

Bis[*N*-(4-nitrophenyl)thiobenz- amidato]mercury(II)

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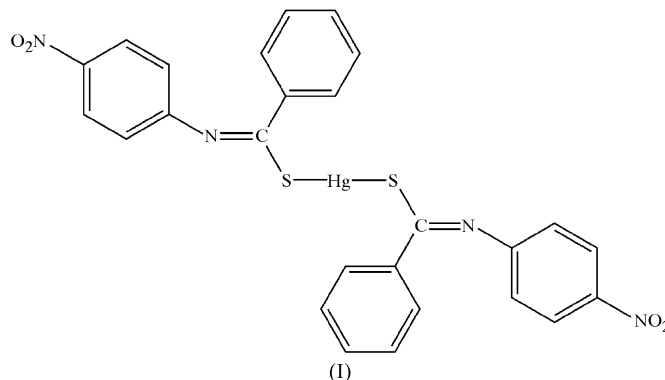
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The molecule of the title compound, [Hg(C₁₃H₉N₂O₂S)₂], has approximate twofold rotation symmetry, with the Hg atom in an essentially linear two-coordinate HgS₂ environment supported by secondary π interactions with the nitrophenyl rings of both ligands. The ligands are in the imine–thiolate rather than the amine–thione tautomeric form.

Comment

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 (Popovic *et al.*, 2000; Kajdan *et al.*, 2000). Interest in the structural chemistry of mercury(II) complexes with ligands containing S-donor atoms, such as 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). Consequently, a number of attempts have been made to explore the coordination chemistry of mercury(II) with diverse sulfur-containing ligands, such as aromatic thiolates (Bell, Branston *et al.*, 2001; Bell, Coles *et al.*, 2001; Bell *et al.*, 2004; Blower & Dilworth, 1987). Extensive use of thionates as bridging ligands stems from the presence of the thioamide NCS 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 nonpolar solvents (Cotton & Walton, 1993). This work describes the synthesis and crystal structure of a mercury(II) complex of such a ligand, the title compound, (I), which is only the second example to be crystallographically characterized.

The molecular structure of (I) is shown in Fig. 1. The molecule has no crystallographic symmetry, but the molecular symmetry is close to *C*₂, with approximately linear coordination of mercury. The Hg–S distances (Table 1) agree well with those in similar mercury(II) complexes, *e.g.* 2.344 (3)–2.351 (3) (Bell, Coles *et al.*, 2001) and 2.338 (3)–2.345 (3) Å (Popovic *et al.*, 2002); the mean value for Hg–S distances in mercury(II) arenethionate complexes in the compilation of Orpen *et al.* (1989) is 2.362 Å. The S–C distances are indicative of single bonds and are in reasonable agreement with the mean value of 1.761 Å reported for related systems by Orpen *et al.* (1989).



The phenyl and nitrophenyl rings make dihedral angles of 19.2 (2) and 68.51 (8)°, respectively, with the SC(N)C thionate unit in the S1 ligand, and the corresponding angles in the S2 ligand are 40.71 (15) and 75.21 (9)°. The dihedral angles between the two aromatic rings within each ligand are 86.75 (12) and 65.28 (12)°, and the nitro group is essentially coplanar with its parent benzene ring in each case, with dihedral angles of 3.0 (2) and 8.3 (3)°. The C–S···S···C pseudo-torsion angle indicating the relative twist of the two ligands in their coordination of mercury is 70.5 (2)°.

The most closely related mercury(II) complex to be crystallographically characterized previously has two thioaceta-

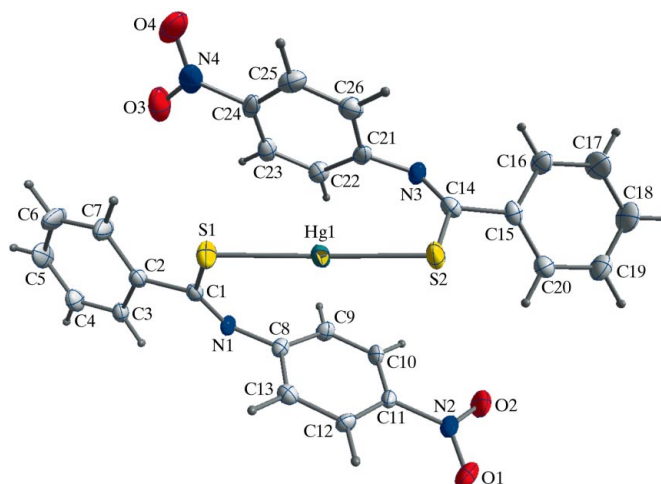


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

nilide ligands (Avalos *et al.*, 1997). It is much less symmetrical, having a weak π coordination of the phenyl ring of one ligand to mercury, while the other is oriented well away from the metal. In the title complex, both nitrophenyl groups lie in orientations such that the shortest Hg \cdots C distance is close to 3 Å [Hg1 \cdots C8 = 2.979 (4) Å and Hg1 \cdots C21 = 3.008 (4) Å] and this Hg \cdots C vector is approximately perpendicular to the ring. The most significant intermolecular interactions include a short S2 \cdots O4($\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$) contact of 3.050 (4) Å, some C—H \cdots π interactions with H \cdots ring-centroid distances less than 3 Å, and a slipped π -stacking interaction between centrosymmetrically related nitrophenyl rings (C21–C26), with a centroid-to-centroid distance of 3.906 (2) Å and a perpendicular interplanar distance of 3.466 Å, the lateral slippage being 1.802 Å.

Experimental

Mercury(II) oxide (0.216 g, 1 mmol) was added to a solution of *N*-(2-methylphenyl)-4-nitrothiobenzamide (0.273 g, 1 mmol) at ambient temperature in chloroform (35 ml) and stirred for 130 min. The completion of the reaction was followed by thin-layer chromatography with CCl₄–CH₃OH (15:1 *v/v*) as eluent. The mixture was filtered through Celite to remove unreacted mercury(II) compounds. The pale-yellow crystals which formed by slow evaporation were separated, recrystallized from chloroform as fine pale-yellow crystals and dried *in vacuo* (yield 95%, m.p. 466–468 K). Analysis calculated for C₂₆H₁₈HgN₄O₄S₂: C 45.28, H 2.96, N 7.55, Hg 26.95%; found: C 45.12, H 3.12, N 7.35, Hg 27.08%.

Crystal data

[Hg(C ₁₃ H ₉ N ₂ O ₂ S) ₂]	$V = 2492.2 (4) \text{ \AA}^3$
$M_r = 715.15$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.7351 (8) \text{ \AA}$	$\mu = 6.39 \text{ mm}^{-1}$
$b = 14.3655 (14) \text{ \AA}$	$T = 150 (2) \text{ K}$
$c = 17.9804 (12) \text{ \AA}$	$0.57 \times 0.19 \times 0.15 \text{ mm}$
$\beta = 97.648 (6)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	27468 measured reflections
Absorption correction: numerical (SHELXTL; Sheldrick, 2005)	4332 independent reflections
$T_{\min} = 0.088, T_{\max} = 0.414$	3779 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.028$

Table 1

Selected geometric parameters (Å, °).

Hg1–S1	2.3415 (11)	C1–N1	1.285 (5)
Hg1–S2	2.3438 (11)	S2–C14	1.787 (4)
S1–C1	1.770 (4)	C14–N3	1.284 (5)
S1–Hg1–S2	174.37 (4)	Hg1–S2–C14	106.10 (15)
Hg1–S1–C1	105.98 (14)	S2–C14–C15	112.0 (3)
S1–C1–C2	113.6 (3)	S2–C14–N3	129.5 (3)
S1–C1–N1	128.7 (3)	C15–C14–N3	118.5 (4)
C2–C1–N1	117.8 (4)	C14–N3–C21	125.6 (4)
C1–N1–C8	124.9 (3)		

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	337 parameters
$wR(F^2) = 0.054$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\text{max}} = 1.07 \text{ e \AA}^{-3}$
4332 reflections	$\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$

All H atoms were located in a difference map, idealized and treated as riding, with C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The crystal was a nonmerohedral twin and the overlap of inequivalent reflections was treated by ROTWIN (Pink & Young, 2000). The largest residual difference electron-density features lie 1.0–1.3 Å from the Hg1 atom.

Data collection: COLLECT (Nonius, 1998); cell refinement: EVALCCD (Duisenberg *et al.*, 2003); data reduction: EVALCCD; program(s) used to solve structure: SHELXTL (Sheldrick, 2005); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2007); software used to prepare material for publication: SHELXTL and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3119). Services for accessing these data are described at the back of the journal.

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