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Bis[μ-1-(2-pyridyl-κN)ethanone 4-phenylthiosemicarbazonato-$\kappa^2 N^1$,S]bis[iodomercury(II)]

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The title compound, $[Hg_2(C_{14}H_{13}N_4S)_2I_2]$, is a dimeric complex of mercury(II) with the *N*,*N*,*S*-tridentate electron-donor Schiff base ligand and lies on a crystallographic twofold axis. The two Hg atoms are linked by two bridging S atoms, forming a rectangular base with Hg—S bond lengths of 2.6490 (12) and 2.6173 (11) Å. The two tridentate ligands are almost perpendicular to the base, resulting in an open box-like structure. The geometry of the Hg atoms is between trigonal bipyramidal and square pyramidal, but closer to the latter.

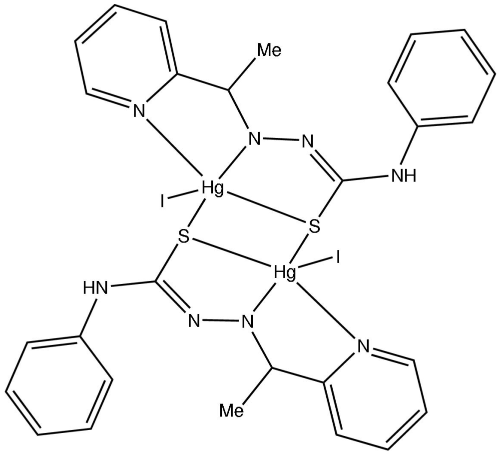
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.026
wR factor = 0.068
Data-to-parameter ratio = 20.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

2-Acetylpyridine 4-phenylthiosemicarbazone is a potential *N*,*N*,*S*-tridentate electron-donor ligand, as shown by the octahedral complex $[Mn(C_{14}H_{13}N_4S_2)_2]$ (Usman *et al.*, 2002). The title compound, (I), is a rare example of a mercury complex with Schiff bases having a coordination number greater than 2, and differs from its zinc and cadmium analogues. The molecule is dimeric with two Hg atoms linked by two S-atom bridges, forming the rectangular base of an open box-like structure (Fig. 1) and lying on a twofold axis. The Hg atom is chelated by the 2-acetylpyridine 4-phenylthiosemicarbazone ligand in an *N*,*N*,*S*-tridentate manner *via* the azomethine N, pyridyl N and thiolate S atoms.



(I)

The geometry of both Hg atoms is between trigonal bipyramidal and square pyramidal, but closer to the latter with some degree of distortion. Atoms N3, N4, S1^{i} (symmetry code in Table 1) and I1 occupy the basal plane, with I1 displaced by 1.491 (1) Å. The other atoms deviate by less than 0.10 Å from the mean plane. The *cis* angles about atom Hg1 are between 67.63 (12) and 107.74 (2)°. The apical position is occupied by atom S1, with the S1—Hg1—(basal atom) angles close to 90° (Table 1).

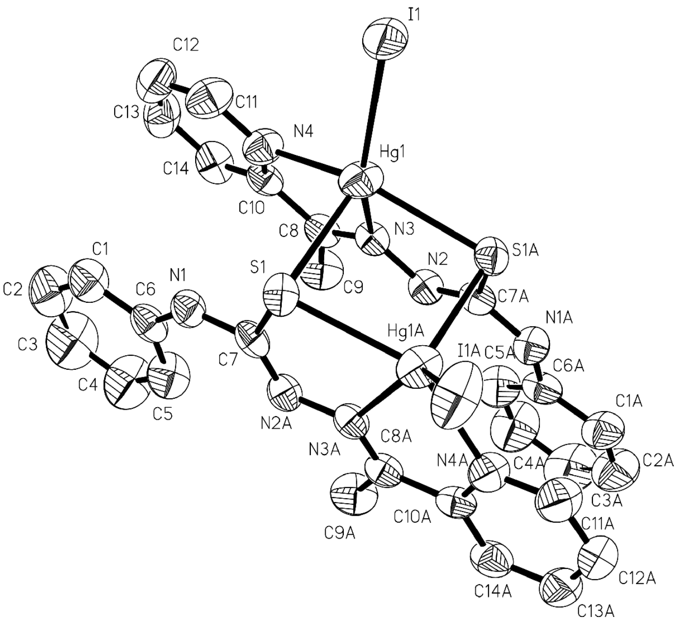


Figure 1
The molecular structure of the title compound, (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. The suffix A corresponds to symmetry code (i) in Table 1.

The Hg—S bond lengths in the complex are shorter than those in the dimeric bis(*o*-chlorophenylbenzoylthiourea-κS)-diiodomercury(II) complex (Yusof & Yamin, 2004) of 2.6840 (16) Å. In addition, the bridging Hg1—S1^{i} bond length is shorter than Hg1—S1. The C7—S1 bond length of 1.768 (4) Å is longer compared to 1.690 (6) Å in bis(*o*-chlorophenylbenzoylthiourea-κS)diiodomercury(II). Other bond lengths and angles are in normal ranges (Allen *et al.*, 1987; Orpen *et al.*, 1989) and in agreement with other metal–bis-Schiff base complexes, such as [Mn($C_{14}H_{13}N_4S_2$)$_2$] (Usman *et al.*, 2002).

The symmetry-related ligands are essentially planar. The S1/N1/C1–C7/N2^{i}/N3^{i}/C8^{i}–C10^{i}/C13^{i}/C14^{i} fragment has a maximum deviation of 0.041 (6) Å for atom C10^{i}. Atoms N4^{i}, C11^{i}, C12^{i} and Hg1^{i} are displaced by 0.144 (5), −0.176 (13), −0.116 (8) and −0.266 (1) Å from the mean plane, respectively. Both ligands make a dihedral angle with each other of 9.07 (11)°. The rectangular base, Hg1—S1—Hg1^{i}—S1^{i}, is also planar, with atoms Hg and S deviating, on opposite sides, by 0.068 (1) Å from the mean plane. The ligands are almost perpendicular to the base with an angle of 85.47 (8)°. In the structure, the molecule is stabilized by the intermolecular hydrogen bond, N1—H1*A*···I1^{ii} [symmetry code: (ii) $\frac{3}{2} - x$, $\frac{1}{2} - y$, $1 - z$; Table 2], forming a zigzag chain parallel to the *a* axis.

Experimental

A solution of pyridylethylenephenylhydrazone (1.50 g, 5.5 mmol) in ethanol (50 ml) was added dropwise to an ethanol solution (50 ml) containing an equimolar amount of mercury iodide in a two-necked round-bottomed flask. The solution was refluxed for about 3 h. The clear solution was filtered and colourless crystals were obtained after evaporation over a period of five days.

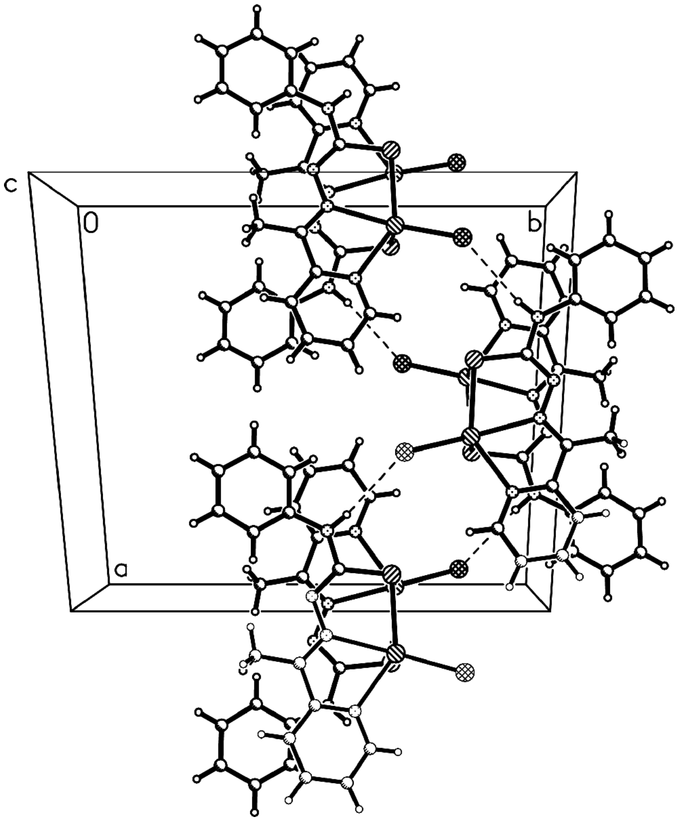


Figure 2
Packing diagram of compound (I), viewed down the *c* axis. Dashed lines denote N—H···I hydrogen bonds.

Crystal data

[$Hg_2(C_{14}H_{13}N_4S)_2I_2$]
M_r = 1193.67
Monoclinic, $C2/c$
a = 18.466 (3) Å
b = 16.745 (2) Å
c = 13.9140 (19) Å
β = 129.174 (2)°
V = 3335.3 (8) Å^3
Z = 4
D_x = 2.377 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8944 reflections
θ = 1.8–27.6°
μ = 11.20 mm^{-1}
T = 293 (2) K
Block, colourless
0.38 × 0.18 × 0.13 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.072, $T_{\max}$ = 0.233
21 199 measured reflections
3875 independent reflections
3277 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.033
$\theta_{\max}$ = 27.6°
$h = -24 \rightarrow 24$
$k = -21 \rightarrow 21$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.068
S = 1.05
3875 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 5.0737P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 1.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.58 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg1—N4	2.387 (4)	Hg1—S1	2.6490 (12)
Hg1—N3	2.398 (3)	Hg1—I1	2.6635 (4)
Hg1—S1^{i}	2.6173 (11)	N2—C7^{i}	1.290 (5)
N4—Hg1—N3	67.63 (12)	N4—Hg1—I1	100.24 (9)
N4—Hg1—S1^{i}	140.71 (9)	N3—Hg1—I1	141.58 (8)
N3—Hg1—S1^{i}	73.32 (9)	S1^{i}—Hg1—I1	107.74 (2)
N4—Hg1—S1	95.73 (9)	S1—Hg1—I1	120.20 (2)
N3—Hg1—S1	97.71 (8)	Hg1^{i}—S1—Hg1	86.22 (3)
S1^{i}—Hg1—S1	93.48 (3)		

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$I1^{ii}	0.86	3.01	3.769 (4)	147

Symmetry code: (ii) $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$.

After their location in a difference map, all H atoms were positioned geometrically and allowed to ride on the parent C or N atoms, with C—H = 0.93–0.96 Å and and N—H = 0.86 Å, and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(methyl C) or 1.2$U_{\rm eq}$(C,N). The highest electron-density peak is located 0.91 Å from atom I1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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