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1-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thioureidothiourea monohydrate

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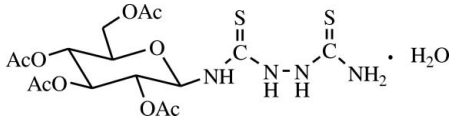
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.055; wR factor = 0.141; data-to-parameter ratio = 12.2.

In the title compound, $C_{16}H_{24}N_4O_9S_2\cdot H_2O$, the hexopyranosyl ring adopts a chair conformation ($^4C_1$), and the five substituents are in equatorial positions. In the crystal structure, extensive O—H···O, N—H···S and N—H···O hydrogen bonding leads to the formation of a three-dimensional network.

Related literature

For cycloaddition and nucleophilic addition, see: Pearson *et al.* (2003); Reitz *et al.* (1989). For the crystal structure of glycosyl isothiosyanate, see: Jiang *et al.* (2003). For the crystal structures of glycosyl isothiosyanate methanol and ethanol derivatives, see: Zhang *et al.* (2001).



Experimental

Crystal data

$C_{16}H_{24}N_4O_9S_2\cdot H_2O$
M_r = 498.53
Monoclinic, $C2$
a = 22.286 (2) Å
b = 7.2005 (7) Å
c = 15.8772 (17) Å
β = 110.119 (2)°
V = 2392.3 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 293 (2) K
0.45 × 0.22 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
6322 measured reflections
3525 independent reflections
3021 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.141
S = 1.07
3525 reflections
289 parameters
7 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Absolute structure: Flack (1983), 1229 Friedel pairs
Flack parameter: −0.16 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H10···O5^{i}	0.87	2.64	3.382 (11)	146
O1W—H20···O9^{ii}	0.87	2.56	3.181 (9)	129
N1—H1A···S2^{iii}	0.86	2.62	3.400 (4)	151
N2—H2A···O3^{iv}	0.86	2.09	2.856 (5)	147
N3—H3A···O1W^{v}	0.86	2.13	2.973 (9)	167
N4—H4B···O1W^{vi}	0.86	2.43	3.244 (9)	159
N4—H4C···O1^{iii}	0.86	2.49	3.323 (5)	164

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

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); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2088).

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supporting information

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1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-3-thioureidothiourea monohydrate

Weidong Sun, Jin Yao, Lifei Bai and Xiaoming Wang

S1. Comment

Over the past decade, many organic chemists have been engaged in the synthesis of glycosyl isothiosyanates and its derivatives. These compound are versatile reagents in organic synthesis and easily undergo many important reactions, such as cycloaddition (Pearson *et al.*, 2003) and nucleophilic addition (Reitz *et al.*, 1989). Recently, the crystal structures of glycosyl isothiosyanate (Jiang *et al.*, 2003) and the methanol and ethanol derivatives (Zhang *et al.*, 2001) have been reported. However, other derivatives of glycosyl isothiosyanate are still rare. Here we report on the synthesis of a new thiosemicarbazide derivative of glycosyl isothiosyanate, 2,3,4,6-tetra-*O*-acetyl- *β*-*D*-glucopyranosyl dithiourea, (I).

The molecular structure of compound (I) is illustrated in Fig. 1. The hexopyranosyl ring adopts a chair conformation ($^4C_1$), and the four substituents are in equatorial positions.

In the crystal extensive O—H···O, N—H···S and N—H···O hydrogen bonding (Table 1) leads to the formation of a three-dimensional network.

S2. Experimental

Compound (I) was prepared by refluxing together equimolar amounts of *β*-*D*-2,3,4,6-tetra-*O*- acetyl-glucopyranosyl isothiocyanate and thiosemicarbazide. After cooling to room temperature, water was added to the mixture and compound (I) was isolated as a white solid. Crystals, suitable for X-ray analysis, were grown from an ethyl acetate and acetonitrile (1:1 / v:v) solution by slow evaporation at room temperature.

S3. Refinement

The compound has a known chiral center [the Flack parameter is -0.16 (12) (Flack, 1983)], and for this reason the Friedel pairs were not merged. The water H-atoms were located in the difference Fourier maps and refined with distance restraintes, O-H = 0.87 (2) Å. The N- and C-bound H-atoms were placed in calculated positions and treated as riding atoms: N—H = 0.86 Å, C—H = 0.96 - 0.98 Å, with U_{iso}(H) = 1.2 or 1.5U_{eq}(parent N- or C-atom).

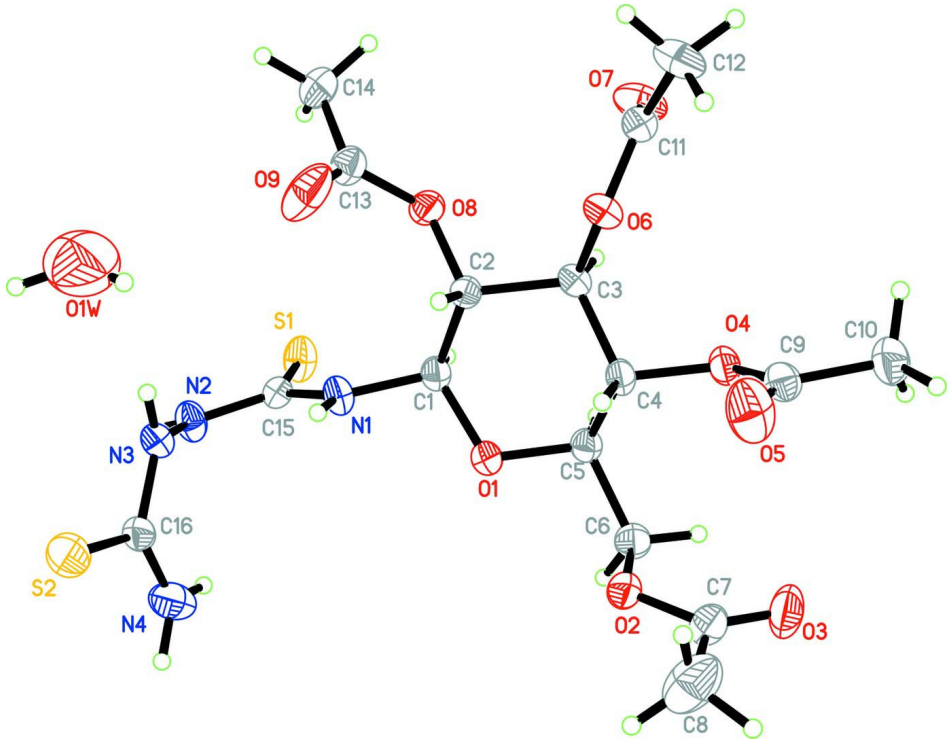

Figure 1

A view of the molecular structure of compound (I), showing the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-3-thioureidothiourea monohydrate

Crystal data

$C_{16}H_{24}N_4O_9S_2{\cdot}H_2O$
$M_r = 498.53$
Monoclinic, *C*2
Hall symbol: C 2y
$a = 22.286\ (2)$ Å
$b = 7.2005\ (7)$ Å
$c = 15.8772\ (17)$ Å
$\beta = 110.119\ (2)°$
$V = 2392.3\ (4)$ Å^3
$Z = 4$
$F(000) = 1048$
$D_x = 1.384$ Mg m^{-3}
Melting point: not measured K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7141 reflections
$\theta = 1.4$–$27.7°$
$\mu = 0.28$ mm^{-1}
$T = 293$ K
Block, colorless
0.45 × 0.22 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ scans, and ω scans
6322 measured reflections
3525 independent reflections
3021 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.4°$
$h = -25\rightarrow26$
$k = -8\rightarrow8$
$l = -18\rightarrow11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.141$
$S = 1.07$
3525 reflections
289 parameters
7 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
$w = 1/[\sigma^2(F_o^2) + (0.0808P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: Flack (1983), 1229 Friedel pairs
Absolute structure parameter: −0.16 (12)

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}
O1W	0.0457 (4)	0.2431 (10)	0.3624 (6)	0.193 (3)
H10	0.0696	0.2068	0.3324	0.232*
H20	0.0081	0.1989	0.3326	0.232*
S1	1.01347 (6)	0.9344 (2)	0.17559 (9)	0.0605 (4)
S2	1.09337 (7)	0.5527 (2)	0.56716 (9)	0.0720 (5)
O1	0.87014 (12)	0.9697 (4)	0.28332 (19)	0.0433 (7)
O2	0.79211 (13)	1.1140 (5)	0.37749 (19)	0.0493 (8)
O3	0.69458 (16)	1.2284 (7)	0.3502 (3)	0.0796 (12)
O4	0.69663 (12)	0.9277 (5)	0.18084 (19)	0.0467 (7)
O5	0.67103 (18)	0.7887 (8)	0.2901 (3)	0.0880 (14)
O6	0.73828 (13)	0.5785 (4)	0.14481 (18)	0.0455 (7)
O7	0.71021 (18)	0.5906 (6)	−0.0050 (2)	0.0732 (11)
O8	0.86480 (13)	0.5944 (4)	0.12682 (18)	0.0464 (7)
O9	0.9131 (2)	0.3601 (6)	0.2159 (3)	0.0902 (14)
N1	0.95480 (15)	0.7892 (5)	0.2819 (2)	0.0427 (9)
H1A	0.9581	0.7239	0.3287	0.051*
N2	1.06247 (16)	0.7629 (6)	0.3289 (2)	0.0490 (10)
H2A	1.0987	0.7961	0.3256	0.059*
N3	1.06233 (17)	0.6483 (6)	0.3986 (2)	0.0496 (10)
H3A	1.0510	0.5342	0.3874	0.060*
N4	1.0852 (2)	0.8905 (7)	0.4975 (3)	0.0695 (13)
H4B	1.0779	0.9645	0.4526	0.083*
H4C	1.0960	0.9345	0.5510	0.083*

C1	0.89174 (18)	0.8500 (6)	0.2278 (3)	0.0396 (10)
H1B	0.8940	0.9195	0.1759	0.047*
C2	0.84790 (19)	0.6840 (6)	0.1959 (3)	0.0387 (10)
H2B	0.8538	0.5977	0.2459	0.046*
C3	0.77758 (18)	0.7409 (6)	0.1562 (3)	0.0387 (10)
H3B	0.7693	0.8028	0.0983	0.046*
C4	0.76213 (18)	0.8694 (6)	0.2203 (3)	0.0396 (10)
H4A	0.7681	0.8044	0.2768	0.047*
C5	0.8067 (2)	1.0374 (6)	0.2378 (3)	0.0423 (10)
H5A	0.8048	1.0902	0.1800	0.051*
C6	0.7926 (2)	1.1884 (7)	0.2936 (3)	0.0487 (11)
H6A	0.8249	1.2848	0.3050	0.058*
H6B	0.7514	1.2436	0.2612	0.058*
C7	0.7401 (3)	1.1452 (8)	0.3977 (4)	0.0586 (13)
C8	0.7464 (4)	1.0653 (12)	0.4877 (5)	0.102 (2)
H8A	0.7080	1.0891	0.5004	0.153*
H8B	0.7820	1.1220	0.5331	0.153*
H8C	0.7532	0.9337	0.4872	0.153*
C9	0.6553 (2)	0.8752 (8)	0.2213 (4)	0.0534 (12)
C10	0.5887 (2)	0.9374 (11)	0.1689 (4)	0.0745 (16)
H10A	0.5601	0.8955	0.1984	0.112*
H10B	0.5758	0.8859	0.1096	0.112*
H10C	0.5874	1.0705	0.1653	0.112*
C11	0.7051 (2)	0.5239 (7)	0.0609 (3)	0.0499 (12)
C12	0.6616 (3)	0.3661 (9)	0.0615 (4)	0.0735 (17)
H12A	0.6389	0.3273	0.0011	0.110*
H12B	0.6316	0.4054	0.0892	0.110*
H12C	0.6864	0.2642	0.0948	0.110*
C13	0.8985 (2)	0.4365 (7)	0.1448 (3)	0.0495 (11)
C14	0.9150 (2)	0.3741 (8)	0.0673 (4)	0.0643 (14)
H14A	0.9387	0.2602	0.0819	0.096*
H14B	0.9405	0.4672	0.0523	0.096*
H14C	0.8765	0.3543	0.0170	0.096*
C15	1.00857 (19)	0.8254 (6)	0.2658 (3)	0.0418 (10)
C16	1.0796 (2)	0.7105 (7)	0.4844 (3)	0.0495 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1W	0.265 (7)	0.099 (4)	0.166 (5)	0.007 (5)	0.012 (5)	−0.014 (4)
S1	0.0520 (7)	0.0731 (9)	0.0629 (8)	0.0127 (7)	0.0280 (6)	0.0215 (7)
S2	0.0840 (10)	0.0872 (11)	0.0403 (7)	0.0242 (8)	0.0154 (6)	0.0036 (7)
O1	0.0333 (14)	0.0484 (18)	0.0460 (17)	−0.0008 (13)	0.0109 (13)	−0.0055 (14)
O2	0.0468 (17)	0.053 (2)	0.0451 (18)	0.0115 (15)	0.0115 (14)	−0.0022 (15)
O3	0.050 (2)	0.104 (3)	0.088 (3)	0.024 (2)	0.029 (2)	0.003 (3)
O4	0.0344 (14)	0.0564 (19)	0.0471 (17)	0.0005 (15)	0.0112 (13)	−0.0011 (16)
O5	0.062 (2)	0.121 (4)	0.089 (3)	−0.011 (2)	0.036 (2)	0.022 (3)
O6	0.0445 (16)	0.0522 (19)	0.0344 (15)	−0.0082 (15)	0.0066 (13)	−0.0036 (14)

O7	0.092 (3)	0.079 (3)	0.0369 (19)	−0.017 (2)	0.0069 (18)	−0.0039 (19)
O8	0.0526 (17)	0.0488 (18)	0.0352 (15)	0.0105 (16)	0.0118 (13)	−0.0008 (14)
O9	0.132 (4)	0.073 (3)	0.081 (3)	0.047 (3)	0.056 (3)	0.023 (2)
N1	0.0352 (18)	0.051 (2)	0.041 (2)	0.0027 (17)	0.0117 (15)	0.0089 (17)
N2	0.0342 (19)	0.069 (3)	0.044 (2)	0.0034 (18)	0.0148 (17)	0.008 (2)
N3	0.046 (2)	0.052 (2)	0.040 (2)	0.0041 (18)	0.0019 (17)	−0.0040 (18)
N4	0.079 (3)	0.073 (3)	0.051 (3)	−0.007 (2)	0.016 (2)	−0.015 (2)
C1	0.038 (2)	0.042 (2)	0.039 (2)	0.0045 (19)	0.0128 (18)	0.0030 (19)
C2	0.041 (2)	0.047 (2)	0.028 (2)	0.0074 (19)	0.0111 (18)	0.0022 (18)
C3	0.036 (2)	0.044 (2)	0.033 (2)	−0.001 (2)	0.0078 (17)	0.0021 (19)
C4	0.031 (2)	0.051 (3)	0.035 (2)	0.0046 (19)	0.0101 (17)	0.0036 (19)
C5	0.042 (2)	0.042 (2)	0.041 (2)	0.001 (2)	0.0108 (19)	0.000 (2)
C6	0.049 (3)	0.041 (3)	0.056 (3)	−0.004 (2)	0.017 (2)	−0.002 (2)
C7	0.059 (3)	0.057 (3)	0.065 (3)	0.003 (3)	0.028 (3)	−0.008 (3)
C8	0.145 (6)	0.096 (5)	0.087 (5)	0.033 (5)	0.068 (4)	0.017 (4)
C9	0.044 (3)	0.060 (3)	0.059 (3)	−0.012 (2)	0.021 (2)	−0.012 (3)
C10	0.041 (3)	0.103 (5)	0.080 (4)	−0.006 (3)	0.022 (3)	−0.016 (4)
C11	0.046 (3)	0.052 (3)	0.045 (3)	0.003 (2)	0.007 (2)	−0.009 (2)
C12	0.068 (3)	0.075 (4)	0.062 (3)	−0.022 (3)	0.003 (3)	−0.018 (3)
C13	0.054 (3)	0.046 (3)	0.047 (3)	0.006 (2)	0.016 (2)	0.006 (3)
C14	0.062 (3)	0.067 (4)	0.070 (3)	0.014 (3)	0.031 (3)	−0.008 (3)
C15	0.037 (2)	0.045 (3)	0.043 (2)	0.007 (2)	0.0136 (19)	−0.005 (2)
C16	0.034 (2)	0.066 (3)	0.045 (3)	0.009 (2)	0.010 (2)	−0.011 (2)

Geometric parameters (Å, º)

O1W—H10	0.868 (10)	C1—C2	1.516 (6)
O1W—H20	0.867 (8)	C1—H1B	0.9800
S1—C15	1.669 (5)	C2—C3	1.530 (5)
S2—C16	1.684 (5)	C2—H2B	0.9800
O1—C1	1.430 (5)	C3—C4	1.501 (6)
O1—C5	1.434 (5)	C3—H3B	0.9800
O2—C7	1.324 (6)	C4—C5	1.528 (6)
O2—C6	1.439 (6)	C4—H4A	0.9800
O3—C7	1.196 (6)	C5—C6	1.503 (6)
O4—C9	1.345 (6)	C5—H5A	0.9800
O4—C4	1.439 (5)	C6—H6A	0.9700
O5—C9	1.200 (6)	C6—H6B	0.9700
O6—C11	1.342 (5)	C7—C8	1.501 (9)
O6—C3	1.435 (5)	C8—H8A	0.9600
O7—C11	1.192 (6)	C8—H8B	0.9600
O8—C13	1.338 (6)	C8—H8C	0.9600
O8—C2	1.430 (5)	C9—C10	1.500 (7)
O9—C13	1.195 (6)	C10—H10A	0.9600
N1—C15	1.335 (5)	C10—H10B	0.9600
N1—C1	1.440 (5)	C10—H10C	0.9600
N1—H1A	0.8600	C11—C12	1.496 (8)
N2—C15	1.349 (5)	C12—H12A	0.9600

N2—N3	1.382 (5)	C12—H12B	0.9600
N2—H2A	0.8600	C12—H12C	0.9600
N3—C16	1.358 (6)	C13—C14	1.471 (7)
N3—H3A	0.8600	C14—H14A	0.9600
N4—C16	1.312 (7)	C14—H14B	0.9600
N4—H4B	0.8600	C14—H14C	0.9600
N4—H4C	0.8600		

H10—O1W—H20	104.6 (8)	O2—C6—C5	110.3 (4)
C1—O1—C5	112.1 (3)	O2—C6—H6A	109.6
C7—O2—C6	116.6 (4)	C5—C6—H6A	109.6
C9—O4—C4	117.9 (4)	O2—C6—H6B	109.6
C11—O6—C3	117.9 (3)	C5—C6—H6B	109.6
C13—O8—C2	119.8 (3)	H6A—C6—H6B	108.1
C15—N1—C1	125.6 (4)	O3—C7—O2	123.8 (5)
C15—N1—H1A	117.2	O3—C7—C8	124.9 (5)
C1—N1—H1A	117.2	O2—C7—C8	111.3 (5)
C15—N2—N3	123.2 (4)	C7—C8—H8A	109.5
C15—N2—H2A	118.4	C7—C8—H8B	109.5
N3—N2—H2A	118.4	H8A—C8—H8B	109.5
C16—N3—N2	121.9 (4)	C7—C8—H8C	109.5
C16—N3—H3A	119.0	H8A—C8—H8C	109.5
N2—N3—H3A	119.0	H8B—C8—H8C	109.5
C16—N4—H4B	120.0	O5—C9—O4	123.2 (5)
C16—N4—H4C	120.0	O5—C9—C10	125.6 (5)
H4B—N4—H4C	120.0	O4—C9—C10	111.2 (5)
O1—C1—N1	106.4 (3)	C9—C10—H10A	109.5
O1—C1—C2	111.5 (3)	C9—C10—H10B	109.5
N1—C1—C2	110.1 (4)	H10A—C10—H10B	109.5
O1—C1—H1B	109.6	C9—C10—H10C	109.5
N1—C1—H1B	109.6	H10A—C10—H10C	109.5
C2—C1—H1B	109.6	H10B—C10—H10C	109.5
O8—C2—C1	107.6 (3)	O7—C11—O6	124.5 (4)
O8—C2—C3	107.9 (3)	O7—C11—C12	124.8 (5)
C1—C2—C3	112.2 (3)	O6—C11—C12	110.7 (4)
O8—C2—H2B	109.7	C11—C12—H12A	109.5
C1—C2—H2B	109.7	C11—C12—H12B	109.5
C3—C2—H2B	109.7	H12A—C12—H12B	109.5
O6—C3—C4	108.4 (3)	C11—C12—H12C	109.5
O6—C3—C2	109.1 (3)	H12A—C12—H12C	109.5
C4—C3—C2	109.1 (3)	H12B—C12—H12C	109.5
O6—C3—H3B	110.1	O9—C13—O8	122.9 (4)
C4—C3—H3B	110.1	O9—C13—C14	125.8 (5)
C2—C3—H3B	110.1	O8—C13—C14	111.4 (4)
O4—C4—C3	108.7 (3)	C13—C14—H14A	109.5
O4—C4—C5	110.3 (3)	C13—C14—H14B	109.5
C3—C4—C5	109.0 (3)	H14A—C14—H14B	109.5
O4—C4—H4A	109.7	C13—C14—H14C	109.5

C3—C4—H4A	109.7	H14A—C14—H14C	109.5
C5—C4—H4A	109.7	H14B—C14—H14C	109.5
O1—C5—C6	108.5 (3)	N1—C15—N2	114.9 (4)
O1—C5—C4	106.8 (3)	N1—C15—S1	125.8 (3)
C6—C5—C4	115.2 (4)	N2—C15—S1	119.3 (3)
O1—C5—H5A	108.7	N4—C16—N3	117.6 (5)
C6—C5—H5A	108.7	N4—C16—S2	124.1 (4)
C4—C5—H5A	108.7	N3—C16—S2	118.2 (4)
C15—N2—N3—C16	−107.9 (5)	C1—O1—C5—C6	−169.4 (3)
C5—O1—C1—N1	−178.7 (3)	C1—O1—C5—C4	65.9 (4)
C5—O1—C1—C2	−58.6 (4)	O4—C4—C5—O1	175.5 (3)
C15—N1—C1—O1	−116.8 (4)	C3—C4—C5—O1	−65.3 (4)
C15—N1—C1—C2	122.3 (5)	O4—C4—C5—C6	54.9 (5)
C13—O8—C2—C1	103.9 (4)	C3—C4—C5—C6	174.1 (4)
C13—O8—C2—C3	−134.9 (4)	C7—O2—C6—C5	−125.6 (4)
O1—C1—C2—O8	168.0 (3)	O1—C5—C6—O2	−64.5 (4)
N1—C1—C2—O8	−74.2 (4)	C4—C5—C6—O2	55.1 (5)
O1—C1—C2—C3	49.5 (4)	C6—O2—C7—O3	0.8 (7)
N1—C1—C2—C3	167.3 (3)	C6—O2—C7—C8	−178.4 (5)
C11—O6—C3—C4	129.2 (4)	C4—O4—C9—O5	2.9 (7)
C11—O6—C3—C2	−112.1 (4)	C4—O4—C9—C10	−176.6 (4)
O8—C2—C3—O6	73.5 (4)	C3—O6—C11—O7	7.1 (7)
C1—C2—C3—O6	−168.1 (3)	C3—O6—C11—C12	−173.9 (4)
O8—C2—C3—C4	−168.2 (3)	C2—O8—C13—O9	3.6 (7)
C1—C2—C3—C4	−49.9 (4)	C2—O8—C13—C14	−175.8 (4)
C9—O4—C4—C3	115.1 (4)	C1—N1—C15—N2	176.3 (4)
C9—O4—C4—C5	−125.6 (4)	C1—N1—C15—S1	−5.0 (7)
O6—C3—C4—O4	−63.5 (4)	N3—N2—C15—N1	8.6 (6)
C2—C3—C4—O4	177.8 (3)	N3—N2—C15—S1	−170.2 (3)
O6—C3—C4—C5	176.4 (3)	N2—N3—C16—N4	12.4 (7)
C2—C3—C4—C5	57.7 (4)	N2—N3—C16—S2	−166.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H10···O5^{i}	0.868 (10)	2.637 (4)	3.382 (11)	144.5 (5)
O1*W*—H20···O9^{ii}	0.867 (8)	2.563 (4)	3.181 (9)	129.1 (5)
N1—H1*A*···S2^{iii}	0.86	2.62	3.400 (4)	151
N2—H2*A*···O3^{iv}	0.86	2.09	2.856 (5)	147
N3—H3*A*···O1*W*^{v}	0.86	2.13	2.973 (9)	167
N4—H4*B*···O1*W*^{vi}	0.86	2.43	3.244 (9)	159
N4—H4*C*···O1^{iii}	0.86	2.49	3.323 (5)	164

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