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Hexaaquacobalt(II) 5,5'-(propane-1,3-diylidithio)bis(1*H*-tetrazole-1-acetate)

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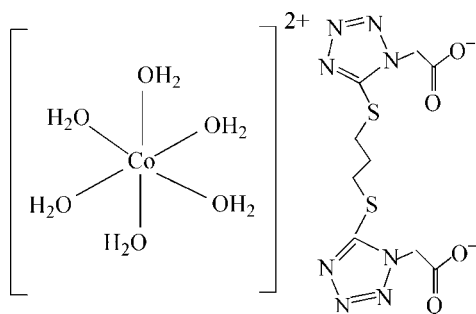
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.025; wR factor = 0.068; data-to-parameter ratio = 12.1.

The asymmetric unit of the title complex, $[\text{Co}(\text{H}_2\text{O})_6]-(\text{C}_9\text{H}_{10}\text{N}_8\text{O}_4\text{S}_2)$, contains one-half of a $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ cation and one-half of a 5,5'-(propane-1,3-diylidithio)bis(1*H*-tetrazole-1-acetate) (battp^{2-}) anion. The Co^{II} center is coordinated by six H_2O molecules in a distorted octahedral coordination environment. In the crystal structure, intra- and intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds link the cations and anions into a three-dimensional network. $\pi-\pi$ contacts between the tetrazole rings [centroid-centroid distance = 3.346 (1) Å] may further stabilize the structure.

Related literature

For related structures, see: Du *et al.* (2004); Jiang & Li (2004); Liu *et al.* (2004).



Experimental

Crystal data

 $[\text{Co}(\text{H}_2\text{O})_6](\text{C}_9\text{H}_{10}\text{N}_8\text{O}_4\text{S}_2)$ $M_r = 525.42$

Monoclinic, $C2/c$
 $a = 19.420$ (2) Å
 $b = 7.9069$ (11) Å
 $c = 13.7356$ (17) Å
 $\beta = 112.957$ (2)°
 $V = 1942.1$ (4) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.17$ mm⁻¹
 $T = 298$ K
 $0.38 \times 0.35 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
 $T_{\text{min}} = 0.665$, $T_{\text{max}} = 0.800$

4714 measured reflections
 1716 independent reflections
 1518 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.068$
 $S = 1.02$
 1716 reflections
 142 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3A}\cdots\text{O1}$	0.85	1.93	2.767 (2)	166
$\text{O4}-\text{H4A}\cdots\text{O2}^{\text{i}}$	0.85	1.90	2.742 (2)	172
$\text{O4}-\text{H4B}\cdots\text{N3}^{\text{ii}}$	0.85	2.19	2.970 (2)	152
$\text{O5}-\text{H5A}\cdots\text{O1}^{\text{i}}$	0.85	1.86	2.7069 (19)	173
$\text{O5}-\text{H5B}\cdots\text{N4}^{\text{iii}}$	0.85	1.99	2.833 (2)	173

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; 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* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2740).

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supporting information

Acta Cryst. (2009). E65, m1006 [doi:10.1107/S1600536809028463]

Hexaaquacobalt(II) 5,5'-(propane-1,3-diyl)dithio)bis(1*H*-tetrazole-1-acetate)

Wan-Ling Liang, Qing Yu, Xiu-Qing Zhang, Jiang-Ke Qin and Hong Liang

S1. Comment

Coordination compounds of the type $[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{10}\text{H}_8\text{O}_6)$, $[\text{Co}(\text{H}_2\text{O})_6](L)_2$ (L = isonicotinate N-oxide, $\text{C}_6\text{H}_4\text{NO}_3$) and $[\text{Co}(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}\cdot 2L\cdot 2\text{ClO}_4$ (L = 1,1'-(propane-1,3-diyl)dipyridinium-4-carboxylate) have been previously prepared and studied by several groups (Liu *et al.*, 2004; Du *et al.*, 2004; Jiang & Li, 2004). We report herein the crystal structure of the new title mononuclear cobalt complex, $[\text{Co}(\text{H}_2\text{O})_6]\cdot(\text{battp})$ [where battp is 1,3-bis(1-acetic acid-1,2,3,4-tetrazole-5-thioether propane)].

The asymmetric unit of the title complex contains one-half of the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ cation and one-half of the $[\text{battp}]^{2-}$ anion (Fig. 1). The Co center is coordinated by six H_2O molecules in a distorted octahedral coordination environment. The average Co-O bond distance is 2.0973 (14) Å.

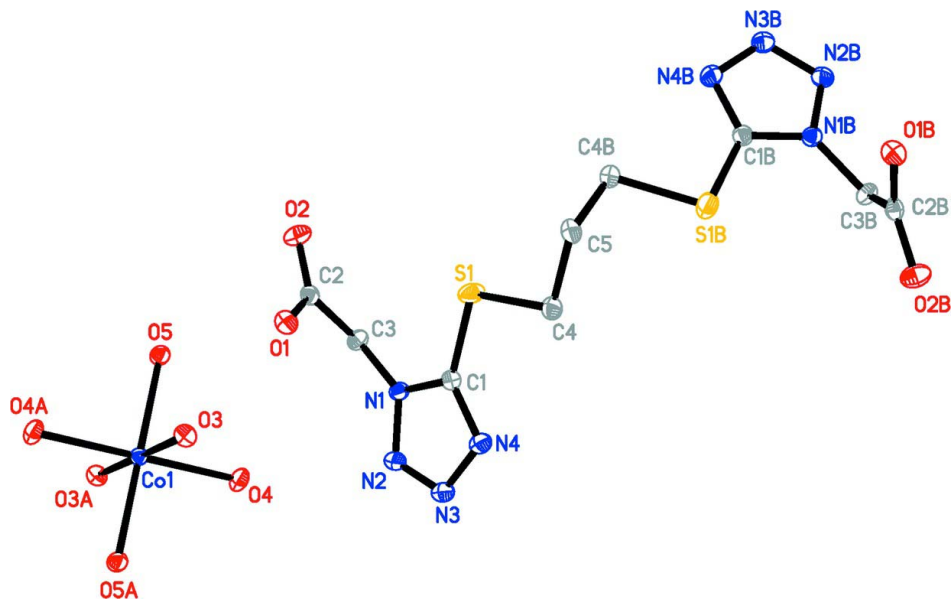
In the crystal structure, intra- and intermolecular O-H \cdots O and O-H \cdots N hydrogen bonds (Table 1) link the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ cations and $[\text{battp}]^{2-}$ anions into a three-dimensional network (Fig. 2), in which they may be effective in the stabilization of the structure. The π - π contact between the tetrazole rings, Cg1—Cg1ⁱ [symmetry code: (i) -x, 2 - y, -z, where Cg1 is centroid of the ring A (N1-N4/C1)] may further stabilize the structure, with centroid-centroid distance of 3.346 (1) Å.

S2. Experimental

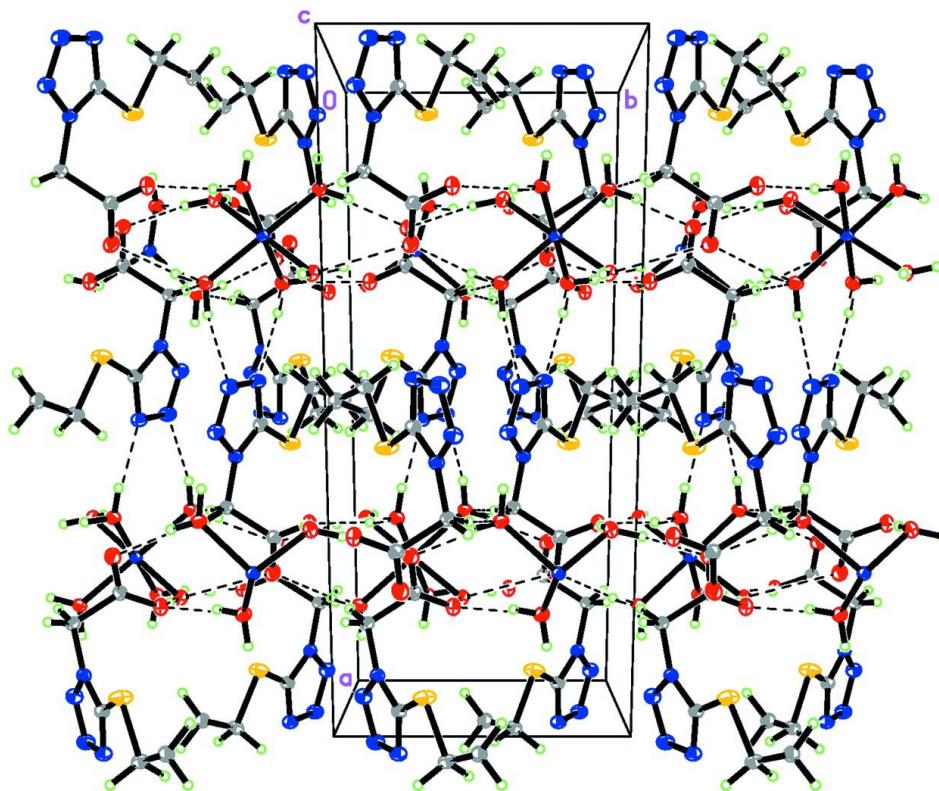
For the preparation of the title compound, H_2battp (0.1440 g, 0.4 mmol) was dissolved in water (5 ml), and the solution of $\text{CoClO}_4\cdot 6\text{H}_2\text{O}$ (0.1832 g, 0.5 mmol) in distilled water (5 ml) was added. The mixture was stirred at 353 K for 3 h, and then cooled and filtered. The filtrate was allowed to slowly evaporate at room temperature. Two weeks later, pink block crystals were obtained.

S3. Refinement

Atom H5 was located in difference Fourier map and refined isotropically. The remaining H atoms were positioned geometrically with O-H = 0.85 Å (for H_2O) and C-H = 0.97 Å for methylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$.

**Figure 1**

The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level [symmetry codes: (A) $1/2 - x, 1/2 - y, -z$; (B) $1 - x, y, 3/2 - z$]. Hydrogen atoms have been omitted for clarity.

**Figure 2**

A partial packing diagram. Hydrogen bonds are shown as dashed lines.

Hexaaquacobalt(II) 5,5'-(propane-1,3-diylthio)bis(1H-tetrazole-1-acetate)

Crystal data

[Co(H₂O)₆](C₉H₁₀N₈O₄S₂)
 $M_r = 525.42$
 Monoclinic, *C2/c*
 Hall symbol: -C 2yc
 $a = 19.420$ (2) Å
 $b = 7.9069$ (11) Å
 $c = 13.7356$ (17) Å
 $\beta = 112.957$ (2)°
 $V = 1942.1$ (4) Å³
 $Z = 4$

$F(000) = 1084$
 $D_x = 1.797$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3230 reflections
 $\theta = 2.8$ – 28.0 °
 $\mu = 1.17$ mm⁻¹
 $T = 298$ K
 Block, pink
 $0.38 \times 0.35 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 1997)
 $T_{\min} = 0.665$, $T_{\max} = 0.800$

4714 measured reflections
 1716 independent reflections
 1518 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 25.0$ °, $\theta_{\text{min}} = 2.3$ °
 $h = -22 \rightarrow 22$
 $k = -5 \rightarrow 9$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.068$
 $S = 1.02$
 1716 reflections
 142 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 atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 3P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.2500	0.2500	0.0000	0.01988 (13)
S1	0.43307 (3)	0.19008 (9)	0.57138 (5)	0.03941 (18)
O1	0.31180 (8)	0.09876 (18)	0.31741 (11)	0.0285 (3)

O2	0.23139 (9)	0.23926 (18)	0.36776 (14)	0.0344 (4)
O3	0.30995 (8)	0.07215 (18)	0.11553 (11)	0.0263 (3)
H3A	0.3132	0.0970	0.1774	0.032*
H3B	0.3001	-0.0328	0.1066	0.032*
O4	0.32343 (8)	0.43840 (19)	0.09350 (12)	0.0298 (3)
H4A	0.3105	0.5351	0.1074	0.036*
H4B	0.3708	0.4302	0.1214	0.036*
O5	0.18294 (8)	0.30070 (18)	0.08298 (11)	0.0262 (3)
H5A	0.1885	0.3941	0.1158	0.031*
H5B	0.1362	0.2841	0.0519	0.031*
N1	0.41422 (9)	0.3568 (2)	0.39209 (13)	0.0222 (4)
N2	0.45252 (10)	0.4106 (2)	0.33400 (14)	0.0284 (4)
N3	0.52125 (10)	0.3673 (2)	0.38552 (14)	0.0314 (4)
N4	0.52993 (10)	0.2844 (2)	0.47718 (14)	0.0287 (4)
C1	0.46251 (12)	0.2798 (3)	0.47931 (16)	0.0237 (4)
C2	0.28859 (12)	0.2281 (2)	0.34801 (15)	0.0225 (4)
C3	0.33493 (11)	0.3904 (3)	0.36361 (17)	0.0246 (4)
H3C	0.3160	0.4558	0.2988	0.030*
H3D	0.3290	0.4578	0.4188	0.030*
C4	0.52031 (11)	0.1138 (3)	0.67099 (16)	0.0282 (5)
H4C	0.5467	0.0439	0.6387	0.034*
H4D	0.5522	0.2081	0.7063	0.034*
C5	0.5000	0.0101 (4)	0.7500	0.0268 (6)
H5	0.5438 (12)	-0.061 (3)	0.7883 (18)	0.033 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0184 (2)	0.0201 (2)	0.0220 (2)	0.00018 (14)	0.00878 (16)	-0.00122 (15)
S1	0.0235 (3)	0.0601 (4)	0.0348 (3)	0.0030 (3)	0.0115 (3)	0.0230 (3)
O1	0.0354 (9)	0.0223 (8)	0.0279 (8)	0.0004 (6)	0.0124 (7)	0.0000 (6)
O2	0.0315 (9)	0.0284 (9)	0.0507 (10)	-0.0033 (7)	0.0239 (8)	0.0010 (7)
O3	0.0293 (8)	0.0234 (7)	0.0267 (8)	0.0031 (6)	0.0115 (6)	0.0008 (6)
O4	0.0196 (7)	0.0275 (8)	0.0386 (9)	-0.0016 (6)	0.0073 (6)	-0.0095 (7)
O5	0.0225 (7)	0.0268 (8)	0.0313 (8)	-0.0010 (6)	0.0126 (6)	-0.0066 (6)
N1	0.0205 (9)	0.0233 (9)	0.0236 (9)	-0.0013 (7)	0.0096 (7)	0.0014 (7)
N2	0.0279 (10)	0.0347 (10)	0.0260 (9)	-0.0019 (8)	0.0141 (8)	0.0019 (8)
N3	0.0265 (10)	0.0405 (11)	0.0302 (10)	-0.0008 (8)	0.0144 (8)	0.0018 (8)
N4	0.0228 (9)	0.0340 (10)	0.0300 (10)	-0.0008 (8)	0.0112 (8)	0.0010 (8)
C1	0.0231 (11)	0.0255 (11)	0.0225 (10)	-0.0012 (8)	0.0089 (9)	-0.0006 (8)
C2	0.0243 (11)	0.0232 (11)	0.0179 (10)	0.0008 (8)	0.0059 (8)	0.0040 (8)
C3	0.0204 (10)	0.0223 (10)	0.0304 (11)	0.0019 (8)	0.0090 (9)	0.0018 (9)
C4	0.0231 (11)	0.0357 (12)	0.0236 (10)	0.0023 (9)	0.0066 (9)	0.0007 (9)
C5	0.0282 (17)	0.0277 (16)	0.0211 (15)	0.000	0.0061 (13)	0.000

Geometric parameters (Å, °)

Co1—O3	2.1000 (14)	O5—H5B	0.8500
Co1—O3 ⁱ	2.1000 (14)	N1—N2	1.354 (2)
Co1—O4 ⁱ	2.1150 (14)	N1—C1	1.345 (3)
Co1—O4	2.1150 (14)	N1—C3	1.458 (3)
Co1—O5 ⁱ	2.0770 (13)	N2—N3	1.290 (2)
Co1—O5	2.0770 (13)	N3—N4	1.370 (3)
S1—C1	1.730 (2)	N4—C1	1.321 (3)
S1—C4	1.816 (2)	C2—C3	1.533 (3)
O1—C2	1.254 (2)	C3—H3C	0.9700
O2—C2	1.245 (3)	C3—H3D	0.9700
O3—H3A	0.8500	C4—C5	1.529 (3)
O3—H3B	0.8500	C4—H4C	0.9700
O4—H4A	0.8499	C4—H4D	0.9700
O4—H4B	0.8499	C5—C4 ⁱⁱ	1.529 (3)
O5—H5A	0.8500	C5—H5	0.98 (2)
O3—Co1—O3 ⁱ	180.00 (12)	H4A—O4—H4B	109.2
O3—Co1—O4 ⁱ	91.78 (6)	Co1—O5—H5A	118.7
O3 ⁱ —Co1—O4 ⁱ	88.22 (6)	Co1—O5—H5B	118.1
O3—Co1—O4	88.22 (6)	H5A—O5—H5B	106.9
O3 ⁱ —Co1—O4	91.78 (6)	C1—S1—C4	102.11 (10)
O4 ⁱ —Co1—O4	180.00 (14)	N4—C1—N1	108.69 (18)
O5 ⁱ —Co1—O3	90.23 (6)	N4—C1—S1	129.81 (17)
O5—Co1—O3	89.77 (6)	N1—C1—S1	121.49 (16)
O5 ⁱ —Co1—O3 ⁱ	89.77 (6)	O2—C2—O1	126.76 (19)
O5—Co1—O3 ⁱ	90.23 (6)	O2—C2—C3	115.80 (18)
O5 ⁱ —Co1—O4 ⁱ	87.10 (6)	O1—C2—C3	117.44 (18)
O5—Co1—O4 ⁱ	92.90 (6)	N1—C3—C2	112.70 (16)
O5 ⁱ —Co1—O4	92.90 (6)	N1—C3—H3C	109.1
O5—Co1—O4	87.10 (6)	C2—C3—H3C	109.1
O5 ⁱ —Co1—O5	180.00 (10)	N1—C3—H3D	109.1
C1—N1—N2	108.35 (16)	C2—C3—H3D	109.1
C1—N1—C3	128.18 (17)	H3C—C3—H3D	107.8
N2—N1—C3	123.36 (16)	S1—C4—H4C	110.4
N3—N2—N1	106.36 (16)	S1—C4—H4D	110.4
N2—N3—N4	111.19 (16)	C5—C4—S1	106.84 (12)
C1—N4—N3	105.41 (17)	C5—C4—H4C	110.4
Co1—O3—H3A	113.8	C5—C4—H4D	110.4
Co1—O3—H3B	121.1	H4C—C4—H4D	108.6
H3A—O3—H3B	107.2	C4—C5—C4 ⁱⁱ	115.2 (3)
Co1—O4—H4A	125.6	C4—C5—H5	106.0 (13)
Co1—O4—H4B	125.1	C4 ⁱⁱ —C5—H5	109.5 (13)
C1—N1—N2—N3	−0.2 (2)	C3—N1—C1—S1	5.2 (3)
C3—N1—N2—N3	176.28 (18)	C4—S1—C1—N4	3.5 (2)
N1—N2—N3—N4	0.3 (2)	C4—S1—C1—N1	−178.16 (17)

N2—N3—N4—C1	-0.2 (2)	C1—N1—C3—C2	-63.3 (3)
N3—N4—C1—N1	0.1 (2)	N2—N1—C3—C2	120.9 (2)
N3—N4—C1—S1	178.55 (17)	O2—C2—C3—N1	150.83 (18)
N2—N1—C1—N4	0.1 (2)	O1—C2—C3—N1	-28.9 (3)
C3—N1—C1—N4	-176.20 (19)	C1—S1—C4—C5	-172.50 (15)
N2—N1—C1—S1	-178.54 (15)	S1—C4—C5—C4 ⁱⁱ	-77.35 (11)

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O3—H3A...O1	0.85	1.93	2.767 (2)	166
O4—H4A...O2 ⁱⁱⁱ	0.85	1.90	2.742 (2)	172
O4—H4B...N3 ^{iv}	0.85	2.19	2.970 (2)	152
O5—H5A...O1 ⁱⁱⁱ	0.85	1.86	2.7069 (19)	173
O5—H5B...N4 ^v	0.85	1.99	2.833 (2)	173

Symmetry codes: (iii) $-x+1/2, y+1/2, -z+1/2$; (iv) $-x+1, y, -z+1/2$; (v) $x-1/2, -y+1/2, z-1/2$.