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Bis(3-phenyl-1,2,4-thiadiazole-5-thiolato)mercury(II)

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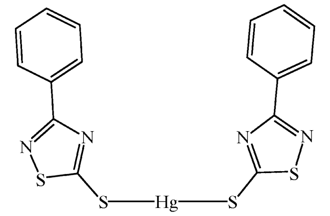
The title compound, [Hg($C_8H_5N_2S_2$)$_2$], has crystallographic C_2 symmetry. The Hg—S distance is 2.353 (2) Å and the coordination geometry is linear, with an S—Hg—S angle of 179.77 (18)°. The exocyclic C—S single-bond distance is 1.749 (6) Å, and intramolecular Hg···N distances of 2.857 (4) Å exist, as well as secondary Hg···C and S···S contacts.

Comment

In recent years, there has been considerable interest in the complexes of heterocyclic thiones and oxadiazole, triazole and related ligands (Raper, 1997; Maravalli & Goudar, 1999; Bell *et al.*, 2000, 2001, 2004). Aromatic nitrogen-containing heterocyclic molecules such as diazines and azolates have been increasingly used in a variety of bridging capacities (Steel, 1990). The fact that mercury(II) ions interact with many biological molecules through coordination with deprotonated thiol, imidazole, disulfide, thioether, amino or carboxylate groups is well known, and a great deal of effort has been devoted to the characterization of these interactions in model molecules and in proteins (Popović *et al.*, 2000; Kajdan *et al.*, 2000). Interest in the structural chemistry of mercury(II) halide complexes with ligands containing S-donor atoms, such as heterocyclic thioamides, is related not only to the toxicological behaviour of the metal and to the detoxification of mercury, but also to their industrial applications, especially in semiconductors or in photovoltaic devices (Hadjikakou *et al.*, 2003). Extensive use of heterocyclic thionates as bridging ligands stems from the presence of the thioamide N—C—S$^-$ group. Parent ligands adopt the thione form in the solid but may exist, at least in part, as the thiol form in solution, particularly in non-polar solvents (Cotton & Walton, 1993).

Our previous reports (Ağırbaş *et al.*, 1992; Dürüst *et al.*, 1991) related to the synthesis of the various thiadiazole derivatives on the basis of thione–thiol rearrangement encouraged us to obtain metal derivatives of the above-mentioned compounds. This work describes the synthesis and crystal structure of the first example, the title compound, (I).



(I)

The molecular structure of (I) is illustrated in Fig. 1. The molecule lies on a crystallographic twofold axis, and although this does not require the coordination geometry to be strictly linear, it is linear within experimental error. No previous examples of complexes of 1,2,4-thiadiazol-5-ylthiolate ligands exist in the Cambridge Structural Database (CSD, Version 5.26, November 2004 release; Allen, 2002), but the Hg1—S1 distance agrees well with those in two recent determinations of bis(1,3-benzothiazole-2-thiolato)mercury(II) (CSD refcode METZUG), *viz.* 2.344 (3)–2.351 (3) Å for three unique values (Bell *et al.*, 2001) and 2.338 (3)–2.345 (3) Å (Popović *et al.*, 2002). The mean value for Hg—S distances in Hg^{II} arenethionate complexes in the compilation of Orpen *et al.* (1989) is 2.362 Å.

The S1—C1 distance is indicative of a single bond, also in reasonable agreement with the mean value of 1.761 Å reported for arenethiolates by Orpen *et al.* (1989) and with the values from the two determinations of METZUG [1.727 (10)–1.751 (9) Å]. Thus, the ligand is established to be a heterocyclic thiolate. Bond distances within the 1,2,4-thiadiazole ring are consisent with those of the only structure in the CSD having an S atom at C1 on this heterocycle, namely 3,5-bis(methylmercapto)-1,2,4-thiadiazole (BICJEC; Gattow *et al.*, 1982), except that BICJEC has C2—N1 slightly longer [1.373 (6) Å] and N2—S2 slightly shorter [1.613 (5) Å]. The 1,2,4-thiadiazole and phenyl rings of (I) are coplanar, and the

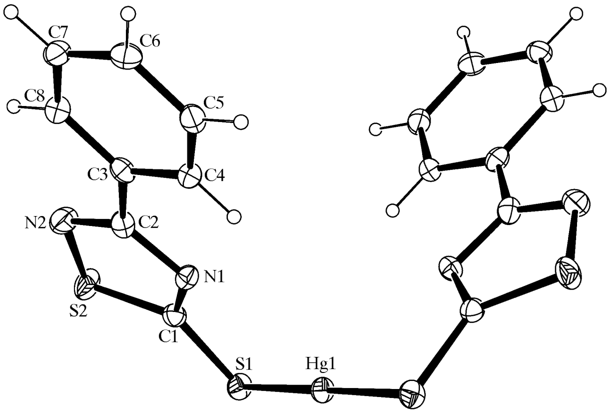


Figure 1
The structure of (I), viewed normal to the twofold axis, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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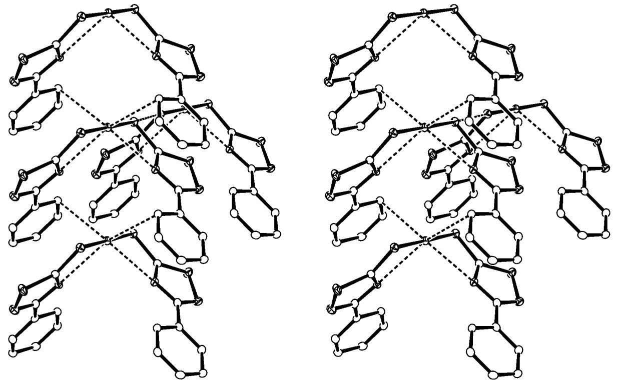

Figure 2
A stereoview, illustrating the secondary interactions in (I). The *b* axis is vertical and the S···S contact lies approximately along *c*.

two thiadiazole rings related by the twofold axis are nearly orthogonal, forming a dihedral angle of 88.2 (1)°. The 1,2,4-thiadiazole ring is planar, with a maximum deviation of 0.005 (4) Å (for C1 and N1), and the Hg atom lies 0.3179 (1) Å out of this plane, such that the Hg···N1 distance is 2.857 (4) Å. Similar, but slightly longer, corresponding distances were found in the two determinations of METZUG, falling in the range 2.970 (8)–3.119 (8) Å, and intermolecular Hg···N contacts of average length 2.9 Å were found in the structure of a linear Hg^{II} aminothiolate complex (Almagro *et al.*, 2001).

In similar linear Hg^{II} complexes with thiolate ligands, Block *et al.* (1990) and Casals *et al.* (1991) noted secondary Hg···S interactions shorter than the sum of the van der Waals radii, increasing the Hg coordination number. The title structure contains none of these, but has close contacts with the phenyl rings of the molecule related by $y + 1$, with the nearest distance being Hg···C4 = 3.289 (3) Å. Along with the aforementioned intramolecular Hg···N contacts, these secondary interactions complete the coordination sphere of Hg, which may be viewed as six-coordinate (Fig. 2). Fig. 2 also shows close S···S contacts along the *c* direction [S1···S1($-x$, y, $1 - z$) = 3.335 (1) Å], which are somewhat shorter than twice the van der Waals radius of sulfur (1.8 Å; Bondi, 1964).

Experimental

A warm solution of $HgCl_2$ (0.5 mmol, 135.7 mg) in aqueous ethanol (10 ml) was added dropwise to a solution of 3-phenyl-1,2,4-thiadiazole-5-thione (Ağırbaş *et al.*, 1992) (1 mmol, 194 mg) in ethanol (10 ml). A white precipitate formed immediately. The reaction mixture was refluxed for 2 h. The solvent was evaporated under reduced pressure, and the crude product was recrystallized from ethyl acetate as colourless needles (m.p. 489–492 K). R_F (EtOAc–light petroleum, 1:1): 0.68; ^1H NMR ($CDCl_3$): δ 7.27–7.35 (*m*, 6H), 7.95–7.98 (*m*, 4H); ^{13}C NMR ($CDCl_3$): δ 127.8, 128.6, 129.2, 130.4, 131.4; IR (KBr, ν, cm^{-1}): 1463, 1432, 1319, 1279, 1113, 1039, 898, 781, 704. Analysis calculated: C 32.73, H 1.72, N 9.54, S 21.85%; found: C 33.20, H 2.21, N 9.53, S 21.66%. MS (EI, 70 eV): 592 (M^+, 2), 386 (15), 283 (2), 225 (17), 219 (23), 135 (100), 122 (26), 103 (65), 77 (20).

Crystal data

$[Hg(C_8H_5N_2S_2)_2]$
$M_r = 587.11$
Monoclinic, $C2$
$a = 23.066$ (2) Å
$b = 5.0026$ (4) Å
$c = 8.0220$ (7) Å
$\beta = 108.871$ (9)°
$V = 875.90$ (14) Å^3
$Z = 2$
$D_x = 2.226$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1083 reflections
$\theta = 2.5$–28.3°
$\mu = 9.27$ mm^{-1}
$T = 105$ K
Lath, colourless
0.17 × 0.05 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer (with an Oxford Cryosystems Cryostream Cooler)
ω scans with κ offsets
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.355$, $T_{max} = 0.757$
4345 measured reflections
1960 independent reflections
1959 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 28.3°$
$h = -29 \rightarrow 30$
$k = -5 \rightarrow 6$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.050$
$S = 1.04$
1960 reflections
115 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 4.7102P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0030 (3)
Absolute structure: Flack (1983), with 746 Friedel pairs
Flack parameter: −0.005 (9)

Table 1
Selected geometric parameters (Å, °).

Hg1—S1	2.353 (2)	N1—C1	1.312 (7)
S1—C1	1.749 (6)	N1—C2	1.365 (6)
S2—N2	1.653 (5)	N2—C2	1.328 (7)
S2—C1	1.724 (5)		
S1—Hg1—S1^i	179.77 (18)	N1—C1—S1	123.6 (4)
C1—S1—Hg1	92.00 (18)	S2—C1—S1	125.1 (3)
N2—S2—C1	92.6 (2)	N2—C2—N1	118.6 (5)
C1—N1—C2	109.6 (4)	N2—C2—C3	122.0 (4)
C2—N2—S2	107.9 (4)	N1—C2—C3	119.4 (4)
N1—C1—S2	111.3 (4)		
Hg1—S1—C1—N1	7.1 (5)	N1—C2—C3—C4	−1.2 (7)

Symmetry code: (i) $-x, y, -z$.

H atoms were placed in idealized positions, with C—H distances of 0.95 Å and displacement parameters assigned as $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM1000). Services for accessing these data are described at the back of the journal.

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