C11	0.0495 (16)	0.090 (2)	0.0579 (16)	0.0248 (15)	0.0144 (13)	0.0093 (16)
C12	0.075 (2)	0.0539 (16)	0.0663 (18)	0.0252 (15)	0.0209 (15)	0.0085 (14)
C13	0.0550 (15)	0.0451 (14)	0.0536 (14)	0.0078 (11)	0.0145 (12)	−0.0023 (12)
C14	0.0591 (15)	0.0446 (13)	0.0481 (13)	0.0048 (11)	0.0258 (12)	0.0084 (11)
C15	0.0572 (14)	0.0372 (12)	0.0530 (14)	0.0043 (10)	0.0309 (12)	−0.0026 (10)
C16	0.0573 (15)	0.0509 (15)	0.0557 (14)	0.0048 (12)	0.0277 (13)	−0.0016 (12)
C17	0.0568 (17)	0.080 (2)	0.0663 (18)	0.0095 (15)	0.0166 (15)	−0.0163 (16)
C18	0.0609 (19)	0.083 (2)	0.113 (3)	−0.0150 (17)	0.045 (2)	−0.037 (2)
C19	0.085 (2)	0.0617 (19)	0.115 (3)	−0.0185 (17)	0.066 (2)	−0.0185 (19)
C20	0.079 (2)	0.0470 (15)	0.0763 (18)	−0.0002 (13)	0.0483 (16)	0.0032 (13)
C21	0.0447 (12)	0.0476 (13)	0.0416 (12)	−0.0001 (10)	0.0198 (10)	−0.0043 (10)
C22	0.0472 (12)	0.0414 (12)	0.0390 (11)	0.0047 (10)	0.0240 (10)	0.0021 (9)
C23	0.0489 (14)	0.0550 (15)	0.0448 (13)	−0.0050 (11)	0.0210 (11)	−0.0044 (11)
C24	0.082 (2)	0.0624 (17)	0.0602 (16)	−0.0189 (15)	0.0406 (15)	−0.0195 (14)
C25	0.111 (3)	0.082 (2)	0.072 (2)	−0.044 (2)	0.037 (2)	−0.0325 (18)
C26	0.076 (2)	0.110 (3)	0.088 (2)	−0.046 (2)	0.032 (2)	−0.019 (2)
C27	0.0567 (14)	0.0395 (12)	0.0550 (14)	0.0068 (10)	0.0316 (12)	−0.0018 (11)
C28	0.0561 (14)	0.0446 (13)	0.0512 (13)	−0.0004 (11)	0.0290 (12)	−0.0095 (11)
C29	0.0671 (19)	0.098 (2)	0.0580 (17)	0.0151 (17)	0.0262 (15)	−0.0092 (17)
C30	0.084 (2)	0.122 (3)	0.0528 (18)	0.013 (2)	0.0128 (17)	−0.0080 (19)
C31	0.112 (3)	0.101 (3)	0.0537 (17)	−0.017 (2)	0.040 (2)	−0.0148 (18)
C32	0.104 (3)	0.093 (2)	0.074 (2)	−0.003 (2)	0.062 (2)	−0.0129 (19)
C33	0.0751 (19)	0.0673 (18)	0.0683 (17)	0.0095 (15)	0.0461 (15)	0.0000 (14)
C34	0.0550 (14)	0.0404 (12)	0.0544 (13)	−0.0022 (10)	0.0366 (12)	−0.0017 (11)
C35	0.0531 (14)	0.0383 (12)	0.0527 (13)	−0.0045 (10)	0.0305 (12)	−0.0040 (10)
C36	0.0674 (17)	0.0714 (18)	0.0568 (15)	0.0016 (14)	0.0353 (14)	−0.0061 (14)
C37	0.086 (2)	0.095 (3)	0.0522 (17)	0.0030 (19)	0.0257 (17)	−0.0060 (16)
C38	0.069 (2)	0.076 (2)	0.071 (2)	0.0052 (16)	0.0100 (17)	−0.0041 (16)
C39	0.0589 (19)	0.097 (3)	0.087 (2)	0.0159 (17)	0.0274 (18)	−0.005 (2)
C40	0.0599 (17)	0.079 (2)	0.0643 (17)	0.0119 (14)	0.0345 (15)	−0.0024 (14)

Geometric parameters (Å, º)

Cu—O1	1.9269 (16)	C15—C16	1.379 (4)
Cu—S1	2.2128 (8)	C15—C20	1.389 (4)
O1—C1	1.257 (3)	C16—C17	1.388 (4)
N1—C1	1.338 (3)	C16—H16	0.93
Cu—O2	1.9230 (18)	C17—C18	1.373 (5)
Cu—S2	2.2272 (7)	C17—H17	0.93
S1—C2	1.726 (2)	C18—C19	1.369 (5)
S2—C22	1.730 (2)	C18—H18	0.93
O2—C21	1.256 (3)	C19—C20	1.367 (5)
O3—C6	1.353 (3)	C19—H19	0.93
O3—C3	1.369 (3)	C20—H20	0.93
O4—C23	1.362 (3)	C21—C23	1.462 (3)
O4—C26	1.364 (4)	C23—C24	1.342 (4)

N1—C2	1.332 (3)	C24—C25	1.412 (4)
N2—C2	1.349 (3)	C24—H24	0.93
N2—C14	1.463 (3)	C25—C26	1.322 (5)
N2—C7	1.472 (3)	C25—H25	0.93
N3—C21	1.326 (3)	C26—H26	0.93
N3—C22	1.342 (3)	C27—C28	1.508 (3)
N4—C22	1.342 (3)	C27—H27A	0.97
N4—C34	1.470 (3)	C27—H27B	0.97
N4—C27	1.474 (3)	C28—C29	1.366 (4)
C1—C3	1.462 (3)	C28—C33	1.380 (4)
C3—C4	1.341 (3)	C29—C30	1.397 (4)
C4—C5	1.425 (4)	C29—H29	0.93
C4—H4	0.93	C30—C31	1.364 (5)
C5—C6	1.325 (4)	C30—H30	0.93
C5—H5	0.93	C31—C32	1.358 (5)
C6—H6	0.93	C31—H31	0.93
C7—C8	1.506 (3)	C32—C33	1.388 (4)
C7—H7A	0.97	C32—H32	0.93
C7—H7B	0.97	C33—H33	0.93
C8—C13	1.376 (3)	C34—C35	1.509 (3)
C8—C9	1.384 (3)	C34—H34A	0.97
C9—C10	1.379 (4)	C34—H34B	0.97
C9—H9	0.93	C35—C40	1.379 (4)
C10—C11	1.376 (4)	C35—C36	1.376 (3)
C10—H10	0.93	C36—C37	1.381 (4)
C11—C12	1.372 (4)	C36—H36	0.93
C11—H11	0.93	C37—C38	1.370 (5)
C12—C13	1.380 (4)	C37—H37	0.93
C12—H12	0.93	C38—C39	1.365 (5)
C13—H13	0.93	C38—H38	0.93
C14—C15	1.513 (4)	C39—C40	1.382 (5)
C14—H14A	0.97	C39—H39	0.93
C14—H14B	0.97	C40—H40	0.93
O2—Cu—O1	89.08 (7)	C16—C17—H17	119.9
O2—Cu—S1	163.52 (7)	C19—C18—C17	119.6 (3)
O1—Cu—S1	93.68 (5)	C19—C18—H18	120.2
O2—Cu—S2	94.35 (5)	C17—C18—H18	120.2
O1—Cu—S2	166.02 (6)	C18—C19—C20	120.4 (3)
S1—Cu—S2	86.86 (2)	C18—C19—H19	119.8
C22—S2—Cu	107.99 (8)	C20—C19—H19	119.8
C2—S1—Cu	108.45 (8)	C19—C20—C15	121.1 (3)
C1—O1—Cu	131.58 (15)	C19—C20—H20	119.4
C21—O2—Cu	130.97 (16)	C15—C20—H20	119.4
C6—O3—C3	106.3 (2)	O2—C21—N3	131.1 (2)
C23—O4—C26	105.7 (2)	O2—C21—C23	115.7 (2)
C2—N1—C1	124.29 (19)	N3—C21—C23	113.0 (2)
C2—N2—C14	122.62 (19)	N3—C22—N4	115.52 (19)

C2—N2—C7	122.24 (19)	N3—C22—S2	127.25 (17)
C14—N2—C7	114.91 (19)	N4—C22—S2	117.15 (17)
C21—N3—C22	125.4 (2)	C24—C23—O4	110.3 (2)
C22—N4—C34	124.03 (19)	C24—C23—C21	131.5 (2)
C22—N4—C27	122.60 (19)	O4—C23—C21	118.1 (2)
C34—N4—C27	113.32 (18)	C23—C24—C25	106.4 (3)
O1—C1—N1	130.5 (2)	C23—C24—H24	126.8
O1—C1—C3	116.3 (2)	C25—C24—H24	126.8
N1—C1—C3	113.16 (19)	C26—C25—C24	106.8 (3)
N1—C2—N2	116.5 (2)	C26—C25—H25	126.6
N1—C2—S1	128.01 (18)	C24—C25—H25	126.6
N2—C2—S1	115.40 (17)	C25—C26—O4	110.9 (3)
C4—C3—O3	109.6 (2)	C25—C26—H26	124.5
C4—C3—C1	133.4 (2)	O4—C26—H26	124.5
O3—C3—C1	116.99 (19)	N4—C27—C28	112.5 (2)
C3—C4—C5	106.7 (2)	N4—C27—H27A	109.1
C3—C4—H4	126.7	C28—C27—H27A	109.1
C5—C4—H4	126.7	N4—C27—H27B	109.1
C6—C5—C4	106.1 (2)	C28—C27—H27B	109.1
C6—C5—H5	126.9	H27A—C27—H27B	107.8
C4—C5—H5	126.9	C29—C28—C33	118.3 (3)
C5—C6—O3	111.3 (2)	C29—C28—C27	120.6 (2)
C5—C6—H6	124.4	C33—C28—C27	121.1 (2)
O3—C6—H6	124.4	C28—C29—C30	120.8 (3)
N2—C7—C8	114.41 (18)	C28—C29—H29	119.6
N2—C7—H7A	108.7	C30—C29—H29	119.6
C8—C7—H7A	108.7	C31—C30—C29	119.9 (3)
N2—C7—H7B	108.7	C31—C30—H30	120.1
C8—C7—H7B	108.7	C29—C30—H30	120.1
H7A—C7—H7B	107.6	C32—C31—C30	120.0 (3)
C13—C8—C9	118.8 (2)	C32—C31—H31	120
C13—C8—C7	120.5 (2)	C30—C31—H31	120
C9—C8—C7	120.6 (2)	C31—C32—C33	120.1 (3)
C10—C9—C8	121.0 (3)	C31—C32—H32	120
C10—C9—H9	119.5	C33—C32—H32	120
C8—C9—H9	119.5	C28—C33—C32	120.9 (3)
C11—C10—C9	119.4 (3)	C28—C33—H33	119.6
C11—C10—H10	120.3	C32—C33—H33	119.6
C9—C10—H10	120.3	N4—C34—C35	113.34 (19)
C12—C11—C10	120.3 (3)	N4—C34—H34A	108.9
C12—C11—H11	119.8	C35—C34—H34A	108.9
C10—C11—H11	119.8	N4—C34—H34B	108.9
C11—C12—C13	119.9 (3)	C35—C34—H34B	108.9
C11—C12—H12	120	H34A—C34—H34B	107.7
C13—C12—H12	120	C40—C35—C36	118.2 (3)
C12—C13—C8	120.6 (3)	C40—C35—C34	119.9 (2)
C12—C13—H13	119.7	C36—C35—C34	121.9 (2)
C8—C13—H13	119.7	C35—C36—C37	120.7 (3)

N2—C14—C15	115.0 (2)	C35—C36—H36	119.6
N2—C14—H14A	108.5	C37—C36—H36	119.6
C15—C14—H14A	108.5	C38—C37—C36	120.5 (3)
N2—C14—H14B	108.5	C38—C37—H37	119.7
C15—C14—H14B	108.5	C36—C37—H37	119.7
H14A—C14—H14B	107.5	C39—C38—C37	119.3 (3)
C16—C15—C20	118.2 (3)	C39—C38—H38	120.3
C16—C15—C14	123.7 (2)	C37—C38—H38	120.3
C20—C15—C14	118.1 (2)	C38—C39—C40	120.3 (3)
C15—C16—C17	120.5 (3)	C38—C39—H39	119.9
C15—C16—H16	119.8	C40—C39—H39	119.9
C17—C16—H16	119.8	C35—C40—C39	120.9 (3)
C18—C17—C16	120.2 (3)	C35—C40—H40	119.5
C18—C17—H17	119.9	C39—C40—H40	119.5

O2—Cu—S2—C22	−9.59 (11)	C15—C16—C17—C18	−0.6 (4)
O1—Cu—S2—C22	94.2 (2)	C16—C17—C18—C19	−0.7 (5)
S1—Cu—S2—C22	−173.12 (9)	C17—C18—C19—C20	1.1 (5)
O2—Cu—S1—C2	89.5 (2)	C18—C19—C20—C15	−0.3 (5)
O1—Cu—S1—C2	−9.81 (11)	C16—C15—C20—C19	−0.9 (4)
S2—Cu—S1—C2	−175.82 (9)	C14—C15—C20—C19	179.6 (3)
O2—Cu—O1—C1	−168.3 (2)	Cu—O2—C21—N3	13.8 (4)
S1—Cu—O1—C1	−4.5 (2)	Cu—O2—C21—C23	−170.15 (19)
S2—Cu—O1—C1	87.3 (3)	C22—N3—C21—O2	−6.4 (4)
O1—Cu—O2—C21	−169.5 (3)	C22—N3—C21—C23	177.5 (2)
S1—Cu—O2—C21	90.5 (3)	C21—N3—C22—N4	170.6 (2)
S2—Cu—O2—C21	−3.1 (3)	C21—N3—C22—S2	−12.8 (4)
Cu—O1—C1—N1	16.9 (4)	C34—N4—C22—N3	175.0 (2)
Cu—O1—C1—C3	−166.58 (16)	C27—N4—C22—N3	−2.1 (3)
C2—N1—C1—O1	−8.8 (4)	C34—N4—C22—S2	−1.9 (3)
C2—N1—C1—C3	174.5 (2)	C27—N4—C22—S2	−179.00 (17)
C1—N1—C2—N2	171.5 (2)	Cu—S2—C22—N3	18.8 (2)
C1—N1—C2—S1	−12.3 (3)	Cu—S2—C22—N4	−164.70 (15)
C14—N2—C2—N1	178.3 (2)	C26—O4—C23—C24	−0.7 (3)
C7—N2—C2—N1	4.1 (3)	C26—O4—C23—C21	−177.1 (3)
C14—N2—C2—S1	1.6 (3)	O2—C21—C23—C24	−172.0 (3)
C7—N2—C2—S1	−172.62 (16)	N3—C21—C23—C24	4.8 (4)
Cu—S1—C2—N1	19.6 (2)	O2—C21—C23—O4	3.4 (4)
Cu—S1—C2—N2	−164.11 (15)	N3—C21—C23—O4	−179.8 (2)
C6—O3—C3—C4	0.4 (3)	O4—C23—C24—C25	0.4 (4)
C6—O3—C3—C1	180.0 (2)	C21—C23—C24—C25	176.1 (3)
O1—C1—C3—C4	−176.3 (3)	C23—C24—C25—C26	0.1 (4)
N1—C1—C3—C4	0.8 (4)	C24—C25—C26—O4	−0.5 (5)
O1—C1—C3—O3	4.2 (3)	C23—O4—C26—C25	0.8 (4)
N1—C1—C3—O3	−178.7 (2)	C22—N4—C27—C28	103.0 (3)
O3—C3—C4—C5	−0.8 (3)	C34—N4—C27—C28	−74.3 (3)
C1—C3—C4—C5	179.7 (3)	N4—C27—C28—C29	−56.7 (3)
C3—C4—C5—C6	0.9 (3)	N4—C27—C28—C33	124.3 (3)

C4—C5—C6—O3	−0.7 (4)	C33—C28—C29—C30	−0.3 (5)
C3—O3—C6—C5	0.2 (3)	C27—C28—C29—C30	−179.4 (3)
C2—N2—C7—C8	−109.9 (2)	C28—C29—C30—C31	0.7 (6)
C14—N2—C7—C8	75.5 (3)	C29—C30—C31—C32	−0.4 (6)
N2—C7—C8—C13	−112.8 (3)	C30—C31—C32—C33	−0.4 (6)
N2—C7—C8—C9	71.2 (3)	C29—C28—C33—C32	−0.4 (5)
C13—C8—C9—C10	−0.4 (4)	C27—C28—C33—C32	178.6 (3)
C7—C8—C9—C10	175.6 (2)	C31—C32—C33—C28	0.8 (5)
C8—C9—C10—C11	−0.1 (4)	C22—N4—C34—C35	101.4 (3)
C9—C10—C11—C12	0.5 (5)	C27—N4—C34—C35	−81.2 (2)
C10—C11—C12—C13	−0.4 (5)	N4—C34—C35—C40	114.7 (3)
C11—C12—C13—C8	−0.1 (4)	N4—C34—C35—C36	−66.7 (3)
C9—C8—C13—C12	0.5 (4)	C40—C35—C36—C37	−0.5 (4)
C7—C8—C13—C12	−175.5 (2)	C34—C35—C36—C37	−179.1 (3)
C2—N2—C14—C15	−84.6 (3)	C35—C36—C37—C38	0.6 (5)
C7—N2—C14—C15	89.9 (2)	C36—C37—C38—C39	−0.5 (6)
N2—C14—C15—C16	5.7 (3)	C37—C38—C39—C40	0.3 (6)
N2—C14—C15—C20	−174.8 (2)	C36—C35—C40—C39	0.2 (5)
C20—C15—C16—C17	1.4 (4)	C34—C35—C40—C39	178.9 (3)
C14—C15—C16—C17	−179.1 (2)	C38—C39—C40—C35	−0.2 (5)