Diiodo(3,4,5,6-tetrahydropyrimidinium-2-thiolato-S)mercury(II)

Dubravka Matković-Čalogović,[a]* Zora Popović,[a] Gordana Pavlović,[a] Željka Soldin[a] and Gerald Giester[b]

[a]Laboratory of General and Inorganic Chemistry, Chemistry Department, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia, and [b]Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstrasse 14, A-1090 Wien, Austria

Correspondence e-mail: dubravka@chem.pmf.hr

The reaction of 3,4,5,6-tetrahydropyrimidine-2-thione (H_4pymtH) with mercury(II) iodide in methanol in a 1:1 molar ratio resulted in the formation of single crystals of the title compound, $[Hg(C_4H_8N_2S)I_2]$. The Hg atom is coordinated by one S atom from H_4pymtH at 2.456 (2) Å and by two I atoms at distances of 2.6872 (7) and 2.7044 (6) Å, and has a characteristic deformed trigonal coordination geometry. The molecule has crystallographic m symmetry but the Hg atom is disordered above and below the mirror plane.

Comment

The chemistry of mercury in a biological medium is dominated by thiolate complexes of low coordination number (Wright *et al.*, 1990). There is also a great deal of evidence pointing to the significance of mercury–halide complexation in biological systems. Our current interest in the coordination chemistry of mercury(II) complexes with S-donor ligands is aimed toward a better understanding of these interactions. Both neutral halides and halogenomercurate anions have been used as probes of biological activity in proteins. Displacement of halide or pseudohalide ions can occur and the mercury cation is then particularly reactive toward the negatively charged and polarizable S-groups. Yet, there are known examples where intact mercurates electrostatically interact with the protein at specific sites, such as the binding of HgI_3^- in myoglobin (Kretsinger *et al.*, 1968).

We have recently synthesized and characterized some mercury(II) halide (X = Cl^-, Br^-, I^-) and pseudohalide (SCN^-, CN^-) complexes with H_4pymtH in the ratios 1:2 and 1:1 (Popović *et al.*, 2000, 2001). Only the chloro and bromo derivatives of the 1:1 complexes have been structurally characterized until now (Popović *et al.*, 2001). Unexpectedly, we found that the structures were made up of tetrahalogenomercurate(II) anions and bis(3,4,5,6-pyrimidinium-2-thiolato-S)mercury(II) cations, $[Hg(H_4pymtH)_2][HgX_4]$. Usually, 1:1 structures are made up of molecules with mercury

coordinated by both sulfur and halide atoms as was found in the structures of the 1:1 mercury(II) halide complexes with other S-donor ligands. These molecules are connected by weak $Hg{\cdots}X$ contacts into dimers (Davidović *et al.*, 1998; Raper *et al.*, 1998, Popović, Matković-Čalogović, Soldin *et al.*, 1999) or polymeric chains (Matković-Čalogović *et al.*, 2000). The halide 1:2 complexes of HgX_2 (X = Cl^-, Br^-, I^-) with H_4pymtH are all monomeric with the tetrahedral coordination of mercury (Popović *et al.*, 2000). Discrete $HgX_2(H_4pymtH)_2$ molecules are interconnected only by hydrogen bonds. Tetrahedral coordination was found also for other mercury complexes of this type with different heterocyclic thiones (Popović, Matković-Čalogović, Hasić & Vikić-Topić, 1999; Pavlović *et al.*, 2000a,b; Bell *et al.*, 2000).

We report here the crystal structure of the title compound, (I), which was prepared in an analogous way to the 1:1 complexes mentioned above yet the structure is very different from that of the bis(3,4,5,6-tetrahydropyrimidinium-2-thiolato-S)mercury(II) tetrachloro- and tetrabromomercurate(II) complexes. The X-ray single-crystal diffractometry study was undertaken at low (200 K) and room temperature. The bond distances in the two data sets are not significantly different. The molecules are packed more densely in the 200 K crystal structure and the volume of the unit cell is lower by 20.4 $Å^3$ in comparison with the room-temperature structure. The distances in the discussion below are for the low-temperature data since it is the better data set. The room temperature data have been deposited [deposition number 142803; Cambridge Structural Database (Allen & Kennard, 1983)].

(I)
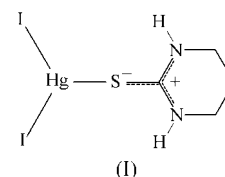
The Hg atom is coordinated by an S atom of the H_4pymtH ligand and two I atoms. The angles reveal the deformed trigonal coordination (Table 1 and Fig. 1). The Hg—I bonds are slightly shorter, and the Hg—S bonds longer than the theoretically calculated values for the sum of the covalent radii of trigonal Hg and the corresponding atoms (2.72 Å for Hg—I and 2.43 Å for Hg—S), indicating strong Hg—I bonds, as was also found in the 1:2 complex. Atoms I, S, C1 and C3 lie
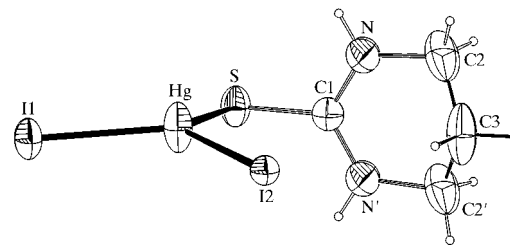

Figure 1
*PLATON*98 (Spek, 1990) drawing of (I) with the atom-numbering scheme. The displacement ellipsoids are at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii. Atoms C2′ and N′ are generated by the mirror-plane symmetry ($x, \frac{1}{2} - y, z$). Only one of the two possible Hg positions is shown.

in the mirror plane but the Hg atom is statistically disordered and situated 0.195 Å out of the mirror plane. This way, the I2 atoms from neighbouring molecules are at short [Hg···I2($-x$, $-y$, $-z$) 3.517 (3) Å] and long distances [Hg···I2($-x$, $1-y$, $-z$) 3.907 (3) Å]. At room temperature, these distances are 3.515 (3) and 3.959 (3) Å, respectively. If the Hg atom was positioned in the mirror plane, two equal but longer contacts would be formed at a distance of 3.712 Å which is, evidently, unfavourable. Taking into account the van der Waals radius of Hg in the range 1.55–1.65 Å (Grdenić, 1981; Matković-Čalogović, 1994), we consider only the short Hg···I interaction as being stronger than the van der Waals type. This way, the effective coordination of mercury can be described as 3+1 implying the existence of discrete, but weakly bound, dimers (Fig. 2). Since Hg is disordered over two positions, this gives two possible modes of dimer formation. If a larger van der Waals radius of Hg is considered (Canty & Deacon, 1980), the longer distance would also be a weak bond and the structure could be described as being made up of endless chains. We found such chains in the 1:1 complex of HgI_2 with benzimidazole-2-thione, but in that structure, Hg is in the mirror plane forming two equal and short Hg···I contacts of 3.378 (1) Å (Matković-Čalogović et al., 2000). A pattern of dimer formation similar to the title complex [disordered Hg atom, 3+1 coordination, same space group, similar b axis, Hg···I = 3.486 (1) Å] is found in the 1:1 complex of HgI_2 with 1,3-imidazole-2-thione ($imtH_2$) (Popović, Matković-Čalogović, Soldin et al., 1999), where the Hg—S bond of 2.460 (2) Å is similar to that in the title compound, but the Hg—I distances are quite different [2.6518 (7) and 2.8187 (7) Å], which is a consequence of the different distortion of the trigonal geometry [the angle S—Hg—I(non-bridging) is 134.63 (5)°]. In both complexes, the longer Hg—I distance involves the bridging I atom.

Analysis of the Cambridge Structural Database (Allen & Kennard, 1993) gave five structures with trigonally coordinated Hg within the $HgSI_2$ fragment of which all form dimers,
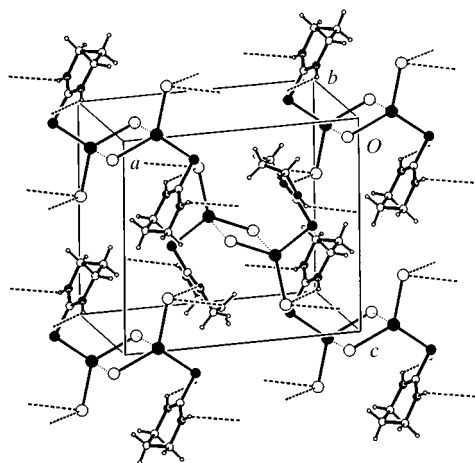
but with Hg···I contacts shorter than 3.4 Å (Hiller *et al.*, 1986; Kergoat *et al.*, 1982).

The thioketo C$=$S bond in free H_4pymtH [1.720 (2) Å, room temperature data (Popović *et al.*, 2001); 1.722 (7) Å at 140–150 K (Dias & Truter, 1964)] has approximately 40% of the π character (Trinajstić, 1968). Upon complexation, there is an increase of the bond length [1.740 (6) Å] which corresponds to a decrease of the π character.

Each monomer has four symmetry-related hydrogen bonds N—H···I1($\frac{1}{2} - x$, $-y$, $z - \frac{1}{2}$) of 3.696 (4) Å (H···A 3.029 Å, N—H···I 136°) (Fig. 2).

Experimental

Crystal data

[Hg(C$_4$H$_8$N$_2$S)I$_2$]	Mo $K\alpha$ radiation
$M_r = 570.57$	Cell parameters from 5843 reflections
Orthorhombic, $Pnma$	tions
$a = 12.826$ (2) Å	$\theta = 3.18$–$28.26°$
$b = 7.3920$ (10) Å	$\mu = 20.007$ mm^{-1}
$c = 11.447$ (2) Å	$T = 200$ (2) K
$V = 1085.3$ (4) Å^3	Prism, yellow
$Z = 4$	$0.2 \times 0.1 \times 0.1$ mm
$D_x = 3.492$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	1428 independent reflections
ω scans	1286 reflections with $I > 2\sigma(I)$
Absorption correction: semi-empirical (*XEMP*; Sheldrick, 1988)	$R_{int} = 0.062$
	$\theta_{max} = 28.26°$
	$h = -15 \rightarrow 17$
	$k = -9 \rightarrow 8$
$T_{min} = 0.059$, $T_{max} = 0.135$	$l = -15 \rightarrow 13$
10 676 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0169P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$\quad + 1.6028P]$
$wR(F^2) = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.116$	$(\Delta/\sigma)_{max} < 0.001$
1428 reflections	$\Delta\rho_{max} = 0.66$ e Å^{-3}
59 parameters	$\Delta\rho_{min} = -0.84$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
	Extinction coefficient: 0.00466 (19)

The Hg atom shows positional disorder and is situated 0.195 Å out of the mirror plane [the distance between the two possible Hg-atom positions is 0.391 (5) Å]. All H atoms were generated at idealized geometrical positions (Nsp^2—H 0.86 Å and Csp^3—H 0.97 Å; $U_{iso} =$

Table 1
Selected geometric parameters (Å, °).

Hg—S	2.456 (2)	C1—N	1.298 (5)
Hg—I1	2.6872 (7)	N—C2	1.477 (7)
Hg—I2	2.7044 (6)	C2—C3	1.490 (7)
S—C1	1.740 (6)		
S—Hg—I1	115.74 (4)	N—C1—S	120.0 (3)
S—Hg—I2	119.53 (4)	C1—N—C2	123.6 (4)
I1—Hg—I2	123.06 (2)	N—C2—C3	108.1 (5)
C1—S—Hg	97.5 (2)	C2^i—C3—C2	109.9 (6)
N—C1—N^i	120.1 (6)		

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

Figure 2
Packing of dimers of (I) in the unit cell. Hg···I contacts are shown by thin dotted lines and the N—H···I hydrogen bonds by dashed lines. Only one of the two possible orientations of dimers generated by the positional disorder of the Hg atom around the mirror plane is shown.

1.2U_{eq} for Nsp^2 and 1.5U_{eq} for Csp^3) and included in the refinement procedure using a riding model.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *KappaCCD Software*; data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1502). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Bell, N. A., Branston, T. N., Clegg, W., Creighton, J. R., Cucurull-Sánchez, L., Elsegood, M. R. J. & Raper, E. R. (2000). *Inorg. Chim. Acta*, **303**, 220–227.
Canty, A. J. & Deacon, G. B. (1980). *Inorg. Chim. Acta*, **45**, L225–227.
Davidović, N., Matković-Čalogović, D., Popović, Z. & Vedrina-Dragojević, I. (1998). *Acta Cryst.* C**54**, 574–576.
Dias, H. W. & Truter, M. R. (1964). *Acta Cryst.* **17**, 937–943.
Grdenić, D. (1981). *Connections in the Crystal Structures of Mercury Compounds*. In *Structural Studies of Molecules of Biological Interest,* edited by G. Dodson, J. P. Glusker & D. Sayre, pp. 207–221. Oxford: Clarendon Press.
Hiller, W., Castineiras, A., Arquero, A. & Masaguer, J. R. (1986). *Acta Cryst.* C**42**, 151–153.
Kergoat, R., Kubicki, M. M., Guerchais, J. E. & Howard, J. A. K. (1982). *J. Chem. Res. (S)*, 340–341.
Kretsinger, R., Watson, H. C. & Kendrew, J. C. (1968). *J. Mol. Biol.* **31**, 305–314.
Matković-Čalogović, D. (1994). PhD thesis (in Croatian; Abstract in English), University of Zagreb, Croatia.
Matković-Čalogović, D., Pavlović, G., Popović, Z., Soldin, Ž. & Giester, G. (2000). 19th European Crystallographic Meeting, Nancy, France, Book of Abstracts, p. 416.
Nonius (1997). *KappaCCD Software*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Pavlović, G., Popović, Z., Soldin, Ž. & Matković-Čalogović, D. (2000a). *Acta Cryst.* C**56**, 61–63.
Pavlović, G., Popović, Z., Soldin, Ž. & Matković-Čalogović, D. (2000b). *Acta Cryst.* C**56**, 801–803.
Popović, Z., Matković-Čalogović, D., Hasić, J. & Vikić-Topić, D. (1999b). *Inorg. Chim. Acta*, **285**, 208–216.
Popović, Z., Matković-Čalogović, D., Pavlović, G., Soldin, Ž. & Giester, G., Rajić, M. & Vikić-Topić, D. (2001). *Croat. Chem. Acta*, **74**. In the press.
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). *Inorg. Chim. Acta*, **306**, 142–152.
Raper, E. S., Creighton, J. R., Bell, N. A., Clegg, W. & Cucurull-Sánchez, L. (1998). *Inorg. Chim. Acta*, **277**, 14–20.
Sheldrick, G. M. (1988). *XEMP*. University of Göttingen, Germany.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Trinajstić, N. (1968). *Tetrahedron Lett.* pp. 1529–1532.
Wright, J. G., Natan, M. J., MacDonell, F. M., Ralston, D. M. & O'Halloran, T. V. (1990). *Prog. Inorg. Chem.* **38**, 323–412.