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(Benzylthiolato-κS)phenylmercury(II)

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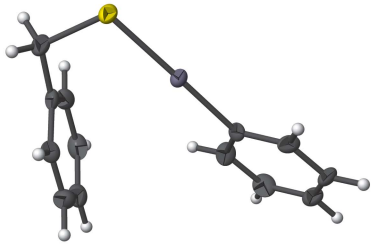
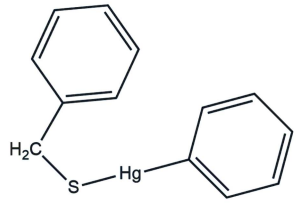
The title complex, $[Hg(C_6H_5)(C_7H_7S)]$, was synthesized from benzyl 4-methylpiperidine-1-carbodithioate. In the complex, the Hg^{II} cation binds to a C atom of a phenyl ring and the S atom of a benzylthiolate ligand in a linear coordination geometry. The molecule is bent at the methylene C atom and the S atom, resulting in a *syn* conformation with respect to the benzyl and phenyl rings. The dihedral angle between the phenyl and benzyl rings is 64.6 (2)°. The crystal structure is stabilized by intermolecular Hg$\cdots$S [3.290 (3) Å] contacts and C—H$\cdots\pi$ interactions, generating a three-dimensional network.

3D view



Chemical scheme



Structure description

Organomercury(II) cations have a high affinity for bonding through the sulfur donor sites present in amino acids, peptides and proteins (Clarkson & Magos, 2006; Hoffmeyer *et al.*, 2006; Rooney, 2007). Crystal structures of several phenylmercury(II) complexes with Hg—S bonds and strong intermolecular Hg$\cdots$S interactions have been reported (Yadav *et al.*, 2014; Bharti *et al.*, 2013; Nath *et al.*, 2016). Mercury has long been used in medicine and industry which has caused toxicity problems. All forms of mercury are toxic in high doses (Clifton, 2007). Compounds with a mercapto group *e.g.* 2,3-dimercaptopropanol (British Anti-Lewisite) are used as antidotes in cases of mercury poisoning (Canty & Kishimoto, 1975). 4-Methyl-piperidinecarbodithioate forms a linear mercury(II) complex in which the dithiosulfur atom coordinates to the mercury(II) ion (Nath *et al.*, 2016; Dar *et al.*, 2015) while in the present work the benzyl ester undergoes cleavage and a sulfur atom from the benzyl mercapto moiety of the ligand coordinates to the mercury(II) cation (Fig. 1). Some complexes of the benzenemethanethiolato ligand have been reported previously (Wong *et al.*, 2005; Papadopoulos *et al.*, 1996; Berg *et al.*, 1979). Sachs

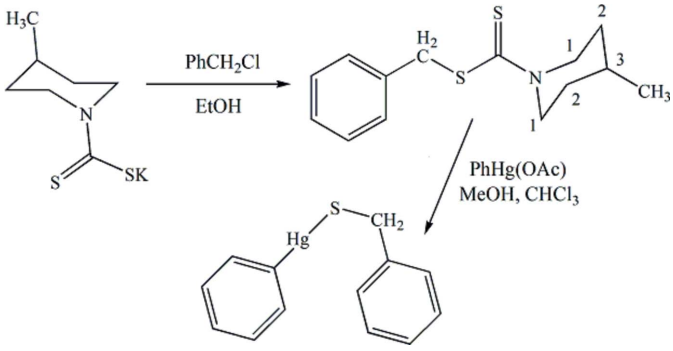


Figure 1
A reaction scheme showing the synthesis of the title compound.

has reported many organo-mercury mercaptides, including this complex, but the crystal structure data was not reported (Sachs, 1923). Therefore, in this work we report the synthesis (Fig. 1), spectroscopic data and crystal structure of the title complex.

The molecular structure of the title complex is shown in Fig. 2. The Hg^{II} cation is bound to the phenyl *ipso*-carbon and the thiolato sulfur atom of a benzenemethanethiolato ligand. This is generated *in situ* during the preparation. The geometry around Hg^{II} is almost linear C1—Hg—S1 = 178.0 (3)°. The phenyl rings (C1–C6 and C8–C13) are inclined to one another at a dihedral angle of 64.6 (2)°. The Hg—S1 bond length is 2.360 (2) Å which is quite similar to other reported Hg—S bonds (Bharti *et al.*, 2013; Nath *et al.*, 2016). The molecule is bent at the sulfur atom and methylene carbon with bond angles of 104.4 (3) and 111.4 (6)°, respectively, which is close to the regular tetrahedral angle. The Hg—S1—C7—C8 torsion angle of 2.7 (9)° reflects the fact that the benzyl and phenylmercury groups are in a *syn* orientation with respect to one another.

Molecules in the crystal structure are stabilized by intermolecular Hg···S interactions [Hg···S^{iv} 3.290 (3) Å; iv = $-x+\frac{3}{2}, -y+\frac{3}{2}, z+1/2$] (Fig. 3) and three C—H···π interactions (Fig. 4, Table 1), leading to a three-dimensional network.

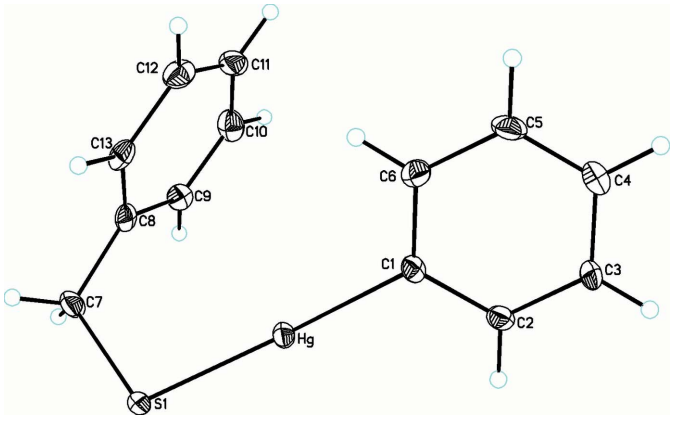


Figure 2
The molecular structure of the title compound, showing 50% probability displacement ellipsoids.

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

*Cg*1, *Cg*2 are the centroids of the benzene C1–C6 and C8–C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*A*···*Cg*1^{i}	0.95	3.00	3.799 (4)	143
C7—H7*A*···*Cg*1^{ii}	0.99	2.98	3.913 (8)	157
C11—H11*A*···*Cg*2^{iii}	0.95	2.63	3.547 (6)	162

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

Synthesis and crystallization

A mixture of potassium 4-methyl-piperidinecarbodithioate (Nath *et al.*, 2016) and benzyl chloride in absolute methanol was stirred for 3 h at room temperature. The solid benzyl 4-methylpiperidine-1-carbodithioate obtained upon removal of the solvent was washed with CCl_4 and dried. A mixture of a methanol–chloroform solution (50:50) of phenylmercury acetate 0.674 g (2 mmol) and benzyl 4-methylpiperidine-1-carbodithioate 0.531 g (2 mmol) was stirred for 2 h at at room temperature. The clear solution was filtered off and kept for crystallization, colourless prismatic crystals of the title compound suitable for X-ray analyses were obtained after 8 d (Fig. 1) Yield: 60%; m.p.: 392–394 K. Analysis found. C, 39.30; H, 3.12; S, 7.83%. Calculated for $C_{13}H_{12}HgS$ (400.88): C, 38.94; H, 3.01; S, 8.00%. IR (selected, KBr): 3063 [ν(C—H)], 2940 [ν(C—H)], 731 [ν(C—S)] cm^{-1}. ^1H NMR ($CDCl_3$): δ [p.p.m.] =

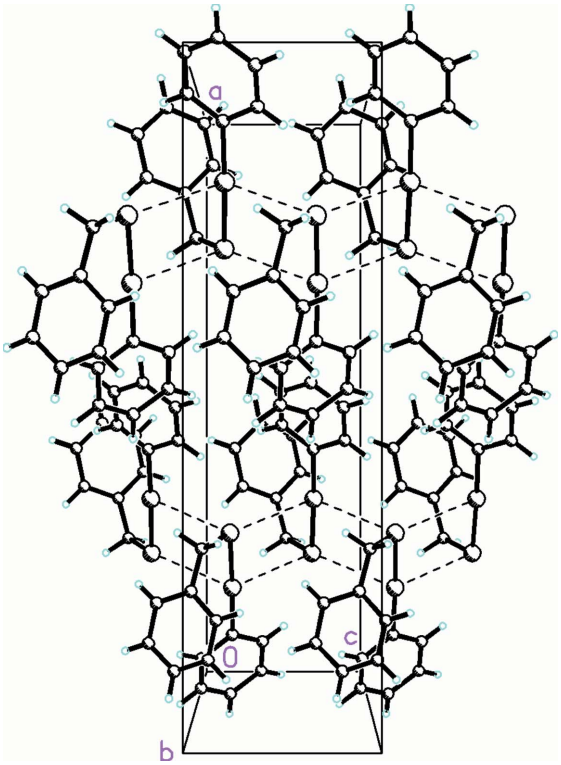


Figure 3
Crystal packing of the title compound, viewed along the *b* axis. Dashed lines indicate intermolecular Hg···S interactions.

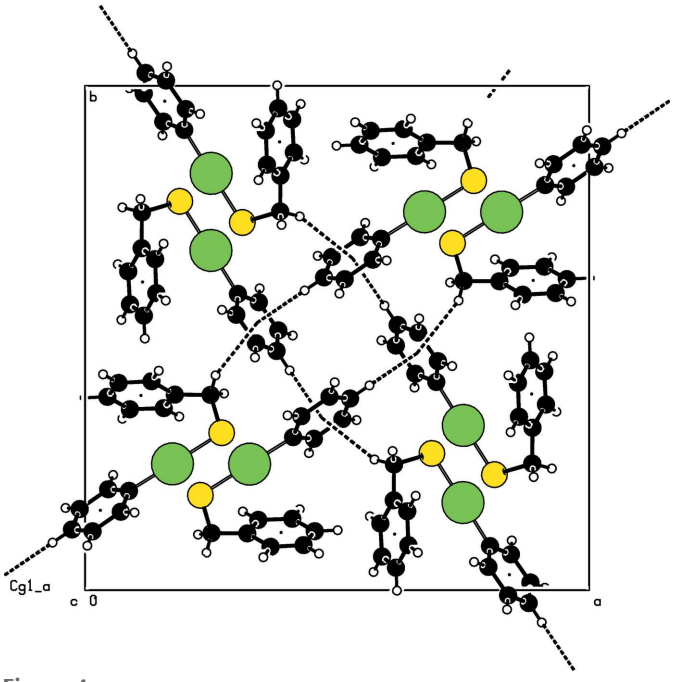


Figure 4
A view of the packing along the *c* axis, showing the C—H···π contacts.

4.23 (*s*, 2H, CH_2), 7.04–7.44 (*m*, 10H, aromatic H). ^{13}C NMR ($CDCl_3$): δ [p.p.m.] = 32.0 (CH_2), 127.2–146.5 (aromatic C).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Hg(C_6H_5)(C_7H_7S)]$
M_r	400.88
Crystal system, space group	Tetragonal, $I\overline{4}$
Temperature (K)	173
a, *c* (Å)	20.4402 (6), 5.7266 (4)
V (Å^3)	2392.6 (2)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	13.00
Crystal size (mm)	0.60 × 0.25 × 0.22
Data collection	
Diffractometer	Rigaku Xcalibur, Eos, Gemini
Absorption correction	Analytical (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.011, 0.123
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4085, 4085, 3706
R_{int}	0.085
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.760
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.035, 0.075, 1.04
No. of reflections	4085
No. of parameters	136
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.96, −1.26
Absolute structure	Flack *x* determined using 1447 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.006 (10)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *SHELXTL* (Sheldrick, 2008).

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170503 [https://doi.org/10.1107/S241431461700503X]

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(Benzylthiolato-κS)phenylmercury(II)

Crystal data

$[Hg(C_6H_5)(C_7H_7S)]$
M_r = 400.88
Tetragonal, $I\overline{4}$
a = 20.4402 (6) Å
c = 5.7266 (4) Å
V = 2392.6 (2) Å^3
Z = 8
$F(000)$ = 1488
D_x = 2.226 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4836 reflections
θ = 3.7–32.2°
μ = 13.00 mm^{-1}
T = 173 K
Prismatic, colourless
0.60 × 0.25 × 0.22 mm

Data collection

Rigaku Xcalibur, Eos, Gemini diffractometer
Radiation source: fine-focus sealed X-ray tube
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: analytical (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.011, T_{max} = 0.123
4085 measured reflections
4085 independent reflections
3706 reflections with $I > 2\sigma(I)$
R_{int} = 0.085
θ_{max} = 32.7°, θ_{min} = 3.2°
h = −29→30
k = −30→31
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.075
S = 1.04
4085 reflections
136 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.96 e Å^{-3}
$\Delta\rho_{min}$ = −1.26 e Å^{-3}
Absolute structure: Flack x determined using 1447 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.006 (10)

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}
Hg	0.67354 (2)	0.75027 (2)	0.68688 (6)	0.02102 (8)
S1	0.77105 (10)	0.81205 (10)	0.6783 (5)	0.0240 (4)
C1	0.5873 (4)	0.6967 (4)	0.6822 (19)	0.0208 (16)
C2	0.5709 (4)	0.6553 (5)	0.8683 (17)	0.026 (2)
H2A	0.5983	0.6536	1.0021	0.031*
C3	0.5150 (4)	0.6166 (5)	0.8591 (18)	0.029 (2)
H3A	0.5047	0.5879	0.9846	0.035*
C4	0.4742 (4)	0.6201 (4)	0.6637 (19)	0.0277 (19)
H4A	0.4357	0.5941	0.6564	0.033*
C5	0.4895 (5)	0.6608 (5)	0.4846 (19)	0.033 (2)
H5A	0.4614	0.6629	0.3525	0.040*
C6	0.5460 (5)	0.6999 (5)	0.4901 (18)	0.030 (2)
H6A	0.5558	0.7283	0.3635	0.036*
C7	0.7490 (4)	0.8871 (5)	0.516 (2)	0.035 (3)
H7A	0.7590	0.9258	0.6136	0.042*
H7B	0.7758	0.8899	0.3724	0.042*
C8	0.6781 (4)	0.8876 (4)	0.4522 (19)	0.0234 (18)
C9	0.6320 (5)	0.9142 (4)	0.6053 (18)	0.026 (2)
H9A	0.6462	0.9349	0.7449	0.031*
C10	0.5666 (5)	0.9108 (5)	0.556 (2)	0.034 (2)
H10A	0.5359	0.9278	0.6652	0.041*
C11	0.5444 (5)	0.8833 (5)	0.351 (2)	0.035 (3)
H11A	0.4988	0.8813	0.3191	0.042*
C12	0.5890 (5)	0.8585 (5)	0.194 (2)	0.033 (2)
H12A	0.5741	0.8399	0.0514	0.039*
C13	0.6563 (5)	0.8609 (5)	0.2429 (16)	0.027 (2)
H13A	0.6869	0.8442	0.1332	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg	0.01884 (15)	0.02023 (16)	0.02399 (15)	−0.00296 (12)	0.00159 (14)	0.00177 (14)
S1	0.0174 (9)	0.0257 (10)	0.0288 (11)	−0.0027 (7)	−0.0027 (10)	0.0064 (11)
C1	0.021 (4)	0.014 (3)	0.028 (4)	−0.003 (3)	−0.001 (4)	−0.004 (4)
C2	0.018 (4)	0.034 (5)	0.026 (5)	0.002 (3)	−0.001 (3)	0.003 (4)
C3	0.017 (4)	0.032 (5)	0.038 (6)	−0.005 (3)	0.004 (4)	0.010 (4)
C4	0.022 (4)	0.029 (4)	0.033 (5)	−0.005 (3)	0.003 (4)	−0.006 (4)
C5	0.029 (5)	0.036 (5)	0.034 (6)	−0.002 (4)	−0.016 (4)	−0.002 (4)
C6	0.032 (5)	0.031 (5)	0.026 (5)	−0.004 (4)	−0.007 (4)	0.005 (4)
C7	0.018 (4)	0.030 (5)	0.058 (8)	−0.005 (3)	−0.003 (5)	0.015 (5)
C8	0.027 (4)	0.014 (4)	0.030 (5)	−0.005 (3)	0.002 (4)	0.003 (4)
C9	0.030 (5)	0.020 (4)	0.027 (5)	−0.001 (3)	−0.001 (4)	−0.003 (4)
C10	0.030 (5)	0.029 (5)	0.044 (6)	0.003 (4)	0.009 (5)	−0.001 (5)
C11	0.029 (5)	0.028 (5)	0.048 (7)	−0.002 (4)	−0.011 (5)	0.011 (5)
C12	0.044 (6)	0.027 (4)	0.027 (5)	−0.005 (4)	−0.009 (6)	0.000 (5)

C13	0.036 (5)	0.027 (4)	0.018 (5)	0.004 (4)	0.008 (4)	0.003 (3)

Geometric parameters (Å, º)

Hg—C1	2.076 (8)	C7—C8	1.496 (12)
Hg—S1	2.360 (2)	C7—H7A	0.9900
S1—C7	1.848 (10)	C7—H7B	0.9900
C1—C6	1.388 (13)	C8—C13	1.390 (13)
C1—C2	1.402 (13)	C8—C9	1.398 (13)
C2—C3	1.390 (12)	C9—C10	1.368 (13)
C2—H2A	0.9500	C9—H9A	0.9500
C3—C4	1.398 (14)	C10—C11	1.378 (16)
C3—H3A	0.9500	C10—H10A	0.9500
C4—C5	1.357 (14)	C11—C12	1.378 (16)
C4—H4A	0.9500	C11—H11A	0.9500
C5—C6	1.404 (13)	C12—C13	1.406 (14)
C5—H5A	0.9500	C12—H12A	0.9500
C6—H6A	0.9500	C13—H13A	0.9500
C1—Hg—S1	178.0 (3)	S1—C7—H7A	109.4
C7—S1—Hg	104.4 (3)	C8—C7—H7B	109.4
C6—C1—C2	119.0 (7)	S1—C7—H7B	109.4
C6—C1—Hg	120.2 (7)	H7A—C7—H7B	108.0
C2—C1—Hg	120.8 (7)	C13—C8—C9	118.5 (8)
C3—C2—C1	120.7 (8)	C13—C8—C7	121.3 (9)
C3—C2—H2A	119.6	C9—C8—C7	120.2 (10)
C1—C2—H2A	119.6	C10—C9—C8	120.7 (9)
C2—C3—C4	119.4 (9)	C10—C9—H9A	119.7
C2—C3—H3A	120.3	C8—C9—H9A	119.7
C4—C3—H3A	120.3	C9—C10—C11	121.2 (10)
C5—C4—C3	119.9 (8)	C9—C10—H10A	119.4
C5—C4—H4A	120.0	C11—C10—H10A	119.4
C3—C4—H4A	120.0	C12—C11—C10	119.3 (9)
C4—C5—C6	121.4 (9)	C12—C11—H11A	120.4
C4—C5—H5A	119.3	C10—C11—H11A	120.4
C6—C5—H5A	119.3	C11—C12—C13	120.3 (10)
C1—C6—C5	119.4 (9)	C11—C12—H12A	119.9
C1—C6—H6A	120.3	C13—C12—H12A	119.9
C5—C6—H6A	120.3	C8—C13—C12	119.9 (9)
C8—C7—S1	111.4 (6)	C8—C13—H13A	120.0
C8—C7—H7A	109.4	C12—C13—H13A	120.0
C6—C1—C2—C3	1.6 (14)	S1—C7—C8—C9	89.2 (10)
Hg—C1—C2—C3	−176.3 (7)	C13—C8—C9—C10	3.6 (14)
C1—C2—C3—C4	−1.2 (14)	C7—C8—C9—C10	−175.4 (9)
C2—C3—C4—C5	0.4 (14)	C8—C9—C10—C11	−2.3 (15)
C3—C4—C5—C6	0.0 (16)	C9—C10—C11—C12	0.2 (15)
C2—C1—C6—C5	−1.1 (14)	C10—C11—C12—C13	0.7 (15)

Hg—C1—C6—C5	176.7 (8)	C9—C8—C13—C12	−2.7 (13)
C4—C5—C6—C1	0.4 (16)	C7—C8—C13—C12	176.2 (9)
Hg—S1—C7—C8	2.7 (9)	C11—C12—C13—C8	0.6 (14)
S1—C7—C8—C13	−89.7 (11)		

Hydrogen-bond geometry (Å, º)

Cg1, Cg2 are the centroids of the benzene C1–C6 and C8–C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*A*···*Cg*1^{i}	0.95	3.00	3.799 (4)	143
C7—H7*A*···*Cg*1^{ii}	0.99	2.98	3.913 (8)	157
C11—H11*A*···*Cg*2^{iii}	0.95	2.63	3.547 (6)	162

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