Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure and Hirshfeld surface analysis of bis[(ethoxymethanethioyl)sulfanido](N,N,N',N'-tetramethylethane-1,2-diamine)mercury(II)

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Received 28 May 2021
Accepted 11 October 2021

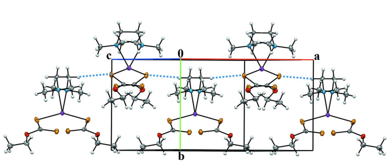
Edited by D. Gray, University of Illinois Urbana-Champaign, USA

Keywords: crystal structure; xanthate; mercury(II); Hirshfeld surface analysis.

CCDC reference: 2115100

Supporting information: this article has supporting information at journals.iucr.org/e

The title four-coordinate mononuclear complex, $[Hg(C_3H_5OS_2)_2(C_6H_{16}N_2)]$ or $[Hg(C_3H_5OS_2)_2(tmeda)]$ (tmeda: N,N,N',N'-tetramethylethane-1,2-diamine), has a distorted tetrahedral geometry. The Hg^{II} ion is coordinated to two N atoms of the N,N,N',N'-tetramethylethylenediamine ligand and two S atoms from two ethylxanthate xanthate ligands. In the crystal, molecules are linked by weak C—H···S hydrogen bonds, forming a two-dimensional supramolecular architecture in the *ab* plane. The most important contributions for the crystal packing are from H···H (59.3%), S···H (27.4%) and O···H (7.5%) interactions.



1. Chemical context

Xanthates (dithiocarbonates) attract the interest of many researchers in the field of coordination chemistry owing to their antidotal, antioxidant and antitumor activities (Shahzadi *et al.*, 2009; Perluigi *et al.*, 2006; Larsson & Oberg, 2011). These ligands exhibit different coordination modes such as monodentate, isobidentate or anisobidentate. Cellulose xanthate has been used for the separation of alcohols by the chromatographic method (Friebolin *et al.*, 2004). It has been reported that metal xanthates exhibit cytotoxic activity on human cancer cells and have the ability to inhibit both DNA and RNA viruses *in vitro* (Efrima & Pradhan, 2003). Mercury represents one of the most toxic heavy metals found in solid and liquid waste from oil refineries and the mining industry. We report herein the synthesis and crystal structure of a new Hg^{II} xanthate containing N,N,N',N'-tetramethylethylenediamine, including the results of a Hirshfeld surface analysis.

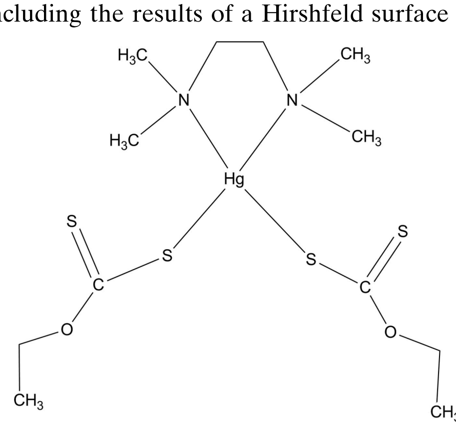


Table 1
Selected bond lengths (Å).

Hg1—S1	2.416 (3)	O1—C1	1.355 (11)
Hg1—N1	2.531 (8)	O1—C2	1.460 (12)
S1—C1	1.727 (9)	N1—C5	1.452 (13)
S2—C1	1.633 (10)	N1—C4	1.479 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···S1^{i}	0.97	2.92	3.845 (11)	160

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

2. Structural commentary

The asymmetric unit of the title complex (Fig. 1) comprises one Hg^{II} ion, one half *N*,*N*,*N*′,*N*′-tetramethylethylenediamine ligand and one ethylxanthate ligand. The Hg^{II} ion is coordinated by two N atoms of the *N*,*N*,*N*′,*N*′-tetramethylethylenediamine ligand and two S atoms from two ethylxanthate xanthate ligands in a distorted tetrahedral environment. The Hg—N and Hg—S bond lengths (Table 1) are 2.531 (8) and 2.416 (3) Å, respectively, whereas the bond angles around the central Hg^{II} ion are in the range 73.8 (3)–149.91 (18)°. The bond lengths and angles of the HgN_2S_2 coordination units correspond to those in the structures of mixed-ligand Hg^{II} coordination compounds (see *Database survey*). The C1—O1 and C2—O1 bond lengths are 1.355 (11) to 1.460 (12) Å, respectively, although all of the C—O bonds show single-bond character. In the {S_2C} section of the xanthate ligands, the C1—S1 distance is 1.727 (9) Å, which is typical of a single bond, whereas the C1═S2 distance of 1.633 (10) Å is typical of a carbon-to-sulfur double bond. The C—N and C—C bond lengths in the *N*,*N*,*N*′,*N*′-tetramethylethylenediamine ligand are normal (Qadir *et al.*, 2020).

3. Supramolecular features

In the crystal, there is a weak intermolecular hydrogen bonding (Table 2) between S atoms and the H atoms of the methylene groups [C4—H4*B*···S1 ($x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$)]. Fig. 2 illustrates the two-dimensional wave-like structure extending in the *ab* plane formed by hydrogen-bonding interactions in [Hg($C_3H_5S_2O_1$)$_2$(tmeda)].

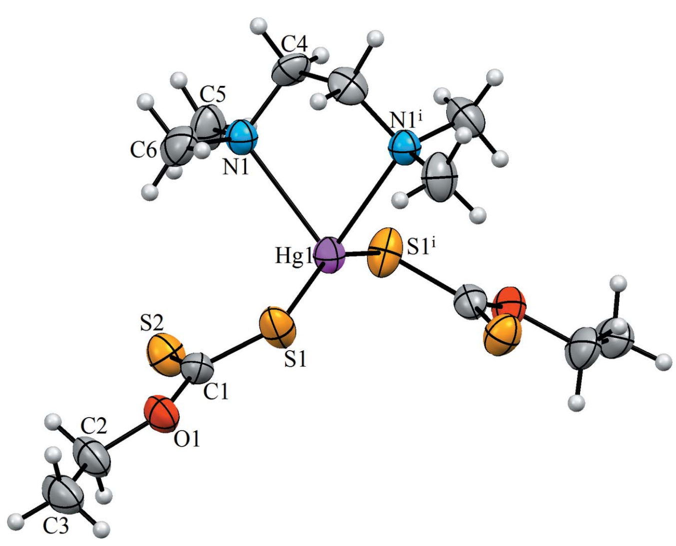


Figure 1
The molecular structure of [Hg($C_3H_5S_2O_1$)$_2$(tmeda)], with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.42, update of November 2020; Groom *et al.*, 2016) for the title complex revealed five similar complexes: [Hg($C_{14}H_{26}O_2S_4$)]$_n$ (BATXOJ; Cox & Tiekink, 1999), [Hg(C_5H_4NSe)$_2$($C_6H_{16}N_2$)] (EKODAK; Sharma *et al.*, 2011), [Hg($C_6H_{16}N_2$)($C_9H_{13}NS$)$_2$](PF_6)$_2$ (POTJOY; Tang *et al.*, 2009), [HgCl(C_7H_7S)($C_6H_{16}N_2$)] (TEVQAM; Kräuter *et al.*, 1996) and [$HgCl_2$($C_6H_{16}N_2$)] (ZZZAJM; Htoon & Ladd, 1976). In BATXOJ, the coordination geometry is distorted tetrahedral with the independent Hg—S distances being 2.413 (5) and 2.842 (5) Å. The range of S—Hg—S angles is 81.8 (2)–150.8 (3)° with the wider angle involving the more tightly bound S1 atoms. In EKODAK, the corresponding mercury complex adopts a severely distorted tetrahedral configuration defined by the two monodentate selenolate and chelating tmeda ligands. The Hg—N bond lengths are in the range 2.573 (17)–2.601 (18) Å. In POTJOY, intermolecular C—H···S hydrogen bonds are important in the crystal packing. Similarly, the molecules are connected to each other *via* C—H···S hydrogen bonds in the title complex. In TEVQAM, the Hg—N and Hg—S bond lengths are 2.54 and 2.34 Å, respectively, comparable to those in the title compound.

5. Hirshfeld surface analysis

A Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was carried out using *CrystalExplorer17.5* (Turner *et al.*, 2017) to quantify the various intermolecular interactions. The Hirshfeld surface mapped over d_{norm} is illustrated in Fig. 3 and the associated two-dimensional fingerprint plots in Fig. 4. The

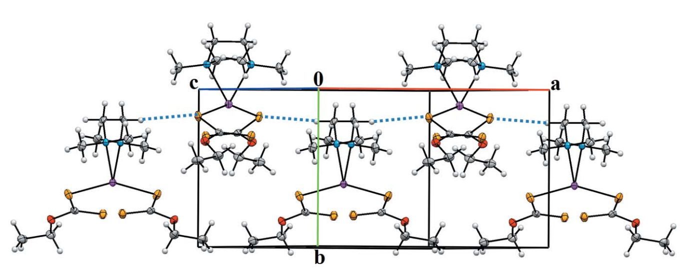


Figure 2
Two-dimensional wave-like structure extending in the *ab* plane formed by hydrogen-bonding interactions in [Hg($C_3H_5S_2O_1$)$_2$(tmeda)].

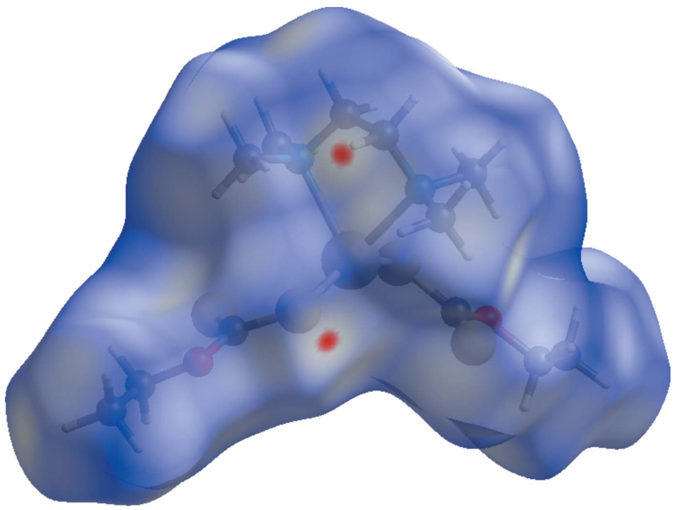


Figure 3
Hirshfeld surface mapped with d_{norm}.

major contributions to the crystal structure are from H···H (59.3%), S···H (27.4%) and O···H interactions (7.5%. The large number of H···H interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing. C···H (3.4%) and S···O (1.9%) contacts are also observed.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Hg(C_3H_5OS_2)_2(C_6H_{16}N_2)]$
M_r	559.18
Crystal system, space group	Orthorhombic, *Pbcn*
Temperature (K)	296
a, *b*, *c* (Å)	12.235 (7), 8.017 (5), 21.251 (17)
V (Å^3)	2084 (2)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	7.79
Crystal size (mm)	0.71 × 0.38 × 0.06
Data collection	
Diffractometer	Bruker D8 Quest with Photon II CPADs detector
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.041, 0.627
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8974, 1946, 1265
R_{int}	0.139
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.147, 1.00
No. of reflections	1946
No. of parameters	99
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.01, −2.73

Computer programs: *APEX3* and *SAINT* (Bruker, 2017), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2017/1* (Sheldrick, 2015*b*), *PLATON* (Spek, 2020) and *WinGX* (Farrugia, 2012).

6. Synthesis and crystallization

Potassium ethylxanthate (4 mmol, 0.64 g) in hot ethanol (10 mL) was added to a hot solution of $Hg(CH_3CO_2)_2$ (2 mmol, 0.64 g) in ethanol (10 mL) under stirring. The formed precipitate was filtered off, washed with water and air-dried. The precipitate was suspended in hot ethanol (10 mL) and tetramethylethylenediamine (2 mmol, 0.23 g) was added under stirring. The colour changed to dark brown. The precipitate was filtered off and dried and then recrystallized from ethanol. Brown rods were formed.

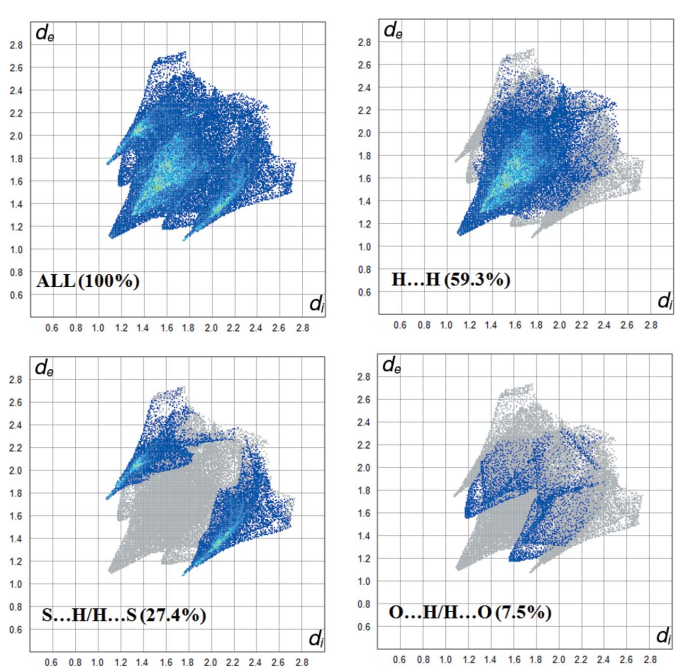


Figure 4
Two-dimensional fingerprint plots for $[Hg(C_3H_5S_2O_1)_2(tmeda)]$.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were positioned geometrically (C—H = 0.96 and 0.97 Å) and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for all others

Acknowledgements

Author contributions are as follows. Conceptualization, SK, AMQ and ES; synthesis, AMQ; writing (review and editing of the manuscript), SK and AMQ, formal analysis, SK, AMQ and ND, validation, SK, AMQ and ND, project administration, SK, AMQ and ES.

Funding information

Funding for this research was provided by: Ondokuz Mayıs University under Project No. PYO.FEN.1906.19.001.

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supporting information

Acta Cryst. (2021). E**77**, 1126-1129 [https://doi.org/10.1107/S2056989021010549]

Crystal structure and Hirshfeld surface analysis of bis[(ethoxymethanethioyl)sulfanido](*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)mercury(II)

Adnan M. Qadir, Sevgi Kansiz, Necmi Dege and Eiad Saif

Computing details

Data collection: *APEX3* (Bruker, 2017); cell refinement: *SAINT* (Bruker, 2017); data reduction: *SAINT* (Bruker, 2017); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Bis[(ethoxymethanethioyl)sulfanido](*N*,*N*,*N*′,*N*′-\ tetramethylethane-1,2-diamine)mercury(II)

Crystal data

$[Hg(C_3H_5OS_2)_2(C_6H_{16}N_2)]$
M_r = 559.18
Orthorhombic, *Pbcn*
a = 12.235 (7) Å
b = 8.017 (5) Å
c = 21.251 (17) Å
V = 2084 (2) Å^3
Z = 4
$F(000)$ = 1088
D_x = 1.782 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 379 reflections
θ = 2.0–24.7°
μ = 7.79 mm^{-1}
T = 296 K
Rod, brown
0.71 × 0.38 × 0.06 mm

Data collection

Bruker D8 Quest with Photon II CPADs detector diffractometer
Radiation source: Incoatec microfocus source
Detector resolution: 7.4074 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.041, T_{max} = 0.627
8974 measured reflections
1946 independent reflections
1265 reflections with $I > 2\sigma(I)$
R_{int} = 0.139
θ_{max} = 25.7°, θ_{min} = 1.9°
h = −14→12
k = −6→9
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.147
S = 1.00
1946 reflections
99 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 1.01 e Å^{-3}
$\Delta\rho_{min}$ = −2.73 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Hg1	0.500000	0.59649 (6)	0.750000	0.0605 (2)
S1	0.6620 (2)	0.6747 (4)	0.69202 (12)	0.0807 (9)
S2	0.4722 (2)	0.7975 (5)	0.61444 (14)	0.0815 (8)
O1	0.6840 (6)	0.8337 (10)	0.5917 (3)	0.0753 (19)
N1	0.4366 (6)	0.3441 (10)	0.6885 (3)	0.0580 (18)
C1	0.6025 (8)	0.7760 (12)	0.6290 (4)	0.063 (2)
C6	0.5057 (9)	0.3204 (18)	0.6319 (5)	0.087 (4)
H6A	0.502245	0.418481	0.606101	0.131*
H6B	0.479686	0.226095	0.608454	0.131*
H6C	0.579968	0.301191	0.644595	0.131*
C4	0.4462 (8)	0.1997 (13)	0.7314 (5)	0.069 (2)
H4A	0.441367	0.097608	0.707118	0.083*
H4B	0.385492	0.201216	0.760778	0.083*
C3	0.7614 (16)	0.9572 (16)	0.5016 (5)	0.101 (5)
H3A	0.747525	1.015326	0.462895	0.152*
H3B	0.795996	0.852358	0.492616	0.152*
H3C	0.808505	1.023299	0.527706	0.152*
C5	0.3232 (9)	0.3668 (17)	0.6701 (5)	0.090 (4)
H5A	0.280086	0.390950	0.706757	0.136*
H5B	0.296750	0.266672	0.650617	0.136*
H5C	0.317899	0.457818	0.640942	0.136*
C2	0.6563 (11)	0.9271 (15)	0.5349 (5)	0.091 (4)
H2A	0.621592	1.031988	0.545653	0.109*
H2B	0.606886	0.863221	0.508546	0.109*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.0589 (4)	0.0689 (4)	0.0536 (3)	0.000	0.0023 (2)	0.000
S1	0.0618 (15)	0.113 (2)	0.0676 (13)	−0.0248 (17)	−0.0088 (11)	0.0231 (15)
S2	0.0674 (17)	0.096 (2)	0.0811 (16)	0.0098 (16)	−0.0023 (13)	0.0141 (16)
O1	0.082 (5)	0.085 (5)	0.059 (3)	−0.011 (4)	0.009 (3)	0.013 (3)
N1	0.056 (5)	0.064 (5)	0.054 (4)	0.000 (4)	0.002 (3)	0.000 (3)
C1	0.075 (6)	0.059 (6)	0.056 (5)	−0.015 (5)	0.004 (4)	0.000 (4)
C6	0.103 (9)	0.088 (9)	0.071 (6)	−0.008 (8)	0.012 (5)	−0.024 (6)
C4	0.057 (6)	0.067 (6)	0.084 (6)	−0.023 (6)	−0.006 (5)	−0.010 (5)
C3	0.142 (13)	0.083 (10)	0.079 (7)	0.005 (8)	0.037 (7)	0.015 (7)
C5	0.075 (8)	0.123 (11)	0.073 (6)	−0.013 (7)	−0.019 (6)	−0.003 (6)
C2	0.115 (10)	0.090 (8)	0.067 (6)	0.005 (8)	0.018 (7)	0.025 (5)

Geometric parameters (Å, º)

Hg1—S1	2.416 (3)	C6—H6C	0.9600
Hg1—S1^{i}	2.416 (3)	C4—C4^{i}	1.53 (2)
Hg1—N1	2.531 (8)	C4—H4A	0.9700
Hg1—N1^{i}	2.531 (8)	C4—H4B	0.9700
S1—C1	1.727 (9)	C3—C2	1.49 (2)
S2—C1	1.633 (10)	C3—H3A	0.9600
O1—C1	1.355 (11)	C3—H3B	0.9600
O1—C2	1.460 (12)	C3—H3C	0.9600
N1—C5	1.452 (13)	C5—H5A	0.9600
N1—C4	1.479 (13)	C5—H5B	0.9600
N1—C6	1.481 (13)	C5—H5C	0.9600
C6—H6A	0.9600	C2—H2A	0.9700
C6—H6B	0.9600	C2—H2B	0.9700
S1—Hg1—S1^{i}	149.91 (18)	N1—C4—H4A	109.1
S1—Hg1—N1	101.26 (18)	C4^{i}—C4—H4A	109.1
S1^{i}—Hg1—N1	102.70 (19)	N1—C4—H4B	109.1
S1—Hg1—N1^{i}	102.70 (19)	C4^{i}—C4—H4B	109.1
S1^{i}—Hg1—N1^{i}	101.26 (18)	H4A—C4—H4B	107.8
N1—Hg1—N1^{i}	73.8 (3)	C2—C3—H3A	109.5
C1—S1—Hg1	99.9 (3)	C2—C3—H3B	109.5
C1—O1—C2	119.2 (9)	H3A—C3—H3B	109.5
C5—N1—C4	109.8 (9)	C2—C3—H3C	109.5
C5—N1—C6	110.1 (8)	H3A—C3—H3C	109.5
C4—N1—C6	110.8 (9)	H3B—C3—H3C	109.5
C5—N1—Hg1	109.3 (7)	N1—C5—H5A	109.5
C4—N1—Hg1	106.4 (5)	N1—C5—H5B	109.5
C6—N1—Hg1	110.3 (6)	H5A—C5—H5B	109.5
O1—C1—S2	124.9 (7)	N1—C5—H5C	109.5
O1—C1—S1	107.7 (7)	H5A—C5—H5C	109.5
S2—C1—S1	127.4 (5)	H5B—C5—H5C	109.5
N1—C6—H6A	109.5	O1—C2—C3	106.0 (11)
N1—C6—H6B	109.5	O1—C2—H2A	110.5
H6A—C6—H6B	109.5	C3—C2—H2A	110.5
N1—C6—H6C	109.5	O1—C2—H2B	110.5
H6A—C6—H6C	109.5	C3—C2—H2B	110.5
H6B—C6—H6C	109.5	H2A—C2—H2B	108.7
N1—C4—C4^{i}	112.7 (7)		
C2—O1—C1—S2	1.9 (13)	C5—N1—C4—C4^{i}	−162.2 (10)
C2—O1—C1—S1	−179.2 (8)	C6—N1—C4—C4^{i}	75.9 (12)
Hg1—S1—C1—O1	178.2 (6)	Hg1—N1—C4—C4^{i}	−44.0 (11)
Hg1—S1—C1—S2	−3.0 (7)	C1—O1—C2—C3	−174.4 (9)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···S1^{ii}	0.97	2.92	3.845 (11)	160

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