

Diiodobis(1-methyl-1,3-imidazolium-2-thiolato-S)mercury(II)

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The reaction of 1-methyl-1,3-imidazole-2-thione (meimtH) with mercury(II) iodide in methanol in a 2:1 molar ratio resulted in the formation of single crystals of the title compound, $[\text{HgI}_2(\text{C}_4\text{H}_6\text{N}_2\text{S})_2]$. The Hg atom is coordinated by two I [2.7809 (9) and 2.7999 (8) Å] and two thione S atoms [2.520 (3) and 2.576 (3) Å] with irregular tetrahedral coordination geometry. The NH groups of the imidazole ring take part in intra- and intermolecular hydrogen bonds with I atoms [N...I 3.596 (8) and 3.611 (9) Å, respectively] joining molecules into infinite chains parallel to the *z* axis.

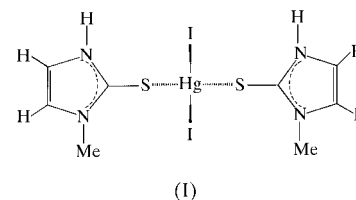
Comment

Heterocyclic thionates are electron-rich polyfunctional ligands (Raper, 1996). Whereas heterocyclic thionates are ambidentate ligands (S- or N-donor atoms), their monosubstituted analogues are S,N-bridging and/or chelating ligands. The N-disubstituted derivatives are exclusively monodentate S donors. Currently available X-ray structural data show that 1-methyl-1,3-imidazole-2-thione (meimtH) can act as a neutral S-donor ligand (Raper & Nowell, 1979, 1980; García-Martínez *et al.*, 1993; Raper *et al.*, 1980; Nowell *et al.*, 1974; Raper & Brooks, 1977; Birker *et al.*, 1982; O'Neill *et al.*, 1982; Oughtred *et al.*, 1984), as an S-bridging ligand (Creighton *et al.*, 1985; Raper & Clegg, 1991) or as an anionic ligand [S-donor: Norris *et al.* (1983); N,S-bridging: Cooper *et al.* (1986), Raper *et al.* (1991), Agnus *et al.* (1980), Castro *et al.* (1995) and Popović *et al.* (1999)]. The structure of the ligand itself, *i.e.* 1-methyl-1,3-imidazole-2-thione (meimtH), is known from two independent studies (Raper *et al.*, 1983; Vampa *et al.* 1995). The C=S bond distances [1.686 (2) and 1.682 (2) Å in two crystallographically independent molecules; Vampa *et al.*, 1995] and the protonation at N3 establish the presence of the thione tautomer in the solid state.

Mercury(II) halides form 1:1 and 1:2 complexes with 1-methyl-1,3-imidazole-2-thione, $\text{HgX}_2(\text{meimtH})$ and $\text{HgX}_2(\text{meimtH})_2$ (Pavlović *et al.*, 2000), whereas mercury(II) acetate forms the complex $\text{Hg}(\text{meimt})_2$ (Popović *et al.*, 1999). Two mercury(II) complexes with 1-methyl-1,3-imidazole-2-thione

derived from HgBr_2 (Raper *et al.*, 1998) and $\text{Hg}(\text{Oac})_2$ (Popović *et al.*, 1999) have been structurally examined. Firstly, $\text{HgBr}_2(\text{meimtH})$ (Raper *et al.*, 1998), with a 4+1 trigonal-bipyramidal mercury coordination, contains bromo-bridged dimers that are further linked into weakly associated polymeric sheets *via* $\text{Hg}\cdots\text{Br}$ contacts of 3.587–3.791 Å. The monodentate meimtH ligand has thione sulfur ligating character, with Hg–S distances in the range 2.405 (4)–2.419 (4) Å. Secondly, $\text{Hg}(\text{meimt})_2$ (Popović *et al.*, 1999) possesses an Hg atom located on a twofold axis coordinated by two S [2.4305 (12) Å] and two N atoms [2.451 (4) Å] from four meimt ligands. The Hg–N bond is longer than the sum of the covalent radii for N and tetrahedral Hg (2.23 Å; Pauling, 1960; Grdenić, 1965). The Hg–S distance of 2.4305 (12) Å lies between expected values for linear and tetrahedral coordination. The meimt ligands bridge two Hg atoms forming infinite chains parallel to the *z* axis.

The coordination of meimtH towards methylmercurio compounds appears to be dependent on pH and on the molar ratio of the reactants. In complexes with a 1:1 mercury-to-meimtH ratio, Hg–S bonds are formed irrespective of the pH of the medium, whereas for the 2:1 ratio under basic conditions, both Hg–S and Hg–N bonds are expected to be formed (Buncel *et al.*, 1982). There are two monomeric complexes containing the $(\text{CH}_3)\text{Hg}^{\text{II}}$ unit, which is bonded to the exocyclic sulfur by Hg–S bonds of 2.382 (2) Å in $[(\text{CH}_3)\text{Hg}(\text{meimtH})(\text{NO}_3)]$ and 2.338 (7) Å in $[(\text{CH}_3)\text{Hg}(\text{meimt})]$ (Norris *et al.*, 1983). Although the ligand in the latter contains an available electron lone pair at the deprotonated N atom, Hg does not form intermolecular contacts with the N atom of adjacent molecules, and the Hg–S bond distance is equal to the sum of the Hg and S covalent radii of 2.34 Å (Grdenić, 1965; Pauling, 1960).



The molecule of $\text{HgI}_2(\text{meimtH})_2$, (I), is situated in a general position (Fig. 1). The Hg atom is tetrahedrally coordinated by two I atoms [Hg–I1 2.7809 (9) Å and Hg–I2 2.7999 (8) Å] and two thione S atoms [Hg–S1 2.520 (3) Å and Hg–S2 2.576 (3) Å]. The Hg–I distances are slightly shorter than the sum of the covalent radii for I and Hg in tetrahedral coordination (2.81 Å; Pauling, 1960; Grdenić, 1965) and correspond well to the Hg–I distance in the red tetrahedral form of HgI_2 [2.783 (3) Å; Jeffrey & Vlasse, 1967]. In contrast, in the 1:1 complex with non-substituted 1,3-imidazole-2-thione, $\text{HgI}_2(\text{imtH}_2)$, Hg displays a 3+1 coordination and the Hg–I bond values are markedly different [2.8187 (7) and 2.6518 (7) Å; Popović *et al.*, 1999] because of participation of one of the I atoms in dimer formation.

The valence angles around the Hg atom of the title compound lie in the range 103.72 (6)–115.14 (6)°, corre-

sponding to a somewhat distorted tetrahedral geometry at mercury. The Hg—S bond values are slightly longer than the sum of the covalent radii for S and tetrahedrally coordinated Hg (1.04 and 1.48 Å, respectively; Pauling, 1960; Grdenić, 1965). The Hg—S bond distance values are longer than in the above-mentioned mercury(II) complexes with meimt[−] or meimtH ligands. Although the Hg atoms in these complexes have different coordination environments, the Hg—S bond values differ according to the nature of the other donor atoms bound to mercury (C, Br or N). The tendency of mercury to form stronger Hg—I and weaker Hg—S bonds has been observed in the iodo complexes with other thiones, such as 3,4,5,6-tetrahydropyrimidine-2-thione (Popović *et al.*, 2000).

The reduction in the π -electron density of the exocyclic C—S bond in the title complex relative to the average bond distance in the free ligand is accompanied by metal coordination. The extent of this reduction, as reflected in the bond lengthening, differs between the title compound and the above-mentioned mercury complexes with meimtH. The lengthening is significant in the HgBr₂(meimtH) [1.73 (2)–1.74 (2) Å; Raper *et al.*, 1998], Hg(meimt)₂ [1.747 (4) Å; Popović *et al.*, 1999], CH₃Hg(meimtH)(NO₃) and CH₃Hg(meimt) complexes [1.741 (8) and 1.75 (2) Å, respectively; Norris *et al.*, 1983], while in the title complex, the C—S bonds are marginally longer than in the free ligand [S1—C11 1.698 (9) Å and S2—C21 1.721 (9) Å *versus* 1.682 (2) and 1.686 (2) Å]. This is a consequence of the observed tendency of mercury to form stronger Hg—I and weaker Hg—S bonds. The lengthened C—S bond is invariably associated with an increase in the double-bond character of the thioamide C—N bonds (Table 1), which are slightly shortened in comparison with the values in the free ligand [1.348 (3) and 1.344 (3) Å; Vampa *et al.*, 1995]. Although the major π -electron density appears to be concentrated in the thioamide fragment, all of the ring bond distances are affected by the extended conjugation, revealing the zwitterionic character of the coordinated ligand [C=S in X₂C=S (X is any atom) 1.671 Å; C_{ar}—Nsp² 1.371 Å; Allen *et al.*, 1987]. The NH groups of the imidazole

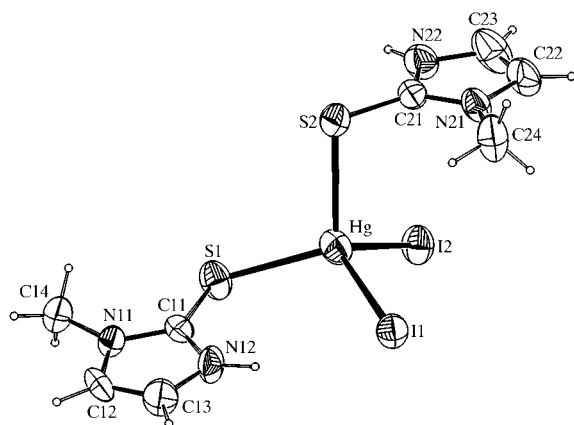


Figure 1
The molecular structure and the atom-numbering scheme of the diiodobis(1-methyl-1,3-imidazolium-2-thiolato-S)mercury(II) complex. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

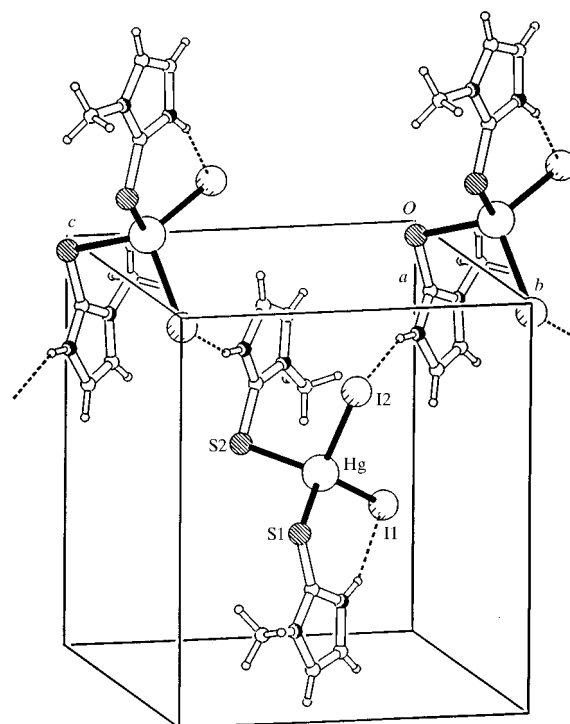


Figure 2
Packing diagram of the title complex. Hydrogen bonds are shown by dashed lines. The intermolecular N—H...I hydrogen bond joins molecules into infinite chains parallel to the *z* axis.

ring take part in intra- and intermolecular hydrogen bonds with the I1 and I2 atoms (Table 2) joining molecules into infinite chains parallel to the *z* axis.

Experimental

The title compound was prepared as described by Popović *et al.* (1999). Crystals suitable for X-ray analysis were formed from a very dilute methanol solution at room temperature on standing for several days.

Crystal data

[HgI₂(C₄H₆N₂S)₂]
 $M_r = 682.73$
 Orthorhombic, $Pca2_1$
 $a = 11.543$ (2) Å
 $b = 13.996$ (5) Å
 $c = 9.9180$ (7) Å
 $V = 1602.3$ (7) Å³
 $Z = 4$
 $D_x = 2.830$ Mg m^{−3}

Mo $K\alpha$ radiation
 Cell parameters from 33 reflections
 $\theta = 10.0$ – 18.6°
 $\mu = 13.706$ mm^{−1}
 $T = 293$ (2) K
 Plate, colourless
 0.696 × 0.382 × 0.050 mm

Data collection

Philips PW1100 diffractometer
 updated by Stoe
 ω scans
 Absorption correction: by integration (*X-RED*; Stoe & Cie, 1995)
 $T_{\min} = 0.074$, $T_{\max} = 0.505$
 5113 measured reflections
 2465 independent reflections (plus 2110 Friedel-related reflections)

3590 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$
 $\theta_{\text{max}} = 30^\circ$
 $h = -16 \rightarrow 16$
 $k = -19 \rightarrow 19$
 $l = -13 \rightarrow 13$
 5 standard reflections
 frequency: 90 min
 intensity decay: 6.4%

Table 1

Selected geometric parameters (Å, °).

Hg—S1	2.520 (3)	N11—C12	1.387 (13)
Hg—S2	2.576 (3)	N12—C11	1.345 (12)
Hg—I1	2.7809 (9)	S2—C21	1.721 (9)
Hg—I2	2.7999 (8)	N21—C21	1.335 (12)
S1—C11	1.698 (9)	N21—C22	1.361 (10)
N11—C11	1.333 (11)	N22—C21	1.325 (12)
S1—Hg—S2	108.49 (9)	S1—Hg—I2	106.39 (6)
S1—Hg—I1	115.14 (6)	S2—Hg—I2	103.72 (6)
S2—Hg—I1	110.76 (7)	I1—Hg—I2	111.63 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N12—H12N...I1	0.86	2.77	3.596 (8)	163
N22—H22N...I2 ¹	0.86	2.80	3.611 (9)	157

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

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0793P)^2 + 0.3812P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.023$	$\Delta\rho_{\max} = 0.99 \text{ e } \text{Å}^{-3}$
4575 reflections	$\Delta\rho_{\min} = -1.45 \text{ e } \text{Å}^{-3}$
156 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = $-0.007 (8)$

The registered intensity data consisted of two octants and included a full set of Friedel opposites. Methyl H atoms were identified from difference syntheses and idealized, and the rigid methyl groups were allowed to rotate but not tip. Other H atoms were included at calculated positions and refined using a riding model; the H-atom isotropic displacement parameters were kept equal to $1.5U_{\text{eq}}$ for Csp^3 and $1.2U_{\text{eq}}$ for Csp^2 . The H atoms at N12 and N22 could be tentatively identified in the difference Fourier map, but were not well defined. They were therefore generated assuming sp^2 hybridization at N and refined with a riding model. The polar axis direction was determined unambiguously by refining the Flack parameter. The maximum and minimum electron-density peaks in the final difference Fourier map are located 0.71 and 0.86 Å, respectively, from the Hg atom.

Data collection: *STADIA* (Stoe & Cie, 1995); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON98* (Spek, 1998); 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: JZ1398). Services for accessing these data are described at the back of the journal.

References

- Agnus, Y., Louis, R. & Weiss, R. (1980). *J. Chem. Soc. Chem. Commun.* pp. 867–869.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Birker, P. J. M. W. L., Reedijk, J., Verschoor, G. C. & Jordanov, J. (1982). *Acta Cryst. B38*, 2245–2247.
- Buncel, E., Norris, A. R., Taylor, S. E. & Racz, W. J. (1982). *Can. J. Chem.* **60**, 3033–3038.
- Castro, R., García-Vázquez, J. A., Romero, J., Sousa, A., Da Chang, Y. & Zubietta, J. (1995). *Inorg. Chim. Acta*, **237**, 143–146.
- Cooper, D. A., Rettig, S. J., Storr, A. & Trotter, J. (1986). *Can. J. Chem.* **64**, 1643–1651.
- Creighton, J. R., Gardiner, D. J., Gorvin, A. C., Gutteridge, C., Jackson, A. R. W., Raper, E. S. & Sherwood, P. M. A. (1985). *Inorg. Chim. Acta*, **103**, 195–205.
- Flack, H. D. (1983). *Acta Cryst. A39*, 876–881.
- García-Martínez, E., Sánchez González, A., Casas, J. S., Sordo, J., Casellato, U., Graziani, R. & Russo, U. (1993). *J. Organomet. Chem.* **463**, 91–96.
- Grdenić, D. (1965). *Quart. Rev.* **19**, 303–328.
- Jeffrey, G. A. & Vlasse, M. (1967). *Inorg. Chem.* **6**, 396–399.
- Norris, A. R., Taylor, S. E., Buncel, E., Bélanger-Gariépy, F. & Beauchamp, A. L. (1983). *Can. J. Chem.* **61**, 1536–1541.
- Nowell, I. W., Cox A. G. & Raper, E. S. (1974). *Acta Cryst. B35*, 3047–3050.
- O'Neill, M. E., Raper, E. S., Daniels, J. A. & Nowell, I. W. (1982). *Inorg. Chim. Acta*, **66**, 79–84.
- Oughtred, R. E., Raper, E. S. & Nowell, I. W. (1984). *Inorg. Chim. Acta*, **84**, L5–8.
- Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell University Press.
- Pavlović, G., Popović, Z., Soldin, Ž. & Matković-Čalogović, D. (2000). *Acta Cryst. C56*, 61–63.
- Popović, Z., Matković-Čalogović, D., Soldin, Ž., Pavlović, G., Davidović, N. & Vikić-Topić, D. (1999). *Inorg. Chim. Acta*, **294**, 35–46.
- Popović, Z., Pavlović, G., Matković-Čalogović, D., Soldin, Ž., Rajić, M., Vikić-Topić, D. & Kovaček, D. (2000). In preparation.
- Raper, E. S. (1996). *Coord. Chem. Rev.* **153**, 199–255.
- Raper, E. S. & Brooks, J. L. (1977). *J. Inorg. Nucl. Chem.* **39**, 2163–2166.
- Raper, E. S. & Clegg, W. (1991). *Inorg. Chim. Acta*, **180**, 239–244.
- Raper, E. S., Creighton, J. R., Bell, N. A., Clegg, W. & Cucurull-Sánchez, L. (1998). *Inorg. Chim. Acta*, **277**, 14–20.
- Raper, E. S., Creighton, J. R. & Clegg, W. (1991). *Inorg. Chim. Acta*, **183**, 179–187.
- Raper, E. S., Creighton, J. R., Oughtred, R. E. & Nowell, I. W. (1983). *Acta Cryst. B39*, 355–360.
- Raper, E. S. & Nowell, I. W. (1979). *Acta Cryst. B35*, 1600–1603.
- Raper, E. S. & Nowell, I. W. (1980). *Inorg. Chim. Acta*, **43**, 165–172.
- Raper, E. S., O'Neill, M. E. & Daniels, J. A. (1980). *Inorg. Chim. Acta*, **41**, 201–205.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, L. (1998). *PLATON98 for Windows*. University of Utrecht, The Netherlands.
- Stoe & Cie (1995). *STADIA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
- Vampa, G., Benvenuti, S., Severi, F., Malmusi, L. & Antolini, L. (1995). *J. Heterocycl. Chem.* **32**, 227–234.