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A new complex of $HgBr_2$ and pyrimidine-2-thione: (pyrimidine-2-thionato-κS)(pyrimidinium-2-thionato-κS)-mercury(II) tetrabromomercury(II)

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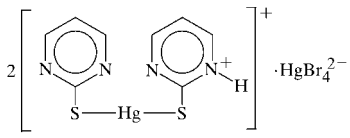
The title compound, $[Hg(C_4H_4N_2S)(C_4H_3N_2S)]_2[HgBr_4]$, consists of $[Hg(pymt)(pymtH)]^+$ complex cations (pymtH is pyrimidine-2-thione) lying across twofold rotation axes in space group *Fddd*, with linearly coordinated mercury at an Hg—S distance of 2.357 (3) Å, and $[HgBr_4]^{2-}$ anions lying at sites of 222 symmetry. The Hg atom is additionally coordinated by two N and two Br atoms, forming a 2+4 effective coordination sphere. The protonated ligand is connected *via* N—H···N hydrogen bonds to the neighbouring unprotonated ligand, thus forming infinite chains of cations.

Comment

It is well known that thio derivatives of pyrimidine play an important role in biological systems. For instance, mercaptopyrimidines exhibit antiviral and antibacterial properties (Rosenfield, Mascharak & Arora, 1987; Rosenfield, Berends *et al.*, 1987) and have been found to inhibit the synthesis of tRNA, thus acting as antitumour and antithyroid agents (Abbot *et al.*, 1978). In many cases, it seems probable that complex formation is implicated in the biological action of these pyrimidine derivatives. Mercury is found to be a strong inhibitor of human pyrimidine nucleoside monophosphate kinase, a polymeric enzyme which catalyzes the phosphorylation of UMP, CMP and dCMP, using ATP as the preferred phosphate donor (Teng *et al.*, 1976).

We have recently reported the synthesis and structural characterization (IR, NMR and X-ray) of various mercury(II) compounds with heterocyclic thiones (Popović, Matković-Čalogović, Hasić & Vikić-Topić, 1999; Popović, Matković-Čalogović, Soldin *et al.*, 1999; Pavlović *et al.*, 2000, 2000*a*,*b*; Popović *et al.*, 2001; Matković-Čalogović *et al.*, 2001; Popović, Pavlović *et al.*, 2002; Popović, Soldin, Matković-Čalogović *et al.*, 2002; Popović, Soldin, Pavlović *et al.*, 2002). Continuing this work, we report here the crystal and molecular structure of the novel title mercury(II) complex with pyrimidine-2-thione (pymtH), (I).



(I)

Although many mercury(II) complexes with pyrimidine-2-thione or its derivatives are known (Battistuzzi & Peyronel, 1980; Khullar & Agarwala, 1974; Contreras *et al.*, 1994), only a few have been characterized by X-ray analysis (Das & Seth, 1997; Romero *et al.*, 1990; Stuart *et al.*, 1980; Tallon *et al.*, 1995). The ability of mercury(II) halides and pseudohalides to form 1:1 and 1:2 complexes with neutral ligands has been known for many years (Dean, 1978; Graddon, 1982). The crystal structures of the 1:2 complexes, HgX_2L_2 (where X is a halide or pseudohalide anion and L is a neutral ligand), usually consist of discrete monomeric molecules with a tetrahedrally coordinated Hg atom (more or less distorted). The structures of the 1:1 complexes, HgX_2L, often consist of discrete halogen-bridged dimeric molecules, with the Hg atom also in a deformed tetrahedral environment. The dimeric structure of the complexes HgX_2(pymtH) (where X is Cl^-, Br^- or I^-) was proposed on the basis of their IR and Raman spectra and also supported by an SCF–MO–MNDO (semi-empirical modified neglected differential overlap) calculation on the HgI_2(pymtH) dimer (Contreras *et al.*, 1994).

The structure of (I) consists of $[Hg(pymt)(pymtH)]^+$ complex cations and $[HgBr_4]^{2-}$ anions. In the cation, the Hg atom lies on a twofold axis and is linearly coordinated by two S atoms from the two ligands, of which one is protonated (pymtH) and the other deprotonated (pymt). The H atom on N2 is statistically disordered, since there is only one pymt/pymtH ligand in the asymmetric unit. The Hg1—S distance (Table 1) is slightly longer than the sum of the covalent radii for linear Hg and S (1.30 + 1.04 Å; Pauling, 1960; Grdenić, 1965). There is also a tetrabromomercurate(2−) anion, where the Hg atom lies at the intersection of three twofold axes. The Hg2—Br distance in this approximately tetrahedral anion corresponds well with the mean value [2.604 (4) Å] of 35 independent Hg—Br distances in tetrabromomercurate(2−) anions found in the Cambridge Structural Database (Version 5.25; Allen, 2002).

The Hg atom in the cation of (I) is additionally coordinated by atoms N1 from the two ligands, at a distance of 2.856 (10) Å, and by two Br atoms from the anion at a distance of 3.4255 (14) Å, which is less than the sum of the van der Waals radii of the corresponding atoms, so the effective coordination can be described as 2+4 (Pauling, 1960; Grdenić, 1981). These contacts are responsible for the elongation of the Hg—S bond and for the slight deviation from linearity. The effect of additional contacts on the lengthening of the Hg—S distance is also found in other Hg complexes coordinated

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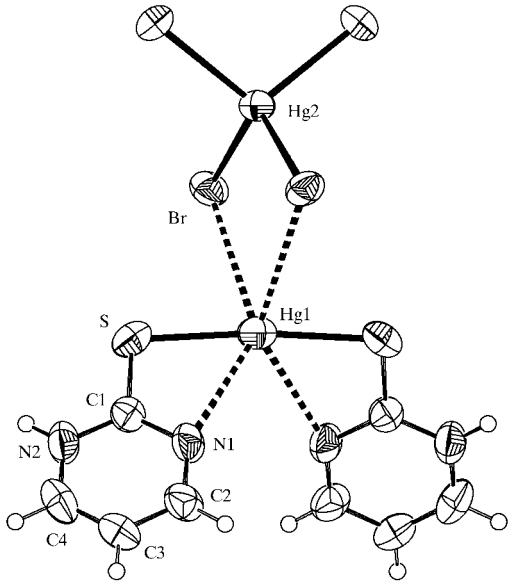

Figure 1
A view of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The Hg···N and Hg···Br contacts are shown by dashed lines.

linearly by different thione ligands. Weak additional Hg···N contacts in the range 2.987 (7)–3.097 (7) Å have little influence on the Hg—S distances [2.338 (3)–2.347 (3) Å] and linearity (178.0 and 180°) in $Hg(btzt)_2$ (where btzt is 1,3-benzothiazole-2-thione; Popović, Soldin, Pavlović *et al.*, 2002). However, two strong Hg···N contacts of 2.451 (4) Å in $Hg(meimt)_2$ (where meimtH is 1-methyl-1,3-imidazole-2-thione) cause the linear coordination to be very deformed toward the tetrahedral [S—Hg—S = 143.15 (5)°], and also cause a much greater elongation of the Hg—S bond [2.4305 (12) Å; Popović, Matković-Čalogović, Soldin *et al.*, 1999).

We have recently characterized the 1:1 complexes $HgX_2(H_4pymtH)$ (where X is Cl^-, Br^-, I^-, SCN^- or CN^-, and H_4pymtH is 3,4,5,6-tetrahydropyrimidine-2-thione; Popović *et al.*, 2001). The chloro and bromo complexes were found to be isostructural and made up of tetrahalogenomercurate(II) anions and bis(3,4,5,6-tetrahydropyrimidinium-2-thiolato-κS)-mercury(II) cations, $[Hg(H_4pymtH)_2][HgX_4]$. In this cation, both N atoms are protonated and cannot form contacts with the Hg atom. The coordination is also 2+4, as in (I), and with comparable Hg—S distances [2.359 (4)–2.370 (4) Å], but all four additional contacts are with halogen atoms [Hg···Br = 3.201 (2)–3.504 (2) Å].

The cations of (I) are connected by N2—H···N2 hydrogen bonds into infinite chains along the [110] direction.

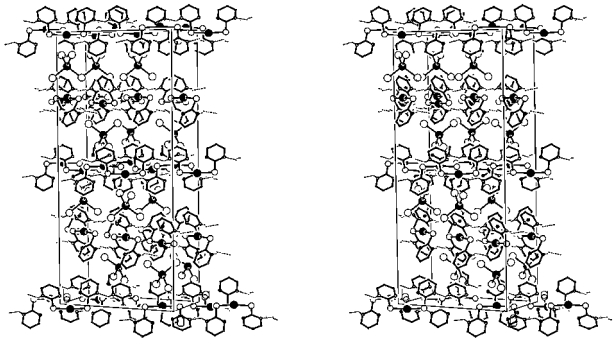

Figure 2
A stereodiagram of the ions in the unit cell of (I), with the hydrogen bonds shown by dashed lines. H atoms attached to C atoms have been omitted for clarity.

Experimental

The reaction of $HgBr_2$ and pymtH in a 1:1 molar ratio gave a mixture of products. Characterization of these compounds is in progress and will be published elsewhere. Crystals of (I) appeared after several weeks from the mother liquor obtained after filtration of the first reaction products.

Crystal data

$[Hg(C_4H_4N_2S)(C_4H_3N_2S)]_2[HgBr_4]$
M_r = 1368.00
Orthorhombic, *Fddd*
a = 9.0573 (7) Å
b = 17.1999 (13) Å
c = 37.754 (9) Å
V = 5881.5 (15) Å^3
Z = 8
D_x = 3.090 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 65 reflections
θ = 10.2–17.6°
μ = 21.37 mm^{-1}
T = 293 (2) K
Plate, yellow
0.49 × 0.40 × 0.05 mm

Data collection

Philips PW1100 diffractometer, updated by Stoe
$\theta/2\theta$ scans
Absorption correction: by integration (*X-RED*; Stoe & Cie, 1995)
T_{min} = 0.022, T_{max} = 0.328
3401 measured reflections
2115 independent reflections
1288 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 29.9°
$h = -3 \rightarrow 12$
$k = -2 \rightarrow 24$
$l = -1 \rightarrow 52$
5 standard reflections
frequency: 90 min
intensity decay: 6.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.145
S = 1.03
2115 reflections
81 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0814P)^2 + 0.022P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.39 e Å^{-3}
$\Delta\rho_{min}$ = −3.63 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg1—S	2.358 (3)	S—C1	1.710 (10)
Hg2—Br	2.6020 (10)		
S—Hg1—S^{i}	174.25 (13)	Br—Hg2—Br^{iii}	108.84 (5)
Br—Hg2—Br^{ii}	113.39 (5)	Br^{ii}—Hg2—Br^{iii}	106.26 (5)

Symmetry codes: (i) $\frac{1}{4}-x, \frac{1}{4}-y, z$; (ii) $x, \frac{1}{4}-y, \frac{1}{4}-z$; (iii) $\frac{1}{4}-x, y, \frac{1}{4}-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H···N2^{iv}	0.86	1.98	2.730 (12)	145

Symmetry code: (iv) $\frac{3}{4}-x, -\frac{1}{4}-y, z$.

The H atom on N2 was found in a difference Fourier map but was not refined. This H atom is disordered and its occupancy was set at 0.5. All other H atoms were treated as riding atoms, with C—H distances of 0.93 Å and N—H distances of 0.86 Å. The residual density in the final difference Fourier map is 0.80 Å from Hg2.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *X-RED* (Stoe & Cie, 1995); data reduction: *X-RED*; 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.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1289). Services for accessing these data are described at the back of the journal.

References

Abbot, J., Goodgame, B. M. L. & Jeeves, I. (1978). *J. Chem. Soc. Dalton Trans.* pp. 880–884.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Battistuzzi, R. & Peyronel, G. (1980). *Spectrochim. Acta A*, **36**, 113–117.

Contreras, J. G., Seguel, G. V. & Alderete, J. B. (1994). *Spectrochim. Acta A*, **50**, 371–374.

Das, A. K. & Seth, S. (1997). *J. Inorg. Biochem.* **65**, 207–218.

Dean, P. A. (1978). *Prog. Inorg. Chem.* **24**, 109–157.

Graddon, D. P. (1982). *Rev. Inorg. Chem.* **4**, 211–282.

Grdenić, D. (1965). *Q. Rev. Chem. Soc.* **19**, 303–328.

Grdenić, D. (1981). *Connections in the Crystal Structures of Mercury Compounds. Structural Studies of Molecules of Biological Interest*, edited by G. Dodson, J. P. Glusker & D. Sayyre, pp. 207–221. Oxford: Clarendon Press.

Khullar, I. P. & Agarwala, U. (1974). *Indian J. Chem.* **12**, 1096–1098.

Matković-Čalogović, D., Popović, Z., Pavlović, G., Soldin, Ž. & Giester, G. (2001). *Acta Cryst.* C**57**, 409–411.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.

Pavlović, G., Popović, Z., Soldin, Ž. & Matković-Čalogović, D. (2000*a*). *Acta Cryst.* C**56**, 61–63.

Pavlović, G., Popović, Z., Soldin, Ž. & Matković-Čalogović, D. (2000*b*). *Acta Cryst.* C**56**, 801–803.

Popović, Z., Matković-Čalogović, D., Hasić, J. & Vikić-Topić, D. (1999). *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**, 359–380.

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.

Popović, Z., Pavlović, G., Soldin, Ž., Popović, J., Matković-Čalogović, D. & Rajić, M. (2002). *Struct. Chem.* **13**, 415–424.

Popović, Z., Soldin, Ž., Matković-Čalogović, D., Pavlović, G., Rajić, M. & Giester, G. (2002). *Eur. J. Inorg. Chem.* pp. 171–180.

Popović, Z., Soldin, Ž., Pavlović, G., Matković-Čalogović, D., Mrvoš-Sermek, D. & Rajić, M. (2002). *Struct. Chem.* **13**, 425–436.

Romero, M. A., Salas, J. M., López, R., Gutiérrez, M. D., Panneerselvam, K., Chacko, K. K., Aoki, K. & Yamazaki, H. (1990). *Inorg. Chim. Acta*, **172**, 253–258.

Rosenfield, S. G., Berends, H. P., Gelmini, L., Stephan, D. W. & Mascharak, P. K. (1987). *Inorg. Chem.* **26**, 2792–2797.

Rosenfield, S. G., Mascharak, P. K. & Arora, S. K. (1987). *Inorg. Chim. Acta*, **129**, 39–46.

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.

Stoe & Cie (1995). *STADI*4 (Version 1.05b) and *X-RED* (Version 1.05b). Stoe & Cie, Darmstadt, Germany.

Stuart, D. A., Nassimbeni, L. R., Hutton, A. T. & Koch, K. R. (1980). *Acta Cryst.* B**36**, 2227–2330.

Tallon, J., Garcia-Vazquez, J. A., Romero, J., Louro, M. S., Sousa, A., Chen, Q., Chang, Y. & Zubieta, J. (1995). *Polyhedron*, **14**, 2309–2317.

Teng, Y.-H., Chen, S.-H. & Scott, C. R. (1976). *J. Biol. Chem.* **251**, 4179–4183.