Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A 1:2 complex of mercury(II) chloride with 1,3-imidazole-2-thione

Gordana Pavlović, Zora Popović,* Željka Soldin and Dubravka Matković-Čalogović

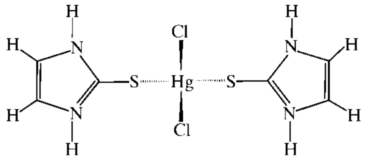
Chemistry Department, Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia
Correspondence e-mail: zpopovic@chem.pmf.hr

Received 23 September 1999
Accepted 25 October 1999

The Hg atom in the title monomeric complex, dichlorobis(3-imidazolium-2-thiolato-*S*)mercury(II), $[HgCl_2(C_3H_4N_2S)_2]$, is four-coordinate having an irregular tetrahedral geometry composed of two Cl atoms [Hg—Cl 2.622 (2) and 2.663 (2) Å] and two thione S atoms [Hg—S 2.445 (2) and 2.462 (2) Å]. The monodentate thione ligand adopts a zwitterionic form and exists as the 3-imidazolium-2-thiolate ion. The bond angle S1—Hg—S2 of 130.87 (8)° has the greatest deviation from ideal tetrahedral geometry. Intermolecular hydrogen bonds between two of the four N—H groups and one of the Cl atoms [3.232 (8) and 3.238 (7) Å] stabilize the crystal structure, while the other two N—H groups contribute through the formation of N—H···Cl intramolecular hydrogen bonds with the other Cl atom [3.121 (7) and 3.188 (7) Å].

Comment

The current interest in the coordination chemistry of mercury(II) complexes containing an exocyclic thione (thioketo) group on a heterocyclic molecule which may contain nitrogen, oxygen or sulfur or a combination of these is related to mercury–cysteine thionate interactions in the toxicological behaviour of mercury (Cheesman *et al.*, 1988), in detoxification of the mercury by metallothioneins (Nielsen *et al.*, 1985), in a DNA-binding protein (Dance, 1986), and in mercury reductase and related proteins (Blower & Dilworth, 1987). Deprotonated heterocyclic thiones, *i.e.* heterocyclic thionates, are ambidentate ligands with exocyclic S or thioamido N donating atoms. The coordination mode depends on the nature of the metal centre, hence N-donor atoms are found in Zn complexes, while in mercury(II) complexes, the S atom is undoubtedly the expected ligating site for Hg^{2+} (Raper, 1996; Popović, Matković-Čalogović, Hasić & Vikić-Topić, 1999; Popović, Matković-Čalogović, Soldin *et al.*, 1999). The structural identification of mercury(II) complexes with thione ligands has, in the past, relied largely on spectroscopic methods such as IR and ^{13}C NMR (Shunmugam & Sathyanarayana, 1983). The crystal structure of the free ligand is not known, but its hemihydrate (Raper *et al.*, 1984), as well as its alkyl and aryl derivatives (Form *et al.*, 1976; Raper *et al.*, 1983; Ansell, 1972) or even its saturated analogue imidazolidine-2-thione (Wheatley, 1953), have been examined. Mercury(II) complexes with 1,3-imidazole-2-thione derivatives and corresponding halides show different HgX_2 and L ratios that can be deduced as $HgX_2{\cdot}L$ and $HgX_2{\cdot}L_2$ [X = halide or pseudo-halide ions; L = $imtH_2$ (1,3-imidazole-2-thione) or meimtH (1-methyl-1,3-imidazole-2-thione)] or HgL_2 (L = $imtH^-$ or $meimt^-$), depending mainly on the stoichiometry of the reactants, the pH and the coordination ability of the ligand. The structural diversity is present too, *i.e.* the complexes may be discrete (Popović, Matković-Čalogović, Soldin *et al.*, 1999), dimeric (Raper *et al.*, 1998; Popović, Matković-Čalogović, Soldin *et al.*, 1999) or polymeric (Popović, Matković-Čalogović, Soldin *et al.*, 1999), reflecting the character of Hg—L and Hg—X interactions. In the context of our previous work on mercury(II) complexes with heterocyclic thiones (Popović, Matković-Čalogović, Hasić & Vikić-Topić, 1999; Popović, Matković-Čalogović, Soldin *et al.*, 1999), the crystal and molecular structure of $[HgCl_2(imtH_2)_2]$, (I), is reported here.



(I)

The molecule (Fig. 1) is built up of a monomeric $HgCl_2$ unit [Hg—Cl1 2.622 (2) Å and Hg—Cl2 2.663 (2) Å], with two thione ligands coordinated to the Hg atom *via* the S atom [Hg—S1 2.445 (2) Å and Hg—S2 2.462 (2) Å] in a distorted tetrahedral environment. The smallest and largest bond angles around the Hg atom are S2—Hg—Cl2 101.07 (7)° and S1—Hg—S2 130.87 (8)°. The Hg—Cl distances are longer than the sum of the covalent radii for Cl and tetrahedrally coordinated Hg atoms (0.99 and 1.48 Å, respectively; Pauling, 1960; Grdenić, 1965). The contribution of the Cl atoms in intramolecular and intermolecular hydrogen-bond formation makes the Hg—Cl bond lengths elongated to some extent. A

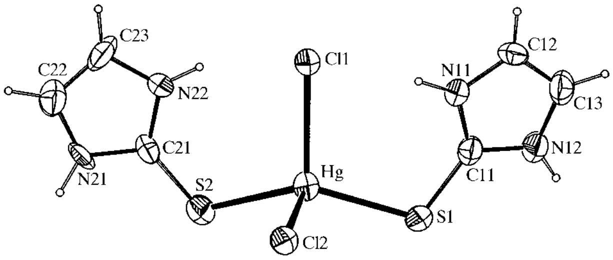


Figure 1
The molecular structure and the atom-numbering scheme of the title complex. Displacement ellipsoids are shown at the 50% probability level. The H atoms are drawn as small circles of arbitrary radii.

similar value is found in the structure of dichlorobis(6-merkaptopurine)mercury(II) [2.622 (3) Å; Lavertue *et al.*, 1976]. Such elongation is probably also due to the existence of N—H···Cl hydrogen bonds. The Hg—S distances are shorter than the sum of the covalent radii of S and tetrahedral Hg (2.52 Å; Pauling, 1960; Grdenić, 1965), indicating that the thione ligand forms a strong covalent bond to Hg. The structural comparison with other analogous mercury(II) complexes is quite difficult due to possible secondary interactions between Hg and halogen atoms. Despite this, there are a few monomeric tetrahedral mercury(II)–chloride complexes that contain sulfur bound to mercury. The S atom in those complexes exists in chemically different environments. The Hg—S values vary between 2.417 (3) Å in the structure of dichlorobis(thiosemicarbazide)mercury(II) (Chieh, 1977) and 2.536 (6) Å in bis(*N,N′*-dimethylthioformamide)mercury(II) (Stålhandske *et al.*, 1997). Similar S—Hg distances to those in (I) are found in mercury(II) chloride complexes of the *N,N′*-diethyl and *N*-ethyl imidazolidine-2-thione derivatives (Hg—S 2.42–2.50 Å; Cannas *et al.*, 1981), while in the di-μ_2-bromobis{*trans*-bromo[1-methyl-imidazoline-2(3*H*)-thione]-mercury(II)} complex (Raper *et al.*, 1998), the Hg—S values are slightly shorter [range 2.405 (4)–2.419 (4) Å]. The S—C bond distances, which retain appreciable double-bond character [S1—C11 1.709 (8) Å and S2—C21 1.717 (9) Å], suggest, along with endocyclic bond-distance values, the zwitterionic nature of the ligand (Allen *et al.*, 1987). The dihedral angle between the two imidazole ring planes amounts to 12.5 (3)°. Such spatial orientation of the imidazole rings is a consequence of the crystal packing of the complex molecules. There are two intramolecular N—H···Cl hydrogen bonds of 3.121 (7) and 3.188 (7) Å (Table 2). Discrete title complex molecules, held together by intermolecular N—H···Cl hydrogen bonds form infinite puckered sheets perpendicular to the *z* axis (Fig. 2 and Table 2). The shortest intermolecular mercury-to-halogen distance of 3.581 (2) Å exists between the Hg and Cl1 atoms, and is longer than the sum of the van der Waals radii for Hg and Cl (3.20–3.36 Å; Matković-Čalogović, 1994; Nyburg & Faerman, 1985).

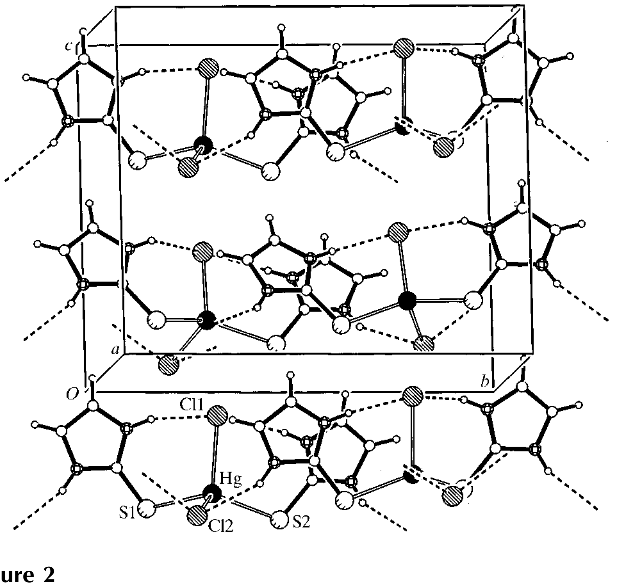


Figure 2
The crystal-packing arrangement of (I) showing the infinite two-dimensional network spreading in the *ab* plane. The intramolecular (N—H···Cl1) and intermolecular (N—H···Cl2) hydrogen bonds are indicated with dashed lines.

Experimental

The title compound was prepared as described elsewhere (Popović, Matković-Čalogović, Soldin *et al.*, 1999). Crystals suitable for X-ray analysis were formed from a dilute ethanol solution of mercury(II) chloride and the thione ligand in a 1:2 molar ratio at room temperature after standing for several days (yield: 89%). The title compound was characterized by IR spectroscopy and elemental analysis (calculated for $C_6H_8Cl_2HgN_4S_2$: C 15.28, H 1.71, Hg 42.54, N 11.88, S 13.57%; found: C 15.89, H 2.44, Hg 42.65, N 11.92, S 13.59%; m.p. 478 K). IR (cm^{-1}): 3298 (*s*), 3250 (*s*), 3190 (*s*), 3131 (*s*, *sh*), 2981 (*m*), 2859 (*m*), 2625 (*m*), 1583 (*vs*), 1477 (*vs*), 1430 (*sh*), 1404 (*s*), 1282 (*m*), 1227 (*m*), 1122 (*m*), 1104 (*w*), 1077 (*s*), 955 (*m*), 918 (*m*), 746 (*s*), 739 (*s*), 683 (*s*), 666 (*vs*), 491 (*m*). The IR spectrum in the region of 4000–450 cm^{-1} was recorded on a Perkin–Elmer FT–IR spectrophotometer Model 1600 using a KBr disk.

Crystal data

$[HgCl_2(C_3H_4N_2S)_2]$
$M_r = 471.77$
Orthorhombic, $Pca2_1$
$a = 7.5296$ (11) Å
$b = 13.7209$ (19) Å
$c = 11.7587$ (16) Å
$V = 1214.8$ (3) Å^3
$Z = 4$
$D_x = 2.579$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 56 reflections
$\theta = 9.0$–$15.4°$
$\mu = 13.425$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.44 × 0.12 × 0.03 mm

Data collection

Philips PW1100 diffractometer updated by Stoe
ω scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1995*a*)
$T_{\min} = 0.158$, $T_{\max} = 0.668$
3067 measured reflections
1847 independent reflections (plus 579 Friedel-related reflections)
1545 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.029$
$\theta_{\max} = 29.89°$
$h = -2 \rightarrow 10$
$k = 0 \rightarrow 19$
$l = -4 \rightarrow 16$
5 standard reflections
frequency: 90 min
intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.064$
$S = 0.897$
2426 reflections
137 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.789$ e Å^{-3}
$\Delta\rho_{\min} = -0.898$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00034 (9)
Absolute structure: Flack (1983)
Flack parameter = −0.022 (10)

The number of Friedel pairs measured (579) corresponds only to a 0.313 fraction of the measured symmetry-unique reflections, nevertheless, there is no reason for rejecting the absolute structure indicated by the Flack (1983) parameter.

Data collection: *STADI*4 (Stoe & Cie, 1995*b*); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1995*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *PLATON*98 (Spek, 1998); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

Hg—S1	2.445 (2)	Hg—Cl2	2.663 (2)
Hg—S2	2.462 (2)	S1—C11	1.709 (8)
Hg—Cl1	2.622 (2)	S2—C21	1.717 (9)
S1—Hg—S2	130.87 (8)	S2—Hg—Cl2	101.07 (7)
S1—Hg—Cl1	108.74 (7)	Cl1—Hg—Cl2	97.17 (7)
S2—Hg—Cl1	108.91 (8)	C11—S1—Hg	107.7 (3)
S1—Hg—Cl2	104.32 (7)	C21—S2—Hg	104.8 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···Cl1	0.86	2.30	3.121 (7)	160
N22—H22N···Cl1	0.86	2.46	3.188 (7)	144
N12—H12N···Cl2^{i}	0.86	2.45	3.238 (7)	152
N21—H21···Cl2^{ii}	0.86	2.42	3.232 (8)	158

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

This research was supported by the Ministry of Science and Technology of the Republic of Croatia (grant No. 119408).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1432). Services for accessing these data are described at the back of the journal.

References

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.

Ansell, G. B. (1972). *J. Chem. Soc. Perkin Trans.* pp. 841–843.

Blower, P. J. & Dilworth, J. R. (1987). *Coord. Chem. Rev.* **76**, 121–185.

Cannas, M., Devillanova, F. A., Marongiu, G. & Verani, G. (1981). *J. Inorg. Nucl. Chem.* **43**, 2383–2388.

Cheesman, B. V., Arnold, A. P. & Rabenstein, D. Z. (1988). *J. Am. Chem. Soc.* **110**, 6359–6364.

Chieh, C. (1977). *Can. J. Chem.* **55**, 1583–1587.

Dance, I. G. (1986). *Polyhedron*, **5**, 1037–1104.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Form, G. R., Raper, E. S. & Downie, T. C. (1976). *Acta Cryst.* B**32**, 345–348.

Grdenić, D. (1965). *Q. Rev.* **19**, 303–329.

Lavertue, P., Hubert, J. & Beauchamp, A. L. (1976). *Inorg. Chem.* **15**, 322–325.

Matković-Čalogović, D. (1994). PhD Thesis (in Croatian, *Abstract* in English), University of Zagreb, Croatia.

Nielsen, K. B., Atkin, C. L. & Winge, D. R. (1985). *J. Biol. Chem.* **260**, 5342–5350.

Nyburg, S. C. & Faerman, C. H. (1985). *Acta Cryst.* B**41**, 274–279.

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

Popović, Z., Matković-Čalogović, D., Hasić, J. & Vikić-Topić, D. (1999). *Inorg. Chim. Acta*, **285**, 208–216.

Popović, Z., Matković-Čalogović, D., Soldin, Ž., Pavlović, G., Davidović, N. & Vikić-Topić, D. (1999). *Inorg. Chim. Acta.* In the press.

Raper, E. S. (1996). *Coord. Chem. Rev.* **153**, 199–255.

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., Oughtred, R. E. & Nowell, I. W. (1983). *Acta Cryst.* B**39**, 355–360.

Raper, E. S., Jackson, A. R. W. & Gardiner, D. J. (1984). *Inorg. Chim. Acta*, **84**, L1–4.

Sheldrick, G. M. (1997*a*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Shunmugam, R. & Sathyanarayana, D. N. (1983). *J. Coord. Chem.* **12**, 151–156.

Spek, A. L. (1998). *PLATON*98 *for Windows*. University of Utrecht, The Netherlands.

Stålhandske, C. M. V., Persson, I., Sandström, M. & Åberg, M. (1997). *Inorg. Chem.* **36**, 4945–4953.

Stoe & Cie (1995*a*). *X-RED*. *Data Reduction Program for Windows*. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1995*b*). *STADI*4. *Diffractometer Control Program*. Stoe & Cie, Darmstadt, Germany.

Wheatley, J. P. (1953). *Acta Cryst.* **6**, 369–377.