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Bis[4-(trimethylammonio)phenyl] disulfide tetraiodomercurate(II)

Jin-Xiang Chen,[a] Wen-Hua Zhang,[a] Zhi-Gang Ren,[a] Yong Zhang[a] and Jian-Ping Lang[a,b]*

[a]Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou Uinversity, Suzhou 215006, Jiangsu, People's Republic of China, and [b]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian, People's Republic of China

Correspondence e-mail: jplang@suda.edu.cn

Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.009 Å
R factor = 0.041
wR factor = 0.101
Data-to-parameter ratio = 25.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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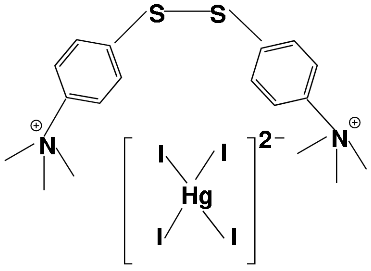
The title compound, ($C_{18}H_{26}N_2S_2$)[HgI_4], consists of a discrete tetraiodomercurate(II) dianion and a bis[4-(trimethylammonio)phenyl] disulfide (Tab-Tab) dication. The geometry about the Hg atom in the dianion is a slightly distorted tetrahedral. The Tab-Tab dications are arranged parallel to each other. Three I atoms of the HgI_4^{2-} dianion are connected to the adjacent H atoms of the methyl and phenyl groups of the Tab-Tab dications to form a two-dimensional network.

Comment

Over recent decades, there has been considerable interest in the coordination chemistry of mercury complexes of organic thiolates, due to their applications in the resistance response in bacteria at the level of gene activation (Casals *et al.*, 1991) and as models for the active site of metallothioneins (Johnson & Armitage, 1987). However, the chemistry of mercury complexes of the zwitterionic organic thiolates is less well explored and only a few compounds have been structurally determined to date (Taylor & Carty, 1977; Casals *et al.*, 1991, 1988; Barrera *et al.*, 1982).

Recently, we have been interested in the preparation of silver clusters from the zwitterionic organic thiolate $TabHPF_6$ [Tab = 4-(trimethylammonio)benzenethiolate; DePamphilis *et al.*, 1974], and several Ag–Tab compounds have been structurally determined (Chen, Xu, Zhang *et al.*, 2004; Chen, Xu, Xu *et al.*, 2004). However, the chemistry of this zwitterionic thiolate with mercury is virtually unknown. Against this background, we carried out the reaction of HgI_2 with $TabHPF_6$ in the presence of Et_4NI. Interestingly, no Hg–Tab complex was formed, but the title compound, (I), containing the HgI_4^{2-} dianion and the oxidized Tab species Tab-Tab dication, was obtained.



(I)

As is well known, many oxidizing agents, such as nitric acid, hydrogen peroxide, oxygen, dimethyl sulfoxide and potassium ferricyanide, can oxidize thiols to disulfides (Yiannos & Karaninos, 1963; Ottersen *et al.*, 1973). In several cases, the

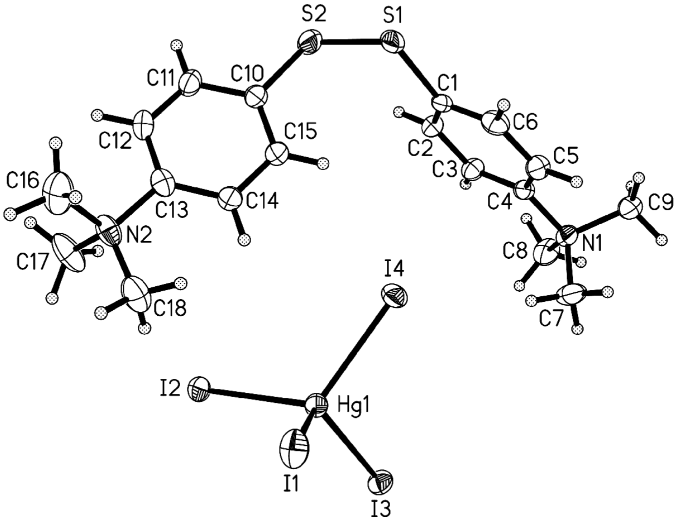


Figure 1
A plot of complex (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

thiol-to-disulfide conversion can also be quickly completed *via* oxygen in the presence of certain metal ions (Chowdhury *et al.*, 1994; Yamamoto & Sekine, 1984). In the present case, the formation of the Tab-Tab dication may be due to the oxidation of Tab *via* oxygen in the presence of Hg^{2+}. It was of interest to determine the structure of the title compound, as there are a limited number of documented metal–organic disulfide salts (Briansó *et al.*, 1981; Casals *et al.*, 1987). Here, we report the crystal structure of the title compound, (I).

The asymmetric unit of (I) contains a Tab-Tab dication and an HgI_4 dianion (Fig. 1). The geometry about the Hg atom in the dianion is slightly distorted tetrahedral (Table 1). Due to the formation of intermolecular C—H···I contacts, the Hg—I bond distances vary from 2.7559 (6) to 2.8003 (5) Å and the I—Hg—I angles vary greatly, from 104.325 (17) to 119.647 (18)°. The mean Hg—I bond length of 2.782 (5) Å is shorter than that observed in $[HgI_4]^{2-}$ in (24-pyrimidinium crown-6)[(DMSO)HgI_3][HgI_4][Hg_2I_7] [2.833 (4) Å; Cramer & Carrie, 1990], but longer than that observed in $[Hg_2I_7]^{3-}$ in the same compound [2.743 (3) Å], and the corresponding distances in [Hg(cryptand 222)][Hg_3I_8] [2.637 (3) Å; cryptand 222 = 4,17,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane; Pickardt & Kühn, 1995].

The Tab-Tab dication has positive charges located on the NMe_3 groups. The torsion angle about the S—S bond [C1—S1—S2—C10] is 92.1 (3)°, which is larger than those reported in *L-L* (86.3°), [Cu(*L-L*)](PF_6) (77.5°) or [Ag(*L-L*)](PF_6) [76.5°; *L-L* = 2,2′-bis[6-(2,2′-bipyridyl)]diphenyldisulfide; Cargill Thompson *et al.*, 1997], $[C_5H_9NH(CH_3)S]_2CuCl_4$ (90°; Briansó *et al.*, 1981) and $[\{(CH_3)_2HN(CH_2)_3\}_2][CdBr_4]$ (75.4°; Casals *et al.*, 1987). The S—S bond length is 2.030 (3) Å, which is comparable with those observed in $[C_5H_9NH(CH_3)S]_2CuCl_4$ [2.02 (2) Å; Briansó *et al.*, 1981], $[\{(CH_3)_2NH(CH_2)_3S\}_2]$-[$CdBr_4$] [2.013 (3) Å; Casals *et al.*, 1987] and bis-[2-(*N*,*N*-dimethylamino)]disulfide dihydrochloride [2.0374 (12) Å; Ottersen *et al.*, 1973].

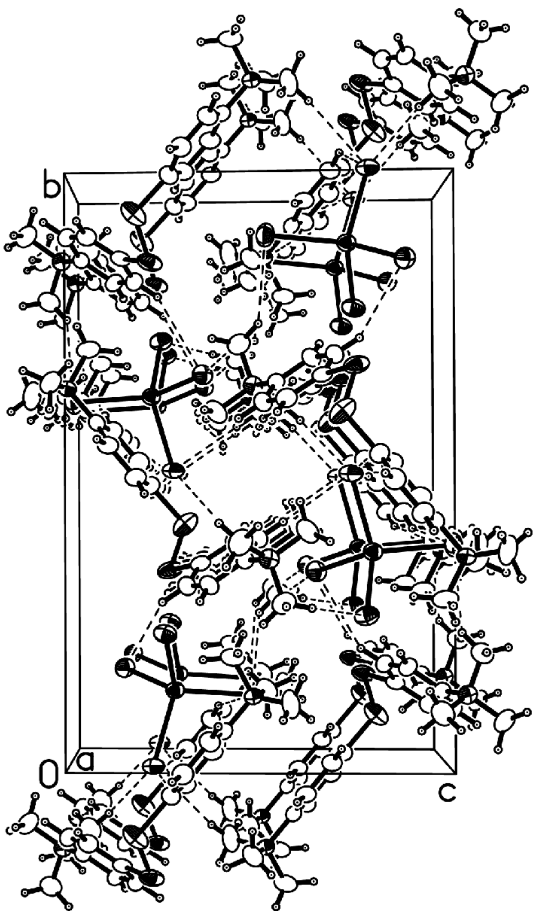


Figure 2
A packing diagram for (I), viewed along the *a* axis, showing the two-dimensional network formed by C—H···I interactions (dashed lines).

The Tab-Tab dications in the crystal of (I) are arranged parallel to each other along the *a* axis, and the HgI_4 dianions are positioned between the cations. Such an arrangement leads to the involvement of I atoms in hydrogen bonds. The I atoms are hydrogen-bond acceptors and the H atoms of the methyl or phenyl groups are hydrogen-bond donors, thereby forming a two-dimensional network (Fig. 2, Table 2).

Experimental

Trimethylammoniumphenyl-4-thiol hexafluorophosphate was prepared according to the literature procedure of DePamphilis *et al.* (1974). To a suspension containing $TabHPF_6$ (62.6 mg, 0.2 mmol) in MeOH (5 ml) was added Et_3N (0.25 ml). The resulting colourless solution was then treated with a solution of HgI_2 (0.045 g, 0.1 mmol) and Et_4NI (0.05 g, 0.2 mmol) in MeCN (10 ml). The mixture was stirred at room temperature for 1 h and then filtered. Diethyl ether (10 ml) was allowed to diffuse into the filtrate. After standing at ambient temperature for several days, colourless block crystals of (I) were formed (yield 0.016 g, 15% based on Hg). The crystal used for the crystal structure determination was obtained directly from the above preparation. Analysis, found: C 20.52, H 2.31, N 3.02%; calculated for $C_{18}H_{26}HgI_4N_2S_2$: C 20.73, H 2.51, N 2.69%. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3011 (*w*), 1485 (*s*), 1465 (*m*), 1406 (*m*), 1120 (*m*), 1007 (*s*), 951 (*s*), 743 (*m*).

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Crystal data

$(C_{18}H_{26}N_2S_2)[HgI_4]$
M_r = 1042.72
Monoclinic, $P2_1/n$
a = 10.4974 (8) Å
b = 20.3856 (13) Å
c = 13.2263 (10) Å
β = 95.332 (2)°
V = 2818.1 (4) Å^3
Z = 4

D_x = 2.458 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 684 reflections
θ = 3.1–27.5°
μ = 10.00 mm^{-1}
T = 193 (2) K
Block, colourless
0.50 × 0.20 × 0.15 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min}$ = 0.104, $T_{\max}$ = 0.223
31 234 measured reflections

6445 independent reflections
5645 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.049
$\theta_{\max}$ = 27.5°
$h = -13 \rightarrow 13$
$k = -22 \rightarrow 26$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
$R(F)$ = 0.041
$wR(F^2)$ = 0.101
S = 1.07
6445 reflections
251 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 3.7432P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 2.35 e Å^{-3}
$\Delta\rho_{\min}$ = −1.93 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg1—I1	2.7559 (6)	S1—C1	1.779 (6)
Hg1—I4	2.7803 (5)	S1—S2	2.030 (3)
Hg1—I2	2.7921 (5)	S2—C10	1.782 (6)
Hg1—I3	2.8003 (5)		
I1—Hg1—I4	104.325 (17)	I4—Hg1—I3	104.449 (16)
I1—Hg1—I2	107.628 (16)	I2—Hg1—I3	104.339 (16)
I4—Hg1—I2	117.143 (16)	C1—S1—S2	106.4 (2)
I1—Hg1—I3	119.647 (18)	C10—S2—S1	104.5 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···I4$^{\rm i}$	0.95	3.03	3.898 (6)	152
C9—H9C···I3$^{\rm ii}$	0.98	3.02	3.934 (7)	155
C12—H12A···I1$^{\rm iii}$	0.95	3.00	3.882 (7)	155
C16—H16A···I4$^{\rm iv}$	0.98	3.10	3.989 (9)	151

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $2-x, 1-y, 1-z$; (iii) $x-1, y, z$; (iv) $1-x, 1-y, 2-z$.

All H atoms were placed in geometrically idealized positions (C—H = 0.98 Å for methyl groups and 0.95 Å for phenyl groups) and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The maximum and minimum electron-density peaks are located 0.86 (1) and 0.76 (2) Å from atom I1.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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