

catena-Poly[[2-methyl-1,3-benzothiazole-*N*)mercury(II)]-di- μ -chloro]

Zora Popović,^{a*} Draginja Mrvoš-Sermek,^a Željka Soldin^a
and Vesna Tralić-Kulenović^b

^aLaboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, HR-10000 Zagreb, Croatia, and ^bFaculty of Textile Technology, University of Zagreb, Pierottijeva 6, HR-10000 Zagreb, Croatia
Correspondence e-mail: zpopovic@chem.pmf.hr

Received 9 August 2000

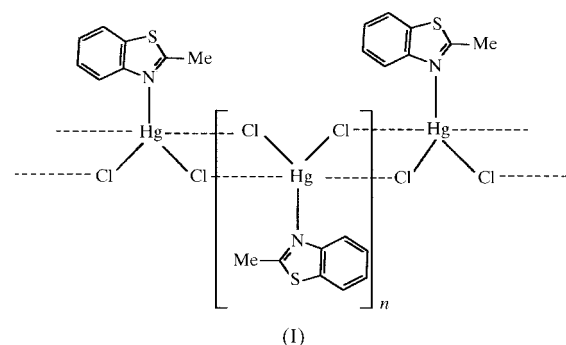
Accepted 4 October 2000

The reaction of 2-methyl-1,3-benzothiazole (mebta) with mercury(II) chloride in methanol in a 1:1 molar ratio resulted in the formation of single crystals of the title compound, [HgCl₂(C₈H₇NS)]_n. The molecules exist as continuous chlorine-bridged chains in which Hg atoms lie in distorted trigonal bipyramidal environments. The equatorial positions are occupied by an N atom from the ligand [2.236 (8) Å] and two Cl atoms [2.428 (3) and 2.459 (3) Å]. The two axial Hg—Cl contacts to two neighbouring molecules [2.874 (3) and 2.964 (3) Å] are significantly shorter than the sum of the respective van der Waals radii, and form close to linear Cl—Hg—Cl sequences [177.80 (7)°].

Comment

Mercury(II) forms complexes with heterocyclic ligands which may contain nitrogen, oxygen, sulfur or a combination of these as parts of endocyclic groups. Such complexes can be used as models for the better understanding of mercury binding in biological systems, as well as of its toxicological behaviour. It is also of interest to get more information on the role of halide ions in such systems. Since the activities of many enzymes depend upon the interaction of a thiazole group with a metal ion, we chose mebta as a model molecule. It is a well known fact that mercury(II) halides form two types of complexes with a neutral ligand depending upon the stoichiometric ratio of the reactants, *i.e.* HgX₂L and HgX₂L₂, respectively. Until now, the only known mercury(II) addition compounds were of the types HgX₂L (X = Cl⁻, Br⁻, I⁻), HgNO₃·L and Hg(ClO₄)₂·1.5L (L = 2-aminobenzothiazole) (Giusti & Peyronel, 1982). On the basis of the IR spectral investigations, the authors exclude a coordination of NH₂-bta (bta is 1,3-benzothiazole) through the amino N atom and support its coordination through the ring nitrogen. Almost as a rule, 2-substituted derivatives of bta act as σ -monodentate ligands through the ring N atom. The only known example of an *N,N'*-bidentate coordination of NH₂-bta is reported for some dimolybdenum 2-aminobenzothiazolate complexes (Cotton & Ilsley, 1981). The 2-aminobenzothiazolate anion is formed

after deprotonation of one amino proton with *n*-butyllithium. It was established that the majority of the structures of 1:1 complexes of mercury(II) halides or pseudohalides with various neutral ligands in the solid state consists of discrete halogen-bridged dimeric molecules with the Hg atom in a tetrahedral environment (Dean, 1978). But this cannot be safely assumed for all 1:1 complexes and other more associated structures are also known (Bell *et al.*, 1981; Einstein *et al.*, 1983; Alvarez-Larena *et al.*, 1997). Recently, we found that due to ring opening of bta by the mercury(II) ion, di- μ -chlorobis[(2-ammonio-benzenethiolato-*S*)chloromercury(II)] was obtained (Davidović *et al.*, 1998), while mebta reacts with the ion in the same manner as the other 2-substituted bta derivatives do, resulting in complexes coordinated through the ring N atom. The structure of (2-mercaptobenzothiazolato)methylmercury(II) is the only one reported so far (Bravo *et al.*, 1985). The stereochemistry of mercury in the solid state is characterized by a few typical modes of ligand binding. The characteristic coordination (*m*) consists of *m* covalently bonded ligands, while the effective coordination (*m* + *n*) includes *n* additionally bonded ligands at distances shorter than the sum of the van der Waals radii of Hg and the donor atom of the ligand (Grdenić, 1965).



The title compound, (I), is a chlorine-bridged polymer (Fig. 1) containing Hg atoms with slightly distorted trigonal

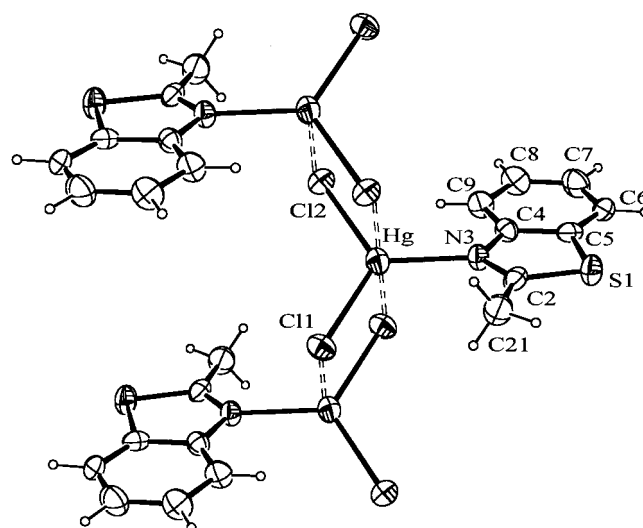


Figure 1
The title molecule with the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level.

bipyramidal coordination (3 + 2). The equatorial positions are occupied by the N atom of the benzothiazole ligand [2.236 (8) Å] and the two terminal Cl atoms [2.428 (3) and 2.459 (3) Å]. The coordination of mercury is an almost regular triangle, with the angles around mercury varying from 118.1 (2) to 122.9 (2)°, and these four atoms are essentially coplanar. The two axial Hg—Cl contacts are close to colinear, with bridging angles of 92.92 (8) and 92.60 (8)°. The Hg—Cl(terminal) and Hg—N distances are longer than expected (sums of the covalent radii are 2.38 and 2.13 Å, respectively) for characteristic trigonal coordination and are in agreement with bond lengths previously reported for chloro-bridged polymeric mercury structures (Biscarini *et al.*, 1977; Bell *et al.*, 1981; Alvarez-Larena *et al.*, 1997).

The molecular parameters for the benzothiazole ligand have expected values. Within the fused benzene ring, the C—C bond lengths range from 1.365 (13) to 1.420 (16) Å; the latter is significantly different from the standard C—C (benzene) value of 1.397 Å. Such differences are common, particularly in fused-ring systems (Oughtred *et al.*, 1982). The C2—S1—C5 angle [90.9 (5)°] is typical of S-containing five-membered heterocyclic molecules. The S1—C2 [1.734 (10) Å] and S1—C5 [1.744 (9) Å] bond lengths imply a partial π character. Significant differences exist between the C2—N3 [1.282 (12) Å] and C4—N3 [1.415 (13) Å] bonds, suggesting localization of π -electron density in the S1—C2—N3 moiety. The solid-state IR spectrum of the title compound in the region of 4000–450 cm^{-1} is in agreement with X-ray diffraction data with respect to the mode of coordination. In the spectral range of 1650–1470 cm^{-1} , which is associated with $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ vibrations, a significant shift of the very strong absorption band toward lower frequencies (from 1529 to 1493 cm^{-1} , and of reduced intensity) is observed. The shift of the $\nu(\text{C}-\text{S})$ vibration toward higher frequencies (from 641 to 654 cm^{-1}) implies an increased $d\pi-p\pi$ contribution between sulfur and the ring π -system.

Experimental

Mercury(II) chloride (0.3 g, 1.1 mmol) was dissolved in methanol (30 ml). Into this solution, a methanol solution of 2-methyl-1,3-benzothiazole (0.36 g, 2.4 mmol; in 20 ml) was added slowly. After a short time, crystallization of the product began. The reaction mixture was left overnight in a cool place. The crystals were filtered off, washed with methanol and dried (yield 75%). Full IR and chemical analysis data are available as supplementary material.

Table 1

Selected geometric parameters (Å, °).

Hg—N3	2.236 (8)	Hg—Cl2 ⁱ	2.874 (3)
Hg—Cl1	2.428 (3)	Hg—Cl1 ⁱⁱ	2.964 (3)
Hg—Cl2	2.459 (3)		
N3—Hg—Cl1	122.9 (2)	N3—Hg—Cl1 ⁱⁱ	87.6 (2)
N3—Hg—Cl2	118.1 (2)	Cl1—Hg—Cl1 ⁱⁱ	87.08 (8)
Cl1—Hg—Cl2	118.84 (9)	Cl2—Hg—Cl1 ⁱⁱ	91.18 (8)
N3—Hg—Cl2 ⁱ	94.6 (2)	Cl2 ⁱ —Hg—Cl1 ⁱⁱ	177.80 (7)
Cl1—Hg—Cl2 ⁱ	92.12 (8)	Hg—Cl1—Hg ⁱⁱ	92.92 (8)
Cl2—Hg—Cl2 ⁱ	87.40 (8)	Hg—Cl2—Hg ⁱ	92.60 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$.

Crystal data

[HgCl₂(C₈H₇NS)]
 $M_r = 420.70$
 Monoclinic, $P2_1/n$
 $a = 7.3460$ (10) Å
 $b = 9.6957$ (6) Å
 $c = 14.9150$ (10) Å
 $\beta = 94.69$ (3)°
 $V = 1058.76$ (17) Å³
 $Z = 4$

$D_x = 2.639$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 27 reflections
 $\theta = 8.2$ – 18.0 °
 $\mu = 15.189$ mm⁻¹
 $T = 293$ (2) K
 Prismatic, colourless
 $0.54 \times 0.22 \times 0.15$ mm

Data collection

Philips PW1100 updated by Stoe diffractometer
 $\theta/2\theta$ scans
 Absorption correction: by integration (Stoe & Cie, 1995)
 $T_{\min} = 0.047, T_{\max} = 0.153$
 2364 measured reflections
 2279 independent reflections
 1629 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 27.02$ °
 $h = -9 \rightarrow 9$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 19$
 4 standard reflections
 frequency: 120 min
 intensity decay: 2.2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.135$
 $S = 1.056$
 2279 reflections
 119 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0887P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 2.18 \text{ e } \text{Å}^{-3}$ (0.92 Å, Hg)
 $\Delta\rho_{\text{min}} = -2.74 \text{ e } \text{Å}^{-3}$ (0.86 Å, Hg)
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0026 (4)

Data collection: *STADIA* (Stoe & Cie, 1995); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1995); structure solution used to solve structure: *SHELXS97* (Sheldrick, 1997); structure refinement used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997)

The authors thank the Ministry of Science and Technology of the Republic of Croatia, Zagreb, for financial support (grant Nos. 119408 and 125003).

Supplementary data, including IR data, for this paper are available from the IUCr electronic archives (Reference: AV1065). Services for accessing these data are described at the back of the journal.

References

- Alvarez-Larena, A., Clegg, W., Cucurull-Sánchez, L., González-Duarte, P., March, R., Piniella, J. F., Pons, J. & Solans, X. (1997). *Inorg. Chim. Acta*, **266**, 81–90.
- Bell, N. A., Goldstein, M., Jones, T. & Nowell, I. W. (1981). *Inorg. Chim. Acta*, **48**, 185–189.
- Biscarini, P., Fusina, L., Nivellini, G. & Pelizzi, G. (1977). *J. Chem. Soc. Dalton Trans.* pp. 664–668.
- Bravo, J., Casas, J. S., Castaño, M. V., Gayoso, M., Mascarenhas, Y. P., Sánchez, A., Santos, C. de O. P. & Sordo, J. (1985). *Inorg. Chem.* **24**, 3435–3438.
- Cotton, F. A. & Ilesley, W. H. (1981). *Inorg. Chem.* **20**, 572–578.
- Davidović, N., Matković-Čalogović, D., Popović, Z. & Vadrina-Dragojević, I. (1998). *Acta Cryst.* **C54**, 574–576.
- Dean, P. A. (1978). *Prog. Inorg. Chem.* **24**, 109–157.
- Einstein, F. W. B., Jones, C. H., Jones, T. & Sharma, R. D. (1983). *Inorg. Chem.* **22**, 3924–3928.
- Farrugia, L. J. (1997). *ORTEP-3 for Windows*. Version 1.02B. University of Glasgow, Scotland.
- Giusti, A. & Peyronel, G. (1982). *Spectrochim. Acta Part A*, **38**, 975–979.
- Grdenić, D. (1965). *Q. Rev.* **19**, 303–328.
- Oughtred, R. E., Raper, E. S., Nowell, I. W. & March, L. A. (1982). *Acta Cryst.* **B38**, 2044–2046.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (1995). *STADIA* and *X-RED*. Versions 1.05B. Stoe & Cie, Darmstadt, Germany.