metal-organic papers

Phenyl(pyrrolinedithiocarbamato)mercury(II)

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Key indicators

Single-crystal X-ray study
$T = 183$ K
Mean σ(C–C) = 0.008 Å
R factor = 0.042
wR factor = 0.108
Data-to-parameter ratio = 26.1

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

An approximately linear geometry around Hg is found in the title compound, $PhHg[S_2CN(CH_2)_4]$ or $[Hg(C_6H_5)(C_5H_8\text{-}NS_2)]$. Distortions in the geometry arise from intra- and intermolecular Hg$\cdots$S interactions, with the latter resulting in the formation of loosely associated dimeric units.

Comment

Owing to varying Hg$\cdots$S supramolecular association, diverse coordination geometries and molecular arrays (monomeric, dimeric, polymeric, two-dimensional layers and three-dimensional networks) are known for the binary 1,1-dithiolates (*e.g.* compounds containing $^-S_2CNR_2$, dithiocarbamate; ^-S_2COR, xanthate; $^-S_2P(OR)_2$ dithiophosphate ligands) of mercury(II) (Cox & Tiekink, 1997, 1999*a,b*). By contrast, significantly reduced molecular aggregation has been found in the organomercury(II) 1,1-dithiolate structures (Chieh & Leung, 1976; Tiekink, 1986, 1987, 1994; Zukerman-Schpector *et al.*, 1991; Vázquez-López *et al.*, 1992; Casas *et al.*, 1994, 2002), where linear C—Hg—S geometries predominate. However, a careful analysis of the crystal structures of these compounds shows that distinctive molecular associations may be delineated (*e.g.* Casas *et al.*, 2002). In this connection, the X-ray analysis of $PhHg[S_2CN(CH_2)_4]$, (I), was undertaken.

(I)
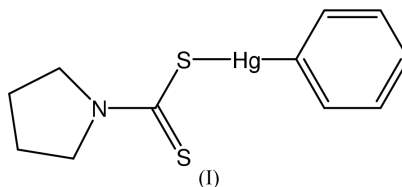
The immediate coordination geometry about the Hg atom in (I) is defined by the *ipso*-C atom of the phenyl group and atom S1 of the dithiocarbamate ligand (Fig. 1 and Table 1). The Hg—S1 bond length of 2.4009 (13) Å is significantly shorter than the Hg$\cdots$S2 distance of 2.9056 (13) Å, a result reflecting the propensity of Hg to exist in linear coordination geometries. The proximity of atom S2 is partly responsible for the deviation from the ideal linear geometry, as seen in the C6—Hg—S1 bond angle of 172.22 (14)°.

The deviations from planarity of atoms Hg, S1, S2 and C1, *i.e.* those defining the 'chelate' ring, are −0.0231 (13), 0.0231 (18), 0.0231 (18) and −0.023 (5) Å, respectively, and the angle between this least-squares plane and that through the Hg-bound phenyl ring is 10.8 (2)°, indicating a certain degree of coplanarity. In addition to the close intramolecular Hg...S2 contact, there is an interaction between a centrosymmetrically related S2 atom ($-x$, $-y$, $1 - z$) and Hg of 3.1178 (13) Å. These secondary bonds lead to the formation of
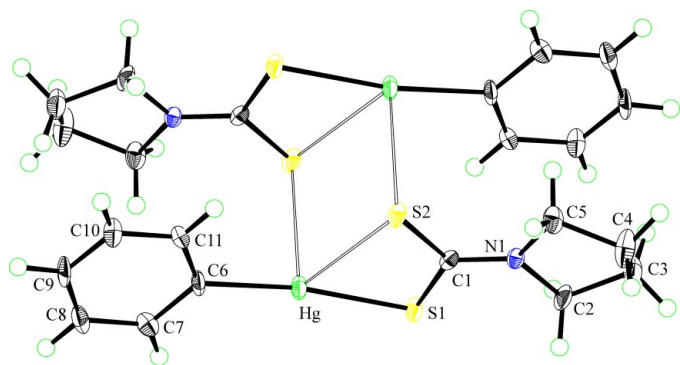
Figure 1
Association between centrosymmetrically related molecules (symmetry code: $-x$, $-y$, $1 - z$) in (I), showing the crystallographic numbering scheme. Displacement ellipsoids are shown at the 50% probability level (Johnson, 1976).

loosely associated dimers, as has been noted for the phenyl-mercury species $PhHg(S_2CNEt_2)$ (Tiekink, 1987), $PhHg-(S_2PPh_2)$ (Zukerman-Schpector *et al.*, 1991) and $PhHg[S_2P-(OEt)_2]$ (Vázquez-López *et al.*, 1992), as well as in the methylmercury analogue of (I), *viz.* $MeHg(S_2CNEt_2)$ (Chieh & Leung, 1976). In contrast with the loosely associated dimers formed in these structures, loosely associated polymeric chains, mediated by weak $Hg\cdots S$ interactions, are found in the remaining organomercury(1,1-dithiolates) cited above.

Experimental

To a stirred solution of $PhHgCl$ (0.1939 g, Aldrich) in CH_2Cl_2 (30 ml) was added a stoichiometric amount of $NH_4S_2CN(CH_2)_4$ (Aldrich) in water (20 ml). After 3 h, the organic layer was separated, dried over $MgSO_4$ and evaporated to dryness. Colourless crystals were obtained from the recrystallization of the precipitate from a $CH_2Cl_2-CH_3OH$ (1/1) solution (m.p. 427–429 K). IR (KBr disc): (C—S) 945 cm^{-1} and (C—N) 1439, 1468 cm^{-1}.

Crystal data

$[Hg(C_6H_5)(C_5H_8NS_2)]$	$D_x = 2.280$ Mg m^{-3}
$M_r = 423.93$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4116
$a = 13.3711$ (10) Å	reflections
$b = 6.3641$ (5) Å	$\theta = 2.2$–$30.0°$
$c = 14.5826$ (11) Å	$\mu = 12.77$ mm^{-1}
$\beta = 95.535$ (2)°	$T = 183$ (2) K
$V = 1235.12$ (16) Å^3	Wedge, colourless
$Z = 4$	$0.39 \times 0.18 \times 0.10$ mm

Data collection

Bruker AXS SMART CCD diffractometer	3574 independent reflections
ω scans	3208 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ($SADABS$; Bruker, 2000)	$R_{int} = 0.051$
$T_{min} = 0.049$, $T_{max} = 0.279$	$\theta_{max} = 30.0°$
9689 measured reflections	$h = -17 \to 18$
	$k = -8 \to 8$
	$l = -18 \to 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.4638P]$
$wR(F^2) = 0.108$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
3574 reflections	$\Delta\rho_{max} = 3.60$ e Å^{-3}
137 parameters	$\Delta\rho_{min} = -4.26$ e Å^{-3}
H-atom parameters constrained	Extinction correction: $SHELXL$97
	Extinction coefficient: 0.0021 (3)

Table 1
Selected geometric parameters (Å, °).

Hg—C6	2.074 (5)	S1—C1	1.741 (5)
Hg—S1	2.4009 (13)	S2—C1	1.715 (5)
Hg—S2	2.9056 (13)	N1—C1	1.307 (6)
C6—Hg—S1	172.22 (14)	C1—S2—Hg	77.93 (17)
C6—Hg—S2	115.68 (16)	C1—N1—C2	124.2 (4)
S1—Hg—S2	68.07 (4)	C1—N1—C5	124.7 (4)
C1—S1—Hg	93.46 (16)	C2—N1—C5	111.1 (4)

H atoms were placed in calculated positions and included in the final refinement in the riding-model approximation. The maximum and minimum residual electron-density peaks were 0.82 and 0.81 Å, respectively, from the Hg atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* and *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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