Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[*N*-benzyl-*N*-(2-phenylethyl)dithiocarbamato-κ^2S,S']lead(II)

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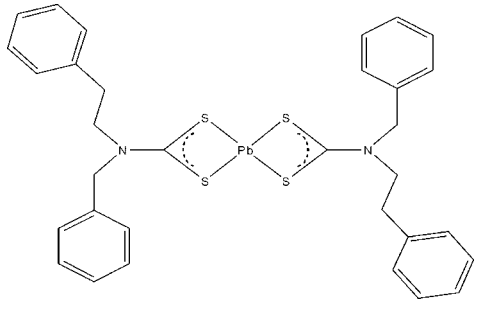
Received 13 July 2012; accepted 17 August 2012

Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.005 Å; R factor = 0.028; wR factor = 0.062; data-to-parameter ratio = 21.0.

The molecule of the title compound, $[Pb(C_{16}H_{16}NS_2)_2]$, is located on a twofold rotation axis, which runs through the Pb^{II} atom. The two dithiocarbamate ligands coordinate the metal in a pyramidal configuration through the S atoms. The two phenyl rings of each dithocarbamate ligand are aligned at a dihedral angle of 78.4 (1)°. The molecular conformation is stabilized by intramolecular C—H···S interactions.

Related literature

For general background of the title compound, see: Davidovich *et al.* (2010); Picket & O'Brien (2001); Srinivasan & Thirumaran (2012); Sathiyaraj & Thirumaran (2012); Green *et al.* (2004); Koh *et al.* (2003). For the preparation, see: Sathiyaraj & Thirumaran (2012). For a related structure, see: Davidovich *et al.* (2010)



Experimental

Crystal data

$[Pb(C_{16}H_{16}NS_2)_2]$ M_r = 780.03
Monoclinic, $C2/c$
a = 28.5467 (12) Å
b = 5.5321 (2) Å
c = 19.4158 (8) Å
β = 101.600 (2)°
V = 3003.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.92 mm^{-1}
T = 292 K
0.20 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.384, T_{max} = 0.384
13027 measured reflections
3711 independent reflections
3006 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.062
S = 1.04
3711 reflections
177 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −1.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···S2	0.97	2.49	2.986 (3)	112
C2—H2B···S1	0.97	2.55	2.990 (4)	107

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

The authors thank the CAS in Crystallography and Biophysics, University of Madras, Chennai for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5972).

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supporting information

Acta Cryst. (2012). E**68**, m1217 [doi:10.1107/S1600536812036161]

Bis[*N*-benzyl-*N*-(2-phenylethyl)dithiocarbamato-$\kappa^2 S,S'$]lead(II)

E. Sathiyaraj, S. Thirumaran and S. Selvanayagam

S1. Comment

The solid state structural chemistry of lead dithiocarbamates is rich and fascinating in that different structural motifs are found ranging from monomeric, dimeric, tetrameric to linear chain (Davidovich *et al.*, 2010). Metal dithiocarbamate complexes have proven to be very successful as single source precursors for the preparation of metal sulfide nanoparticles (Picket & O′Brien, 2001; Srinivasan & Thirumaran, 2012). The title compound was also used as single source precursor for the synthesis of PbS nanoparticles (Sathiyaraj & Thirumaran, 2012). There is an indication that the molecular structure of the synthetic precursor may influence both the size and morphology of the nanoparticles (Green *et al.*, 2004; Koh *et al.*, 2003). In view of these importance we have undertaken the crystal structure determination of 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 structure consists of monomeric molecules composed of one Pb atom and two chelating dithiocarbamate ligands. The two dithiocarbamate ligands are coordinated through S atoms to the metal pyramidally and in each chelate ring one Pb-S bond is significantly shorter than other. The relative bond distances and angles for the title compound agree with the presence of an electron lone pair at an equatorial position of a distorted trigonal bipyramid PbS_4. Evidence for the presence of a stereochemically active electron lone pair of the lead atom has also been reported for other lead complexes (Davidovich *et al.*, 2010).

The sum of the angles at N1 [359.8°] is in accordance with sp^2 hybridization. Two phenyl rings in dithiocarbmate ligand is make a dihedral angle of 78.4 (1) °.

In addition to the van der Waals interactions, the molecular structure is influenced only by intramolecular C—H···S hydrogen bonds involving atoms S1 and S2. (Fig. 2 and Table 1).

S2. Experimental

The title compound was prepared according to the literature procedure (Sathiyaraj & Thirumaran, 2012). Single crystals 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 Uiso(H) = $1.2U_{eq}$(C) for H atoms.

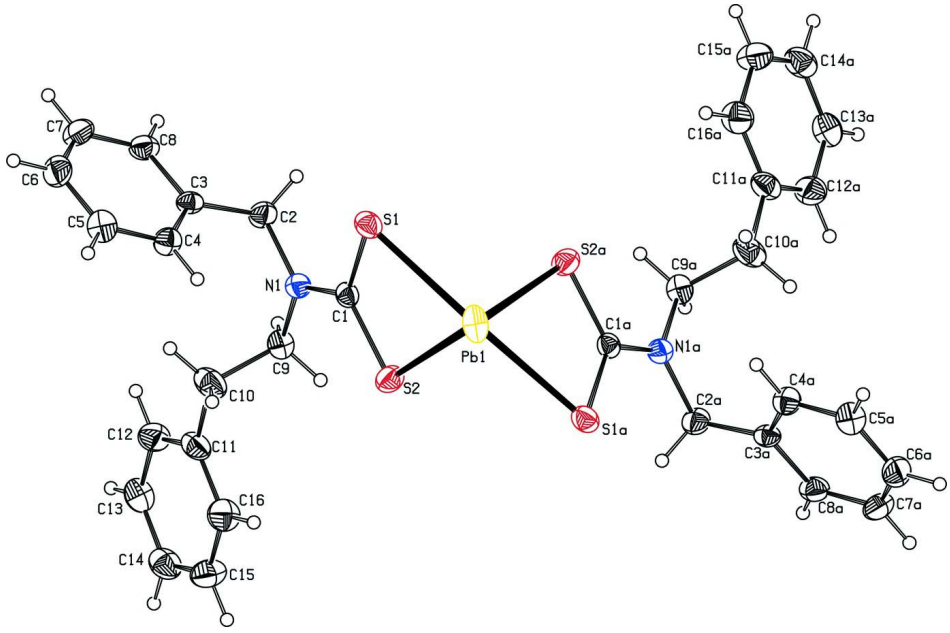

Figure 1

The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

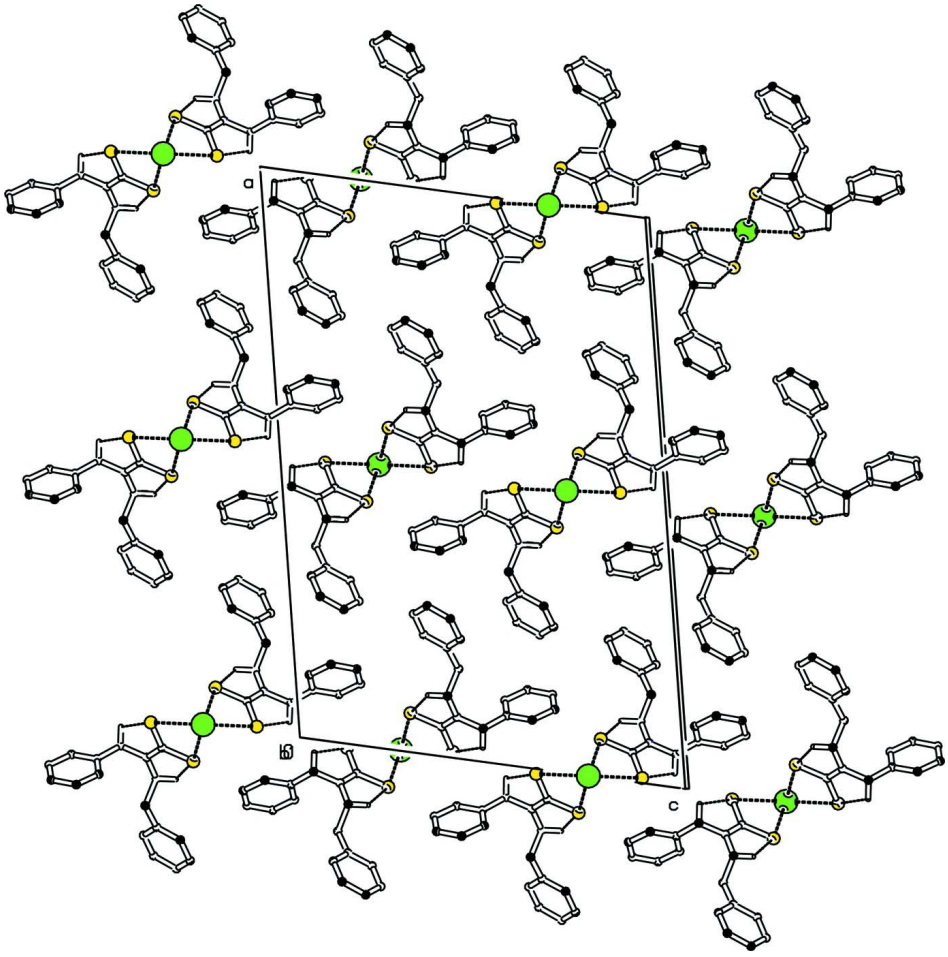

Figure 2

Molecular packing of the title compound, viewed along the *b* axis; H-bonds are shown as dashed lines. For the sake of clarity, H atoms, not involved in hydrogen bonds, have been omitted.

Bis[*N*-benzyl-*N*-(2-phenylethyl)dithiocarbamato- κ^2S,S']lead(II)

Crystal data

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$M_r = 780.03$
Monoclinic, *C*2/*c*
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$a = 28.5467\ (12)$ Å
$b = 5.5321\ (2)$ Å
$c = 19.4158\ (8)$ Å
$\beta = 101.600\ (2)°$
$V = 3003.6\ (2)$ Å^3
$Z = 4$
$F(000) = 1536$
$D_x = 1.725$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5527 reflections
$\theta = 1.5–28.3°$
$\mu = 5.92$ mm^{-1}
$T = 292$ K
Block, brown
0.20 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.384$, $T_{max} = 0.384$

13027 measured reflections
3711 independent reflections
3006 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 28.3°$, $\theta_{min} = 1.5°$
$h = -37 \rightarrow 31$
$k = -7 \rightarrow 7$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.062$
$S = 1.04$
3711 reflections
177 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 1.657P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -1.25$ 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.

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pb1	1.0000	1.14280 (3)	0.7500	0.05084 (8)
S1	0.99115 (3)	0.94809 (17)	0.61154 (4)	0.04494 (19)
S2	0.93213 (3)	0.80487 (16)	0.71424 (4)	0.0473 (2)
N1	0.92789 (9)	0.5899 (4)	0.59107 (12)	0.0373 (6)
C1	0.94871 (10)	0.7651 (6)	0.63419 (14)	0.0339 (6)
C2	0.94211 (11)	0.5417 (6)	0.52408 (15)	0.0440 (7)
H2A	0.9397	0.3691	0.5153	0.053*
H2B	0.9755	0.5862	0.5287	0.053*
C3	0.91358 (11)	0.6706 (5)	0.46061 (15)	0.0343 (6)
C4	0.88722 (12)	0.8758 (5)	0.46490 (17)	0.0427 (7)
H4	0.8853	0.9369	0.5089	0.051*
C5	0.86360 (12)	0.9926 (6)	0.40547 (17)	0.0498 (8)
H5	0.8460	1.1317	0.4095	0.060*
C6	0.86593 (13)	0.9041 (7)	0.34018 (18)	0.0571 (10)
H6	0.8501	0.9832	0.2999	0.069*
C7	0.89154 (14)	0.6993 (8)	0.33484 (17)	0.0569 (10)
H7	0.8931	0.6391	0.2906	0.068*
C8	0.91528 (12)	0.5799 (6)	0.39433 (16)	0.0453 (8)
H8	0.9323	0.4393	0.3900	0.054*
C9	0.89245 (11)	0.4222 (6)	0.61033 (17)	0.0419 (7)
H9A	0.8957	0.4225	0.6610	0.050*

H9B	0.8992	0.2598	0.5962	0.050*
C10	0.84215 (12)	0.4865 (8)	0.5771 (2)	0.0612 (10)
H10A	0.8382	0.4756	0.5264	0.073*
H10B	0.8360	0.6523	0.5888	0.073*
C11	0.80629 (12)	0.3225 (6)	0.60110 (19)	0.0492 (8)
C12	0.78865 (14)	0.1181 (7)	0.5636 (2)	0.0564 (9)
H12	0.8000	0.0762	0.5236	0.068*
C13	0.75473 (12)	−0.0232 (7)	0.58444 (19)	0.0542 (9)
H13	0.7434	−0.1599	0.5585	0.065*
C14	0.73735 (13)	0.0338 (7)	0.6428 (2)	0.0579 (9)
H14	0.7137	−0.0608	0.6561	0.070*
C15	0.75511 (14)	0.2325 (8)	0.68166 (19)	0.0629 (10)
H15	0.7439	0.2719	0.7220	0.075*
C16	0.78937 (14)	0.3730 (6)	0.6612 (2)	0.0584 (10)
H16	0.8015	0.5057	0.6885	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.05114 (13)	0.03239 (11)	0.05977 (12)	0.000	−0.01087 (8)	0.000
S1	0.0350 (4)	0.0494 (5)	0.0505 (4)	−0.0041 (4)	0.0088 (3)	0.0104 (4)
S2	0.0515 (5)	0.0542 (5)	0.0374 (4)	−0.0131 (4)	0.0120 (4)	−0.0068 (4)
N1	0.0362 (14)	0.0397 (14)	0.0366 (12)	−0.0003 (11)	0.0088 (11)	−0.0024 (11)
C1	0.0303 (15)	0.0344 (15)	0.0355 (14)	0.0031 (13)	0.0033 (12)	0.0036 (13)
C2	0.0473 (19)	0.0463 (18)	0.0398 (15)	0.0094 (16)	0.0121 (14)	−0.0061 (15)
C3	0.0352 (16)	0.0323 (16)	0.0381 (14)	−0.0058 (12)	0.0142 (13)	−0.0051 (12)
C4	0.0476 (19)	0.0378 (18)	0.0431 (16)	−0.0015 (14)	0.0100 (14)	−0.0079 (14)
C5	0.054 (2)	0.0366 (19)	0.0565 (19)	0.0008 (15)	0.0067 (16)	0.0025 (16)
C6	0.055 (2)	0.068 (3)	0.0470 (19)	−0.0091 (19)	0.0068 (17)	0.0178 (18)
C7	0.062 (2)	0.075 (3)	0.0374 (17)	−0.008 (2)	0.0185 (17)	−0.0050 (17)
C8	0.0453 (19)	0.0483 (19)	0.0460 (17)	−0.0039 (15)	0.0182 (15)	−0.0098 (15)
C9	0.0423 (18)	0.0355 (16)	0.0459 (16)	0.0000 (14)	0.0045 (14)	−0.0028 (14)
C10	0.041 (2)	0.067 (3)	0.076 (2)	0.0087 (18)	0.0135 (18)	0.030 (2)
C11	0.0356 (18)	0.052 (2)	0.061 (2)	0.0064 (15)	0.0116 (16)	0.0140 (17)
C12	0.052 (2)	0.063 (3)	0.057 (2)	0.0107 (18)	0.0173 (18)	−0.0014 (19)
C13	0.049 (2)	0.043 (2)	0.066 (2)	−0.0022 (16)	0.0033 (17)	−0.0008 (18)
C14	0.047 (2)	0.057 (2)	0.071 (2)	−0.0051 (18)	0.0141 (19)	0.016 (2)
C15	0.069 (3)	0.069 (3)	0.058 (2)	−0.007 (2)	0.029 (2)	−0.001 (2)
C16	0.058 (2)	0.054 (2)	0.063 (2)	−0.0103 (17)	0.0127 (19)	−0.0096 (17)

Geometric parameters (Å, º)

Pb1—S2^{i}	2.6813 (8)	C7—C8	1.384 (5)
Pb1—S2	2.6813 (8)	C7—H7	0.9300
Pb1—S1^{i}	2.8597 (9)	C8—H8	0.9300
Pb1—S1	2.8597 (9)	C9—C10	1.494 (4)
S1—C1	1.703 (3)	C9—H9A	0.9700
S2—C1	1.727 (3)	C9—H9B	0.9700

N1—C1	1.339 (4)	C10—C11	1.510 (5)
N1—C2	1.463 (4)	C10—H10A	0.9700
N1—C9	1.475 (4)	C10—H10B	0.9700
C2—C3	1.512 (4)	C11—C16	1.378 (5)
C2—H2A	0.9700	C11—C12	1.384 (5)
C2—H2B	0.9700	C12—C13	1.368 (5)
C3—C4	1.373 (4)	C12—H12	0.9300
C3—C8	1.391 (4)	C13—C14	1.362 (5)
C4—C5	1.375 (4)	C13—H13	0.9300
C4—H4	0.9300	C14—C15	1.372 (6)
C5—C6	1.373 (5)	C14—H14	0.9300
C5—H5	0.9300	C15—C16	1.369 (5)
C6—C7	1.363 (5)	C15—H15	0.9300
C6—H6	0.9300	C16—H16	0.9300

$S2^{i}$—Pb1—S2	91.59 (4)	C8—C7—H7	119.6
$S2^{i}$—Pb1—$S1^{i}$	64.61 (2)	C7—C8—C3	119.8 (3)
S2—Pb1—$S1^{i}$	84.46 (2)	C7—C8—H8	120.1
$S2^{i}$—Pb1—S1	84.46 (2)	C3—C8—H8	120.1
S2—Pb1—S1	64.61 (2)	N1—C9—C10	112.9 (3)
$S1^{i}$—Pb1—S1	135.74 (4)	N1—C9—H9A	109.0
C1—S1—Pb1	85.08 (10)	C10—C9—H9A	109.0
C1—S2—Pb1	90.43 (11)	N1—C9—H9B	109.0
C1—N1—C2	121.3 (3)	C10—C9—H9B	109.0
C1—N1—C9	122.5 (2)	H9A—C9—H9B	107.8
C2—N1—C9	116.0 (2)	C9—C10—C11	112.1 (3)
N1—C1—S1	121.2 (2)	C9—C10—H10A	109.2
N1—C1—S2	119.2 (2)	C11—C10—H10A	109.2
S1—C1—S2	119.63 (17)	C9—C10—H10B	109.2
N1—C2—C3	116.0 (2)	C11—C10—H10B	109.2
N1—C2—H2A	108.3	H10A—C10—H10B	107.9
C3—C2—H2A	108.3	C16—C11—C12	117.3 (3)
N1—C2—H2B	108.3	C16—C11—C10	121.0 (3)
C3—C2—H2B	108.3	C12—C11—C10	121.7 (3)
H2A—C2—H2B	107.4	C13—C12—C11	121.1 (3)
C4—C3—C8	118.4 (3)	C13—C12—H12	119.5
C4—C3—C2	123.5 (3)	C11—C12—H12	119.5
C8—C3—C2	118.1 (3)	C14—C13—C12	120.8 (3)
C3—C4—C5	121.3 (3)	C14—C13—H13	119.6
C3—C4—H4	119.3	C12—C13—H13	119.6
C5—C4—H4	119.3	C13—C14—C15	119.2 (3)
C6—C5—C4	120.0 (3)	C13—C14—H14	120.4
C6—C5—H5	120.0	C15—C14—H14	120.4
C4—C5—H5	120.0	C16—C15—C14	120.1 (3)
C7—C6—C5	119.5 (3)	C16—C15—H15	119.9
C7—C6—H6	120.2	C14—C15—H15	119.9
C5—C6—H6	120.2	C15—C16—C11	121.5 (3)
C6—C7—C8	120.9 (3)	C15—C16—H16	119.2

C6—C7—H7	119.6	C11—C16—H16	119.2
S2^{i}—Pb1—S1—C1	91.43 (10)	C3—C4—C5—C6	0.3 (5)
S2—Pb1—S1—C1	−2.98 (10)	C4—C5—C6—C7	0.4 (5)
S1^{i}—Pb1—S1—C1	47.21 (10)	C5—C6—C7—C8	−0.1 (6)
S2^{i}—Pb1—S2—C1	−80.18 (10)	C6—C7—C8—C3	−0.8 (5)
S1^{i}—Pb1—S2—C1	−144.48 (10)	C4—C3—C8—C7	1.4 (5)
S1—Pb1—S2—C1	2.93 (10)	C2—C3—C8—C7	−176.9 (3)
C2—N1—C1—S1	2.6 (4)	C1—N1—C9—C10	101.6 (3)
C9—N1—C1—S1	177.5 (2)	C2—N1—C9—C10	−83.3 (3)
C2—N1—C1—S2	−177.3 (2)	N1—C9—C10—C11	−176.3 (3)
C9—N1—C1—S2	−2.4 (4)	C9—C10—C11—C16	87.0 (4)
Pb1—S1—C1—N1	−175.1 (2)	C9—C10—C11—C12	−93.8 (4)
Pb1—S1—C1—S2	4.81 (16)	C16—C11—C12—C13	1.9 (5)
Pb1—S2—C1—N1	174.8 (2)	C10—C11—C12—C13	−177.3 (3)
Pb1—S2—C1—S1	−5.11 (17)	C11—C12—C13—C14	0.1 (5)
C1—N1—C2—C3	−92.9 (3)	C12—C13—C14—C15	−1.5 (6)
C9—N1—C2—C3	91.9 (3)	C13—C14—C15—C16	1.0 (6)
N1—C2—C3—C4	20.9 (5)	C14—C15—C16—C11	1.1 (6)
N1—C2—C3—C8	−160.9 (3)	C12—C11—C16—C15	−2.5 (5)
C8—C3—C4—C5	−1.1 (5)	C10—C11—C16—C15	176.7 (4)
C2—C3—C4—C5	177.0 (3)		

Symmetry code: (i) −*x*+2, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···S2	0.97	2.49	2.986 (3)	112
C2—H2*B*···S1	0.97	2.55	2.990 (4)	107