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N-(4-Methylpiperazin-4-ium-1-yl)dithiocarbamate sesquihydrate

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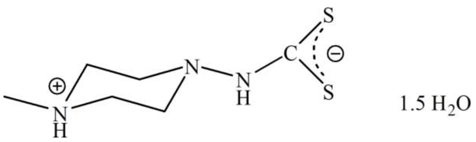
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.041; wR factor = 0.113; data-to-parameter ratio = 14.5.

In the crystal structure of the title compound, $C_6H_{13}N_3S_2\cdot1.5H_2O$, weak N—H⋯S interactions between the zwitterionic molecules are observed, leading to an extensively folded layered arrangement parallel to (100). There are three crystallographically independent water molecules in the asymmetric unit, which are disordered and only half occupied.

Related literature

For the synthesis and structures of a series of $^{-}S_2CNR$-type zwitterionic dithiocarbamic acids, see: Schramm *et al.* (1984) for R = $C_3H_6NH^+(Me)_2$; Kokkou *et al.* (1988) for R = $C_3H_6NH^+(Et)_2$ and R=$C_2H_4NH^+(Et)_2$; Stergioudis *et al.* (1989) for R=$C_2H_4NH^+(Me)_2$; Yamin *et al.* (2002) for R=$C_2H_4NH_3^+$. For structures of dithiocarbamates incorporating a hydrazine-based skeleton, see: Braibanti *et al.* (1969); Mattes & Füsser (1984); Kiel *et al.* (1985). For the synthesis of dithiocarbamates, see: Coucouvanis (1979); Hogarth (2005); Eul *et al.* (1987); Hulanicki (1967); Ivanov *et al.* (1999). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$C_6H_{13}N_3S_2\cdot1.5H_2O$
M_r = 218.34
Monoclinic, $C2/c$
a = 23.3560 (18) Å
b = 6.8191 (3) Å
c = 15.7067 (10) Å
β = 119.920 (9)°
V = 2168.2 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.46 mm^{-1}
T = 120 K
0.48 × 0.23 × 0.21 mm

Data collection

Kuma KM-4-CCD Sapphire2 diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2008)
$T_{\min}$ = 0.952, $T_{\max}$ = 1
3755 measured reflections
2024 independent reflections
1674 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.113
S = 1.08
2024 reflections
140 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.60 e Å^{-3}
$\Delta\rho_{\min}$ = −0.21 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N⋯S2^{i}	0.80 (3)	2.60 (3)	3.375 (2)	164 (2)
N3—H3N⋯S1^{ii}	0.76 (2)	2.67 (2)	3.3131 (18)	143 (2)
N3—H3N⋯S2^{ii}	0.76 (2)	2.67 (2)	3.2846 (18)	140 (2)

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2008); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (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: NC2276).

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supplementary materials

Acta Cryst. (2012). E**68**, o1717   [doi:10.1107/S1600536812020521]

N-(4-Methylpiperazin-4-ium-1-yl)dithiocarbamate sesquihydrate

Anna Mietlarek-Kropidłowska, Jarosław Chojnacki, Paweł Wityk, Miłosz Wieczór and Barbara Becker

Comment

During our work on the synthesis of organic molecules which may serve as building blocks of more complex structures (*e.g.* coordination compounds) we have focused on dithiocarbamates. These are known to be versatile ligands (Coucouvanis, 1979; Hogarth, 2005) easily bonding to metal soft centres, as well as to be potentially useful chemotherapeutics, pesti- and fungicides (Hulanicki, 1967; Ivanov *et al.*, 1999). Dithiocarbamates (dtc) are amongst the most frequently used bidentate sulfur ligands. More than 2500 compounds with at least one such dtc group can be found in the Cambridge Structural Database (Version 5.33, Nov. 2011, updated to Feb. 2012; Allen, 2002). However, the number of structurally characterized dithiocarbamic acids (invariably present in a form of zwitterionic species) is surprisingly small. These include compounds of ^-S_2CNR type with $R = C_3H_6NH^+(Me)_2$ (Schramm *et al.*, 1984), $R = C_3H_6NH^+(Et)_2$ and $R{=}C_2H_4NH^+(Et)_2$ (Kokkou *et al.*, 1988), $R{=}C_2H_4NH^+(Me)_2$ (Stergioudis *et al.*, 1989), $R{=}C_2H_4NH_3^+$ (Yamin *et al.*, 2002) and *N*-acetimidoyl dithiocarbamic acid (Eul *et al.*, 1987). Here we describe the structure of new, 1-(4*H*,4-methylpiperazinium)dithiocarbamate sesquihydrate, the first zwitterionic species with N—N bond. The only other structurally characterized dithiocarbamates incorporating hydrazine-based skeleton are salts with potassium (Mattes & Füsser, 1984; Kiel *et al.*, 1985) or hydrazinium (Braibanti *et al.*, 1969) cations.

There are no significant differences in NCS_2 group geometry compared to other compounds of this type. The notable feature of the title compound is the presence of the intermolecular interactions (Table 1). Eeach molecule of the title compound serves to its close neighbors as a hydrogen bond donor (*via* N—H groups) and acceptor (*via* S atoms, see Figure 2). As a result, all of the NH-groups are engaged in the formation of the network of N—H···S interactions between the pairs of antiparallel chains what leads to the extensively folded layered arrangement observed within the crystal. Additional water molecules are present in vicinity of the twofold axis and are disordered (see experimental refinement section for details).

Experimental

A stoichiometric amount (0.325 g, 0.26 cm^3) of carbon disulfide, CS_2, was added dropwise to a methanol/H_2O (10:1, *v*/*v*) solution containing 0.5 g (0.52 cm^3) 1-amino-4-methylpiperazine and 0.24 g potassium hydroxide. The mixture had been stirred for *ca* 25 min until a white precipitate appeared. The clear filtrate was then left at temperature of 5°C for crystallization. After 5 days, well shaped, colorless needle-like crystals suitable for X-ray analysis were collected. Then, the mother liquor was concentrated and after few days more product was isolated. The overall yield was *ca* 50%. The presence of O—H groups was confirmed by FTIR analysis of single crystals taken from the mother liquor using Mattson Genesis II Gold spectrometer equipped with Momentum Microscope as detector (a broad maximum of absorption at 3434 cm^{-1} together with a sharp one at 3239 cm^{-1}). However, the product, when taken from the mother liquor and dried using the filter paper, changes - becomes at first opaque and finally takes the form of a powder (most probably because of the removal of the solvent molecules). The microanalysis of such product was also conducted using Vario El Cube CHNS, Elementar (found: %H 6.55, %N 17.04, %C 29.82; calc. for $C_6H_{13}N_3S_2.1.5H_2O$: %H 7.38, %N 19.24, %C 33.00). The melting point for the title compound (for 10 °/min heating rate) was determined to be 129°C.

Refinement

All C—H atoms were placed in calculated positions (methyl H atoms allowed to rotate but not to tip) and refined as riding on their carrier atoms with respective bond lengths and U_{iso}(H) values: C—H = 0.96 Å (CH_3) and U_{iso}(H) = 1.5 U_{eq}(C), C—H = 0.97 Å (CH_2) and U_{iso}(H) = 1.2 U_{eq}(C). Refirement of N—H was carried out withouth restrains.

After refinement of the zwitterionic molecule three electron density peaks are observed that were assigned to three disordered and half-occupied oxygen atoms with distances O1—O2 and O2—O3 2.734 (5) and 2.845 (5) Å, respectively. The symmetry equivalent atoms constitute the second disorder part. The connectivity table was adjusted by using PART -1 *SHELX* instruction to avoid creating bonds to symmetry equivalent oxygen atoms (generated by the twofold axis). Hydrogen atoms bound to O1 and O2 are directed towards acceptor atoms and could have been found and refined as restrained. Positions of H3C and H3D hydrogen atoms were restrained to target 0.85 (2) Å O—H bond lengths and to 1.300 Å H3C—H3D distance to maintain proper H—O—H valence angle.

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2008); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2008); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia,1997) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

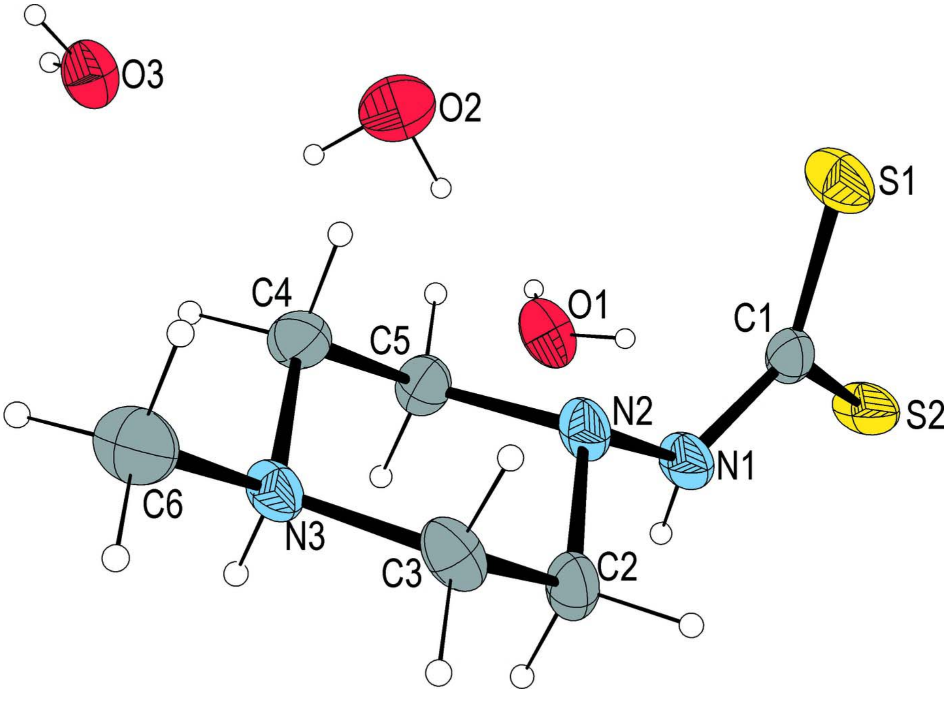

Figure 1

Molecular structure and atom-numbering scheme for the title compound with displacement ellipsoids drawn at 50% probability level. H atoms are represented as arbitrary circles. Only one set of disordered half-occupied water molecules is shown for clarity.

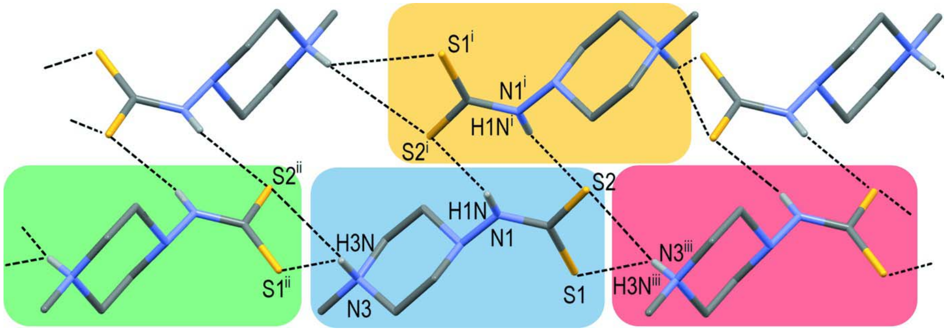

Figure 2

Hydrogen bond network within the crystal of $C_6N_3H_{13}S_2$×$1.5H_2O$. Dashed lines denote the assumed N—H···S hydrogen bonds. Water molecules are omitted for clarity. [Symmetry codes: (i) 1/2-*x*, 1.5-*y*, 2-*z*; (ii) *x*, 1-*y*, -1/2+*z*); (iii) *x*, 1-*y*, 1/2+*z*.]

N-(4-Methylpiperazin-4-ium-1-yl)dithiocarbamate sesquihydrate

Crystal data

$C_6H_{13}N_3S_2 \cdot 1.5H_2O$
$M_r = 218.34$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 23.3560$ (18) Å
$b = 6.8191$ (3) Å
$c = 15.7067$ (10) Å
$\beta = 119.920$ (9)°
$V = 2168.2$ (2) Å^3
$Z = 8$

$F(000) = 936$
$D_x = 1.338$ Mg m^{-3}
Melting point: 402 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2050 reflections
$\theta = 2.6$–28.7°
$\mu = 0.46$ mm^{-1}
$T = 120$ K
Block, colourless
0.48 × 0.23 × 0.21 mm

Data collection

Kuma KM-4-CCD Sapphire2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.1883 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2008)
$T_{\min} = 0.952$, $T_{\max} = 1$

3755 measured reflections
2024 independent reflections
1674 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.021$
$\theta_{\max} = 25.5°$, $\theta_{\min} = 2.7°$
$h = -18 \rightarrow 28$
$k = -8 \rightarrow 7$
$l = -19 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.113$
$S = 1.08$
2024 reflections
140 parameters
5 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0755P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Special details

Experimental. Absorption correction: CrysAlis PRO (Oxford Diffraction, 2008). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.11286 (3)	0.40172 (9)	1.02811 (4)	0.0315 (2)	
S2	0.21612 (3)	0.71645 (9)	1.10583 (4)	0.0325 (2)	
N1	0.18466 (9)	0.5160 (3)	0.94834 (12)	0.0253 (4)	
H1N	0.2097 (12)	0.592 (4)	0.9456 (16)	0.030*	
N2	0.14708 (9)	0.3938 (3)	0.86627 (11)	0.0228 (4)	
N3	0.10268 (9)	0.2586 (3)	0.67082 (12)	0.0219 (4)	
H3N	0.1226 (12)	0.321 (4)	0.6552 (17)	0.026*	
C1	0.17032 (10)	0.5395 (3)	1.02061 (13)	0.0237 (5)	
C2	0.19188 (11)	0.2838 (3)	0.84347 (14)	0.0262 (5)	
H2A	0.2237	0.2077	0.9017	0.031*	
H2B	0.2172	0.3759	0.8260	0.031*	
C3	0.15206 (11)	0.1465 (3)	0.75862 (14)	0.0267 (5)	
H3A	0.1820	0.0742	0.7422	0.032*	
H3B	0.1289	0.0497	0.7777	0.032*	
C4	0.06052 (11)	0.3844 (3)	0.69519 (14)	0.0267 (5)	
H4A	0.0324	0.3003	0.7107	0.032*	
H4B	0.0312	0.4664	0.6377	0.032*	
C5	0.10291 (10)	0.5152 (3)	0.78231 (13)	0.0237 (5)	
H5A	0.1291	0.6054	0.7657	0.028*	
H5B	0.0744	0.5950	0.7989	0.028*	
C6	0.06125 (13)	0.1260 (4)	0.58698 (16)	0.0375 (6)	
H6A	0.0899	0.0443	0.5725	0.056*	
H6B	0.0321	0.2046	0.5290	0.056*	
H6C	0.0345	0.0420	0.6042	0.056*	
O1	0.1228 (2)	0.9907 (5)	0.9238 (3)	0.0331 (8)	0.50
H1A	0.1408	0.9093	0.9682	0.050*	0.50
H1B	0.1038	1.0904	0.9270	0.050*	0.50
O2	−0.00204 (19)	0.8579 (6)	0.8020 (3)	0.0426 (8)	0.50
H2C	−0.027 (3)	0.891 (10)	0.742 (2)	0.064*	0.50
H2D	0.0350 (19)	0.920 (9)	0.834 (4)	0.064*	0.50
O3	−0.0827 (2)	0.9861 (6)	0.6047 (3)	0.0323 (8)	0.50
H3C	−0.1054	0.8903	0.5705	0.048*	0.50
H3D	−0.1127	1.0731	0.5844	0.048*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0393 (4)	0.0359 (3)	0.0276 (3)	−0.0079 (3)	0.0229 (3)	−0.0077 (2)
S2	0.0284 (3)	0.0499 (4)	0.0237 (3)	−0.0104 (3)	0.0164 (2)	−0.0164 (2)
N1	0.0264 (9)	0.0334 (11)	0.0183 (8)	−0.0050 (9)	0.0127 (7)	−0.0060 (7)
N2	0.0284 (9)	0.0253 (9)	0.0162 (8)	0.0016 (8)	0.0123 (7)	−0.0031 (6)
N3	0.0251 (10)	0.0253 (9)	0.0183 (8)	−0.0077 (8)	0.0130 (7)	−0.0053 (7)
C1	0.0226 (11)	0.0309 (11)	0.0170 (9)	0.0063 (9)	0.0094 (8)	0.0007 (8)
C2	0.0302 (12)	0.0306 (11)	0.0176 (9)	0.0090 (10)	0.0117 (9)	0.0012 (8)
C3	0.0385 (13)	0.0234 (10)	0.0258 (10)	0.0027 (10)	0.0217 (10)	0.0003 (9)
C4	0.0221 (11)	0.0350 (12)	0.0240 (10)	0.0003 (10)	0.0123 (9)	−0.0060 (9)
C5	0.0242 (10)	0.0247 (11)	0.0206 (10)	0.0033 (9)	0.0101 (8)	−0.0027 (8)
C6	0.0364 (13)	0.0467 (15)	0.0334 (12)	−0.0175 (12)	0.0204 (11)	−0.0225 (11)
O1	0.053 (2)	0.0193 (16)	0.0324 (19)	−0.001 (2)	0.025 (2)	−0.0003 (14)
O2	0.035 (2)	0.040 (2)	0.048 (2)	−0.0038 (17)	0.0176 (18)	−0.0047 (17)
O3	0.040 (2)	0.0276 (18)	0.0301 (19)	0.005 (2)	0.0184 (18)	0.0021 (14)

Geometric parameters (Å, º)

S1—C1	1.690 (2)	C4—C5	1.516 (3)
S2—C1	1.721 (2)	C4—H4A	0.9900
N1—C1	1.344 (2)	C4—H4B	0.9900
N1—N2	1.413 (2)	C5—H5A	0.9900
N1—H1N	0.80 (3)	C5—H5B	0.9900
N2—C5	1.460 (2)	C6—H6A	0.9800
N2—C2	1.470 (3)	C6—H6B	0.9800
N3—C6	1.489 (3)	C6—H6C	0.9800
N3—C4	1.492 (3)	O1—O2	2.724 (5)
N3—C3	1.493 (3)	O1—H1A	0.8236
N3—H3N	0.76 (2)	O1—H1B	0.8269
C2—C3	1.510 (3)	O2—O3	2.845 (5)
C2—H2A	0.9900	O2—H2C	0.86 (2)
C2—H2B	0.9900	O2—H2D	0.86 (2)
C3—H3A	0.9900	O3—H3C	0.8435
C3—H3B	0.9900	O3—H3D	0.8498
C1—N1—N2	122.54 (18)	N3—C4—H4A	109.5
C1—N1—H1N	117.8 (17)	C5—C4—H4A	109.5
N2—N1—H1N	118.1 (17)	N3—C4—H4B	109.5
N1—N2—C5	109.09 (16)	C5—C4—H4B	109.5
N1—N2—C2	109.24 (16)	H4A—C4—H4B	108.1
C5—N2—C2	109.73 (14)	N2—C5—C4	109.32 (17)
C6—N3—C4	110.78 (17)	N2—C5—H5A	109.8
C6—N3—C3	111.58 (18)	C4—C5—H5A	109.8
C4—N3—C3	111.21 (15)	N2—C5—H5B	109.8
C6—N3—H3N	106.9 (18)	C4—C5—H5B	109.8
C4—N3—H3N	110.4 (19)	H5A—C5—H5B	108.3
C3—N3—H3N	105.7 (19)	N3—C6—H6A	109.5
N1—C1—S1	122.25 (16)	N3—C6—H6B	109.5

N1—C1—S2	114.87 (16)	H6A—C6—H6B	109.5
S1—C1—S2	122.86 (11)	N3—C6—H6C	109.5
N2—C2—C3	109.37 (18)	H6A—C6—H6C	109.5
N2—C2—H2A	109.8	H6B—C6—H6C	109.5
C3—C2—H2A	109.8	O2—O1—H1A	106.6
N2—C2—H2B	109.8	O2—O1—H1B	84.1
C3—C2—H2B	109.8	H1A—O1—H1B	124.5
H2A—C2—H2B	108.2	O1—O2—O3	123.96 (18)
N3—C3—C2	110.47 (17)	O1—O2—H2C	126 (4)
N3—C3—H3A	109.6	O3—O2—H2D	114 (4)
C2—C3—H3A	109.6	H2C—O2—H2D	116 (6)
N3—C3—H3B	109.6	O2—O3—H3C	108.7
C2—C3—H3B	109.6	O2—O3—H3D	126.7
H3A—C3—H3B	108.1	H3C—O3—H3D	99.4
N3—C4—C5	110.62 (17)		

C1—N1—N2—C5	101.4 (2)	C4—N3—C3—C2	−53.9 (2)
C1—N1—N2—C2	−138.6 (2)	N2—C2—C3—N3	58.0 (2)
N2—N1—C1—S1	8.7 (3)	C6—N3—C4—C5	178.46 (17)
N2—N1—C1—S2	−172.63 (15)	C3—N3—C4—C5	53.8 (2)
N1—N2—C2—C3	177.53 (16)	N1—N2—C5—C4	−177.72 (15)
C5—N2—C2—C3	−62.9 (2)	C2—N2—C5—C4	62.6 (2)
C6—N3—C3—C2	−178.18 (17)	N3—C4—C5—N2	−57.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···S2^{i}	0.80 (3)	2.60 (3)	3.375 (2)	164 (2)
N3—H3*N*···S1^{ii}	0.76 (2)	2.67 (2)	3.3131 (18)	143 (2)
N3—H3*N*···S2^{ii}	0.76 (2)	2.67 (2)	3.2846 (18)	140 (2)

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