

Bis{N-benzyl-N-[2-(thiophen-2-yl)ethyl]-dithiocarbamato- κ^2S,S' }lead(II)

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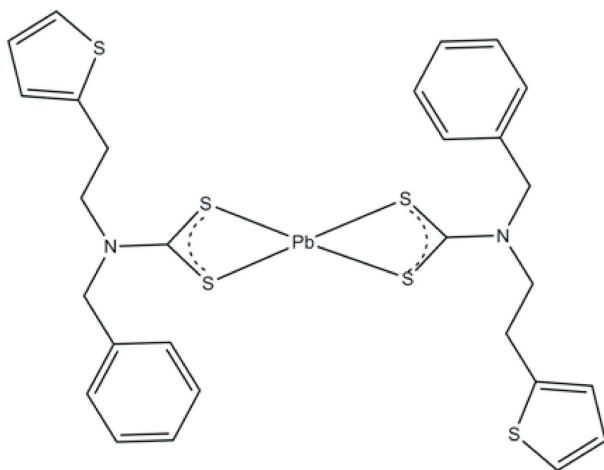
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Key indicators: single-crystal X-ray study; $T = 292$ K; mean $\sigma(C-C) = 0.003$ Å; disorder in main residue; R factor = 0.026; wR factor = 0.074; data-to-parameter ratio = 20.3.

The molecule of the title compound, $[Pb(C_{14}H_{14}NS_3)_2]$, is located on a twofold rotation axis. The dithiocarbamate anion S,S' -chelates to the Pb^{II} atom, which shows a Ψ -trigonal-bipyramidal coordination. The thiophene ring is disordered over two positions, the major component having 71.3 (7)% occupancy. The molecular conformation is stabilized by intramolecular $C-H \cdots S$ interactions.

Related literature

For a related structure, see: Sathiyaraj *et al.* (2012). For the superposition of structures, see: Gans & Shalloway (2001).



Experimental

Crystal data

$[Pb(C_{14}H_{14}NS_3)_2]$
 $M_r = 792.07$
 Monoclinic, $C2/c$
 $a = 27.459$ (2) Å
 $b = 5.5580$ (4) Å
 $c = 19.4670$ (15) Å
 $\beta = 100.168$ (2)°

$V = 2924.3$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 6.22$ mm⁻¹
 $T = 292$ K
 $0.20 \times 0.08 \times 0.06$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.699$, $T_{\max} = 0.707$

16187 measured reflections
 3487 independent reflections
 3089 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.074$
 $S = 1.01$
 3487 reflections
 172 parameters

23 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.91$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.84$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C2-H2A \cdots S1$	0.97	2.47	2.998 (4)	114
$C8-H8B \cdots S2$	0.97	2.53	2.988 (4)	109

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL2013 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5336).

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
 Bruker (2001). SMART, SADABS and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
 Gans, J. D. & Shalloway, D. (2001). *J. Mol. Graph. Model.* **19**, 557–559.
 Sathiyaraj, E., Thirumaran, S. & Selvanayagam, S. (2012). *Acta Cryst.* **E68**, m1217.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supporting information

Acta Cryst. (2013). E69, m457 [doi:10.1107/S1600536813019259]

Bis{N-benzyl-N-[2-(thiophen-2-yl)ethyl]dithiocarbamato- κ^2 S,S'}lead(II)

E. Sathiyaraj, S. Thirumaran, B. Sridhar and S. Selvanayagam

S1. Comment

In continuation of our work on the crystal structure analysis of lead complexes, we have undertaken a single-crystal X-ray diffraction study for the title compound, and the results are presented here.

The X-ray study confirmed the molecular structure and atomic connectivity for (I), as illustrated in Fig. 1. The Pb atom is coordinated by four sulfur atom from two dithiocarbamate anions. The asymmetry in Pb-S bonds suggests that the lone pair on Pb(II) is stereochemically active. The geometry of this coordination PbS₄ polyhedron is trigonal bipyramid. The geometry is similar to that reported for bis[N-benzyl-N-(2-phenylethyl)dithiocarbamato]lead(II) (Sathiyaraj *et al.*, 2012). The superposition of the coordination polyhedron (PbS₄) of (I) with this related reported structure, using Qmol (Gans & Shalloway, 2001) shows the r.m.s. deviation is 0.005 Å.

The sum of the angles at N1 [359.7°] is in accordance with sp² hybridization. The thiophene ring is disordered over two positions, with a major component being 71.3 (7)%. The dihedral angles between the phenyl and the major and minor components of the thiophene ring are 74.8 (1) and 74.7 (1)°, respectively.

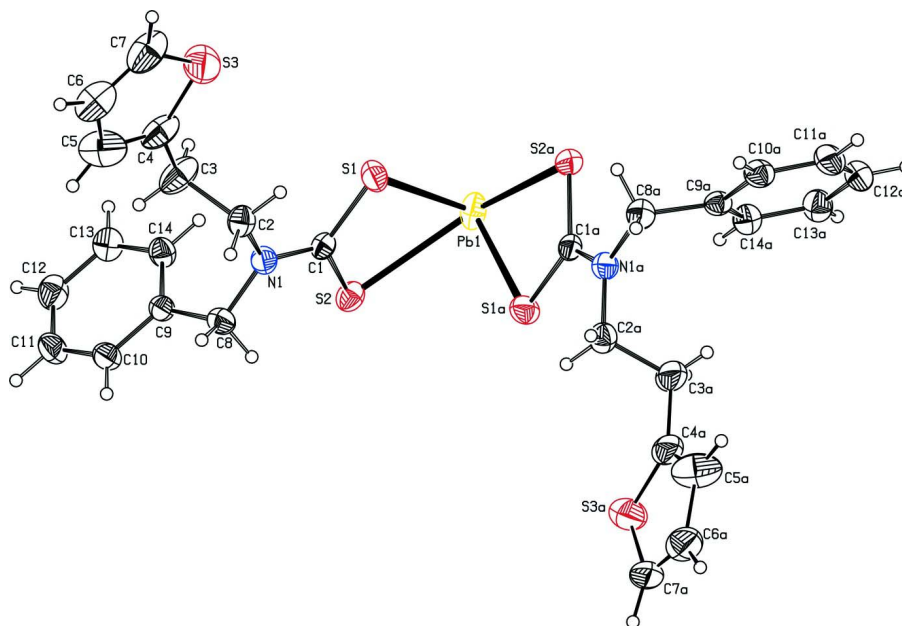
In addition to the van der Waals interactions, the molecular structure is influenced only by intramolecular C—H⋯S hydrogen bonds.

S2. Experimental

Benzyl(2-(thiophene-2-yl)ethyl)amine (4 mmol) and carbon disulfide (4 mmol) were dissolved in ethanol (20ml) and stirred for 30 minutes. To this solution, an aqueous solution (100 ml) of Pb(NO₃)₂ (2 mmol) was added with constant stirring. A pale yellow powder precipitated that was filtered and dried. Single crystals of (I) were obtained by slow evaporation of dichloromethane and acetone (1:1) solution of the title compound at room temperature.

S3. Refinement

H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.93–0.97 Å, and U_{iso}(H) = 1.2U_{eq}(C) for H atoms. The thiophene ring is disordered over two positions, with a major component being 71.3 (7)%. Pairs of C—S, C—C and C=C bond distances were restrained to 1.74 (1), 1.43 (1) and 1.37 (1) Å, respectively. The bond distances C3—C4 and C3—C4' were restrained to within 0.01 Å of each other. The temperature factors of C5' was set to those of S3 (as were these pairs: C4' to C4, S3' to C5, C6' to C6 and C7' to C7). The planarity of thiophene ring atoms were restrained to within 0.01 Å³ of each other. Pairs of C—S and C—C 1,3 bond distances were restrained to the values of 2.58 (1) and 2.33 (1) Å, respectively.

**Figure 1**

The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The minor occupied atoms of the disordered part have been omitted for clarity

Bis{*N*-benzyl-*N*-[2-(thiophen-2-yl)ethyl]dithiocarbamate- κ^2 S,S'}lead(II)

Crystal data

[Pb(C₁₄H₁₄NS₃)₂]

$M_r = 792.07$

Monoclinic, *C2/c*

$a = 27.459$ (2) Å

$b = 5.5580$ (4) Å

$c = 19.4670$ (15) Å

$\beta = 100.168$ (2)°

$V = 2924.3$ (4) Å³

$Z = 4$

$F(000) = 1552$

$D_x = 1.799$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8428 reflections

$\theta = 2.5$ – 27.6 °

$\mu = 6.22$ mm⁻¹

$T = 292$ K

Needle, yellow

$0.20 \times 0.08 \times 0.06$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2001)

$T_{\min} = 0.699$, $T_{\max} = 0.707$

16187 measured reflections

3487 independent reflections

3089 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 28.0$ °, $\theta_{\min} = 2.1$ °

$h = -35$ → 35

$k = -7$ → 7

$l = -25$ → 25

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.074$

$S = 1.01$

3487 reflections

172 parameters

23 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 2.5197P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.91 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.84 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Pb1	0.5000	1.14399 (3)	0.7500	0.06000 (9)	
S1	0.42993 (3)	0.80812 (17)	0.71606 (4)	0.0567 (2)	
S2	0.49150 (3)	0.95155 (16)	0.61228 (4)	0.05250 (18)	
N1	0.42564 (10)	0.5970 (5)	0.59289 (13)	0.0471 (5)	
C1	0.44701 (10)	0.7691 (6)	0.63555 (14)	0.0422 (5)	
C2	0.38975 (13)	0.4246 (6)	0.61323 (18)	0.0540 (7)	
H2A	0.3901	0.4389	0.6630	0.065*	
H2B	0.4000	0.2623	0.6042	0.065*	
C3	0.33791 (14)	0.4638 (10)	0.5748 (3)	0.0812 (13)	
H3A	0.3287	0.6302	0.5805	0.097*	
H3B	0.3370	0.4356	0.5255	0.097*	
S3	0.28129 (10)	0.3223 (5)	0.67259 (11)	0.0953 (8)	0.713 (7)
C4	0.3015 (4)	0.3061 (14)	0.5993 (4)	0.0749 (18)	0.713 (7)
C5	0.2819 (4)	0.1084 (14)	0.5602 (4)	0.098 (2)	0.713 (7)
H5	0.2893	0.0692	0.5168	0.118*	0.713 (7)
C6	0.2487 (2)	-0.0298 (10)	0.5950 (4)	0.087 (2)	0.713 (7)
H6	0.2320	-0.1674	0.5766	0.105*	0.713 (7)
C7	0.2449 (3)	0.0673 (15)	0.6581 (4)	0.096 (3)	0.713 (7)
H7	0.2256	0.0057	0.6887	0.115*	0.713 (7)
S3'	0.2817 (3)	0.0438 (10)	0.5716 (4)	0.098 (2)	0.287 (7)
C4'	0.3056 (10)	0.273 (4)	0.5972 (14)	0.0749 (18)	0.287 (7)
C5'	0.2874 (9)	0.372 (3)	0.6629 (9)	0.0953 (8)	0.287 (7)
H5'	0.2978	0.5133	0.6868	0.114*	0.287 (7)
C6'	0.2511 (6)	0.204 (3)	0.6800 (6)	0.087 (2)	0.287 (7)
H6'	0.2344	0.2224	0.7174	0.105*	0.287 (7)
C7'	0.2443 (6)	0.015 (3)	0.6342 (9)	0.096 (3)	0.287 (7)
H7'	0.2226	-0.1114	0.6364	0.115*	0.287 (7)
C8	0.44094 (12)	0.5488 (6)	0.52616 (16)	0.0519 (7)	
H8A	0.4392	0.3766	0.5180	0.062*	
H8B	0.4753	0.5963	0.5298	0.062*	
C9	0.41122 (7)	0.6731 (3)	0.46313 (8)	0.0426 (6)	
C10	0.41287 (8)	0.5775 (3)	0.39761 (10)	0.0541 (7)	
H10	0.4307	0.4373	0.3936	0.065*	
C11	0.38794 (9)	0.6913 (4)	0.33807 (8)	0.0647 (9)	
H11	0.3890	0.6273	0.2942	0.078*	
C12	0.36135 (9)	0.9008 (4)	0.34405 (9)	0.0665 (9)	

H12	0.3447	0.9769	0.3042	0.080*
C13	0.35970 (8)	0.9964 (3)	0.40957 (11)	0.0597 (8)
H13	0.3419	1.1366	0.4136	0.072*
C14	0.38463 (8)	0.8826 (3)	0.46911 (8)	0.0513 (7)
H14	0.3835	0.9466	0.5129	0.062*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.06332 (13)	0.04215 (11)	0.06445 (13)	0.000	−0.01642 (8)	0.000
S1	0.0622 (5)	0.0666 (5)	0.0418 (4)	−0.0148 (4)	0.0101 (3)	−0.0066 (3)
S2	0.0442 (4)	0.0575 (4)	0.0549 (4)	−0.0057 (3)	0.0064 (3)	0.0094 (3)
N1	0.0475 (13)	0.0506 (13)	0.0428 (12)	−0.0029 (10)	0.0064 (10)	−0.0014 (10)
C1	0.0369 (12)	0.0451 (14)	0.0425 (13)	0.0017 (11)	0.0009 (10)	0.0046 (12)
C2	0.0555 (17)	0.0498 (16)	0.0543 (17)	−0.0029 (14)	0.0028 (14)	0.0007 (14)
C3	0.0510 (19)	0.089 (3)	0.101 (3)	0.0012 (19)	0.0061 (19)	0.044 (3)
S3	0.0902 (14)	0.1277 (18)	0.0723 (11)	−0.0234 (11)	0.0257 (9)	0.0052 (10)
C4	0.046 (2)	0.079 (4)	0.098 (3)	0.007 (3)	0.009 (2)	0.036 (3)
C5	0.103 (2)	0.046 (3)	0.157 (4)	−0.014 (2)	0.054 (3)	−0.011 (3)
C6	0.070 (3)	0.071 (4)	0.119 (6)	−0.005 (3)	0.011 (4)	0.031 (4)
C7	0.062 (3)	0.120 (6)	0.103 (7)	−0.022 (3)	0.011 (4)	0.056 (6)
S3'	0.103 (2)	0.046 (3)	0.157 (4)	−0.014 (2)	0.054 (3)	−0.011 (3)
C4'	0.046 (2)	0.079 (4)	0.098 (3)	0.007 (3)	0.009 (2)	0.036 (3)
C5'	0.0902 (14)	0.1277 (18)	0.0723 (11)	−0.0234 (11)	0.0257 (9)	0.0052 (10)
C6'	0.070 (3)	0.071 (4)	0.119 (6)	−0.005 (3)	0.011 (4)	0.031 (4)
C7'	0.062 (3)	0.120 (6)	0.103 (7)	−0.022 (3)	0.011 (4)	0.056 (6)
C8	0.0540 (16)	0.0537 (17)	0.0485 (15)	0.0076 (14)	0.0106 (13)	−0.0070 (14)
C9	0.0415 (13)	0.0436 (14)	0.0439 (14)	−0.0071 (11)	0.0109 (11)	−0.0057 (11)
C10	0.0554 (17)	0.0604 (18)	0.0488 (16)	−0.0032 (14)	0.0157 (14)	−0.0080 (14)
C11	0.071 (2)	0.084 (3)	0.0416 (16)	−0.0063 (19)	0.0158 (16)	−0.0065 (16)
C12	0.066 (2)	0.081 (2)	0.0514 (18)	−0.0083 (18)	0.0062 (16)	0.0150 (17)
C13	0.0651 (19)	0.0493 (17)	0.0624 (19)	−0.0014 (15)	0.0049 (16)	0.0041 (15)
C14	0.0577 (18)	0.0453 (16)	0.0498 (16)	−0.0026 (13)	0.0062 (14)	−0.0076 (12)

Geometric parameters (Å, °)

Pb1—S1 ⁱ	2.6785 (9)	C7—H7	0.9300
Pb1—S1	2.6785 (9)	S3'—C4'	1.48 (2)
Pb1—S2	2.8575 (9)	S3'—C7'	1.733 (9)
Pb1—S2 ⁱ	2.8576 (9)	C4'—C5'	1.56 (3)
S1—C1	1.727 (3)	C5'—C6'	1.446 (9)
S2—C1	1.709 (3)	C5'—H5'	0.9300
N1—C1	1.333 (4)	C6'—C7'	1.369 (9)
N1—C8	1.459 (4)	C6'—H6'	0.9300
N1—C2	1.478 (4)	C7'—H7'	0.9300
C2—C3	1.502 (5)	C8—C9	1.515 (4)
C2—H2A	0.9700	C8—H8A	0.9700
C2—H2B	0.9700	C8—H8B	0.9700

C3—C4	1.471 (6)	C9—C10	1.3900
C3—C4'	1.497 (10)	C9—C14	1.3900
C3—H3A	0.9700	C10—C11	1.3900
C3—H3B	0.9700	C10—H10	0.9300
S3—C4	1.622 (7)	C11—C12	1.3900
S3—C7	1.728 (7)	C11—H11	0.9300
C4—C5	1.389 (8)	C12—C13	1.3900
C5—C6	1.449 (7)	C12—H12	0.9300
C5—H5	0.9300	C13—C14	1.3900
C6—C7	1.361 (7)	C13—H13	0.9300
C6—H6	0.9300	C14—H14	0.9300
S1 ⁱ —Pb1—S1	91.64 (5)	S3—C7—H7	125.1
S1 ⁱ —Pb1—S2	84.65 (2)	C4'—S3'—C7'	97.1 (11)
S1—Pb1—S2	64.63 (2)	S3'—C4'—C3	140 (2)
S1 ⁱ —Pb1—S2 ⁱ	64.63 (2)	S3'—C4'—C5'	113.3 (10)
S1—Pb1—S2 ⁱ	84.65 (2)	C3—C4'—C5'	106.3 (15)
S2—Pb1—S2 ⁱ	136.04 (3)	C6'—C5'—C4'	107.1 (7)
C1—S1—Pb1	90.74 (10)	C6'—C5'—H5'	126.4
C1—S2—Pb1	85.25 (10)	C4'—C5'—H5'	126.4
C1—N1—C8	121.5 (3)	C7'—C6'—C5'	111.3 (6)
C1—N1—C2	122.7 (3)	C7'—C6'—H6'	124.3
C8—N1—C2	115.5 (3)	C5'—C6'—H6'	124.3
N1—C1—S2	121.2 (2)	C6'—C7'—S3'	111.1 (7)
N1—C1—S1	119.7 (2)	C6'—C7'—H7'	124.4
S2—C1—S1	119.17 (18)	S3'—C7'—H7'	124.4
N1—C2—C3	113.0 (3)	N1—C8—C9	116.0 (2)
N1—C2—H2A	109.0	N1—C8—H8A	108.3
C3—C2—H2A	109.0	C9—C8—H8A	108.3
N1—C2—H2B	109.0	N1—C8—H8B	108.3
C3—C2—H2B	109.0	C9—C8—H8B	108.3
H2A—C2—H2B	107.8	H8A—C8—H8B	107.4
C4—C3—C2	113.0 (5)	C10—C9—C14	120.0
C4'—C3—C2	108.1 (12)	C10—C9—C8	117.94 (16)
C4—C3—H3A	109.0	C14—C9—C8	122.00 (16)
C2—C3—H3A	109.0	C11—C10—C9	120.0
C4—C3—H3B	109.0	C11—C10—H10	120.0
C2—C3—H3B	109.0	C9—C10—H10	120.0
H3A—C3—H3B	107.8	C12—C11—C10	120.0
C4—S3—C7	95.1 (3)	C12—C11—H11	120.0
C5—C4—C3	120.9 (7)	C10—C11—H11	120.0
C5—C4—S3	111.5 (4)	C11—C12—C13	120.0
C3—C4—S3	127.6 (5)	C11—C12—H12	120.0
C4—C5—C6	112.2 (5)	C13—C12—H12	120.0
C4—C5—H5	123.9	C14—C13—C12	120.0
C6—C5—H5	123.9	C14—C13—H13	120.0
C7—C6—C5	111.4 (5)	C12—C13—H13	120.0
C7—C6—H6	124.3	C13—C14—C9	120.0

C5—C6—H6	124.3	C13—C14—H14	120.0
C6—C7—S3	109.8 (4)	C9—C14—H14	120.0
C6—C7—H7	125.1		
C8—N1—C1—S2	3.1 (4)	C7'—S3'—C4'—C3	-169 (4)
C2—N1—C1—S2	175.4 (2)	C7'—S3'—C4'—C5'	0.01 (16)
C8—N1—C1—S1	-176.5 (2)	C4—C3—C4'—S3'	132 (12)
C2—N1—C1—S1	-4.1 (4)	C2—C3—C4'—S3'	-102 (3)
Pb1—S2—C1—N1	-175.3 (2)	C4—C3—C4'—C5'	-38 (9)
Pb1—S2—C1—S1	4.30 (16)	C2—C3—C4'—C5'	88.1 (9)
Pb1—S1—C1—N1	175.0 (2)	S3'—C4'—C5'—C6'	0.0 (2)
Pb1—S1—C1—S2	-4.57 (17)	C3—C4'—C5'—C6'	173 (2)
C1—N1—C2—C3	110.3 (4)	C4'—C5'—C6'—C7'	0.0 (4)
C8—N1—C2—C3	-76.9 (4)	C5'—C6'—C7'—S3'	0.0 (5)
N1—C2—C3—C4	-175.1 (5)	C4'—S3'—C7'—C6'	0.0 (4)
N1—C2—C3—C4'	177.4 (13)	C1—N1—C8—C9	-94.7 (3)
C4'—C3—C4—C5	-48 (9)	C2—N1—C8—C9	92.4 (3)
C2—C3—C4—C5	-104.5 (6)	N1—C8—C9—C10	-159.4 (2)
C4'—C3—C4—S3	129 (10)	N1—C8—C9—C14	23.5 (4)
C2—C3—C4—S3	71.9 (10)	C14—C9—C10—C11	0.0
C7—S3—C4—C5	0.00 (15)	C8—C9—C10—C11	-177.2 (2)
C7—S3—C4—C3	-176.7 (11)	C9—C10—C11—C12	0.0
C3—C4—C5—C6	177.2 (10)	C10—C11—C12—C13	0.0
S3—C4—C5—C6	0.2 (2)	C11—C12—C13—C14	0.0
C4—C5—C6—C7	-0.4 (4)	C12—C13—C14—C9	0.0
C5—C6—C7—S3	0.4 (4)	C10—C9—C14—C13	0.0
C4—S3—C7—C6	-0.2 (3)	C8—C9—C14—C13	177.1 (2)

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

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C2—H2 <i>A</i> \cdots S1	0.97	2.47	2.998 (4)	114
C8—H8 <i>B</i> \cdots S2	0.97	2.53	2.988 (4)	109