Acta Chemica Scandinavica, 1995: 49: 391–398
Printed in Belgium – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Structure of the Triiodomercurate(II) Ion in the Solid and Liquid State

Lars A. Bengtsson,[a,†] Bertil Norén[a] and Harald Stegemann[b,†]

[a]Inorganic Chemistry 1, University of Lund, PO Box 124, S-221 00 Lund, Sweden and [b]Institut für Anorganische Chemie, FR Chemie, Ernst-Moritz-Arndt-Universität Greifswald, Soldtmannstr. 16, D-17489 Greifswald, Germany

Bengtsson, L. A., Norén B., Stegemann H., 1995. Structure of the Triiodomercurate(II) Ion in the Solid and Liquid State. – Acta Chem. Scand. 49: 391–398 © Acta Chemica Scandinavica 1995.

The crystal structures of $(Me_3S)HgI_3$ and $(Et_3S)HgI_3$ have been determined at room temperature, and both crystallise in the space group $P2_1/n$ (No. 14) with the unit-cell parameters $a = 8.496(1)$, $b = 15.500(2)$ and $c = 9.324(1)$ Å, $\beta = 97.96(1)°$, $Z = 4$ and $a = 8.766(1)$, $b = 13.126(1)$ and $c = 12.998(2)$ Å, $\beta = 91.63(1)°$, $Z = 4$, respectively. The trimethyl sulfonium compound consists of discrete cations and chains of HgI_3^- anions along the *c*-axis. The structure of the triethyl sulfonium compound is related, but consists of discrete cations and dimeric anions $Hg_2I_6^{2-}$, which are fragments of the HgI_3^- chains in the corresponding trimethyl sulfonium salt. Theoretical studies indicate that the HgI_3^- state is energetically the more stable. The small change in cation size most likely induces structural changes because of packing requirements. This observation is supported by the fact that isolated HgI_3^- anions predominate in melts and acetone solutions of both salts, as indicated by the results of liquid X-ray scattering, Raman and NMR spectroscopy.

Research into the effects of iodide-accepting cations on the local structure and conductivity properties of trialkyl sulfonium-based polyiodide systems has led to synthesis of compounds such as $(R_3S)I_x$–HgI_2 (various *x*) and their structural characterisation.[1,2] The polyiodide compound $(Et_3S)I_7$–HgI_2(s) has been shown to consist of $Hg_2I_6^{2-}$ dimers bridged into a three-dimensional network by iodine molecules. In the present work the structures of the non-I_2-containing analogues $(R_2S)I$–HgI_2, R = Me and Et, have been determined and analysed in the solid and liquid state.

The effect of transition or post-transition metal cations on polyiodide structures has previously primarily been confined to so-called screened cations, e.g. $Co(NH_3)_6^{3+}$ or $Pt(en)_2^{2+}$,[3,4] with a few exceptions such as Tl_6PbI_{10}.[5]

The structure of $(Me_3S)I$–HgI_2, or rather $(Me_3S)HgI_3$(s), has been known since the mid-sixties and consists of trigonal HgI_3^- units stacked into chains.[6,7] Since the structural moiety in the triethyl sulfonium polyiodide $(Et_3S)HgI_9$ described above contains $Hg_2I_6^{2-}$ dimers instead of chains of trigonal HgI_3^- units, we considered it of interest to investigate whether this difference in iodomercurate structure depends on the inclusion of iodine into the structure or on the size of the trialkyl sulfonium cation. The previously reported structure of $(Me_3S)HgI_3$ has also been redetermined.

Triiodomercurate(II) compounds are known to crystallise in four different ways; as discrete HgI_3^- anions, HgI_3^- chains, distorted HgI_3^- chains which are better described as chains of corner-sharing HgI_4^{2-} tetrahedra, and discrete $Hg_2I_6^{2-}$ dimers (*vide infra*). The coordination chemistry of mercury(II) and iodide has been reviewed thoroughly and recently.[2,8,9] The HgX_3^- compounds for the other halides, $X = Cl^-$ and Br^-, are also known. The structures of such compounds will not be discussed here, but it is noted that a trend to form HgX_3^- chains with small cations and $Hg_2X_6^{2-}$ dimers with large ones has been addressed on the basis of vibrational spectroscopic and crystallographic results.[10,11] However, the data presented in the literature are not easily generalized in terms of halomercury anion and cation size, and many of the conclusions are speculative. This work is devoted to the synthesis and detailed structural study of two analogous trialkyl sulfonium-based compounds on the borderline of structural rearrangement in order to shed some light on the stability of the triiodomercurate(II) ion configuration.

In this study the structures of the trialkyl sulfonium triiodomercurate(II) compounds are studied by X-ray diffraction and Raman spectroscopy in the solid state, and X-ray scattering, Raman and NMR spectroscopy in the liquid state.

† To whom correspondence should be addressed.

Experimental

Chemicals. The trialkyl sulfonium triiodomercurates, $(R_3S)HgI_3$, were prepared by mixing stoichiometric amounts of an aqueous slurry of HgI_2 (BDH, *p.A.* grade) and an acetone solution of the trialkyl sulfonium iodide to give a pale yellow solution.[12] The $(R_3S)I$ reactants (Janssen, 98%) were purified by recrystallisation from a hot ethanol solution before use. Single crystals were grown by slow evaporation. The crystals are transparent and yellow. The trimethyl sulfonium solution gives only one product, the intended $(Me_3S)HgI_3$(s), whereas the triethyl sulfonium solution produces crystals of $(Et_3S)_2HgI_4$(s), $(Et_3S)HgI_3$(s) and $(Et_3S)Hg_2I_5$(s), as identified by visual observation of the crystals, chemical analysis and Raman spectroscopy. The crystal structures of the other compound have been determined.[13,14]

Crystal structure determination. The intensity data sets were collected at room temperature on an Enraf-Nonius CAD4 diffractometer employing graphite monochromatised Mo*K*α radiation (λ = 0.7107 Å). The ω–2Θ scan technique was used, and the scan interval, Δω, was extended 25% at both ends for the background measurements. Three standard reflections were measured at regular intervals. A random variation within ±3% in the intensities was observed in both data collections. [For $(Me_3S)HgI_3$ the intensities increased non-linearly during the first 40 h of X-ray exposure time; thus the data collection was restarted and thereafter no systematic variation was observed]. Information on the collection and reduction of the data is given in Table 1. The values of I and $\sigma(I)$ were corrected for Lorentz, polarisation and absorption effects. Reflections with $I<3\sigma(I)$ were considered to be insignificantly different from the background and were excluded from all subsequent calculations. The cell dimensions were determined by least-squares methods from the Θ-angles of 25 reflections for both compounds. The Θ-values were obtained as $\Theta_{hkl} = (\omega_{hkl} - \omega_{\overline{hkl}})/2$ with $\omega_{\overline{hkl}}$ measured at negative Θ-angles. Both compounds belong to the Laue class $2/m$. Systematic extinctions are consistent with the space group $P2_1/n$. The structures were refined by full-matrix least-squares calculations employing programs compiled and amended by Lundgren.[15] In the final refinement, anisotropic temperature factors were applied to all non-hydrogen atoms. Hydrogens could not be located in the final difference Fourier map. Scattering factors with corrections for

Table 1. Unit-cell parameters and experimental crystal data for $(R_3S)HgI_3$(s), R=Me and Et.

	R=Me	R=Et
Formula	$C_3H_9HgI_3S$	$C_6H_{15}HgI_3S$
M (g mol^{-1})	658.47	700.55
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Laue symmetry	$2/m$	$2/m$
a (Å)	8.496(1)	8.766(1)
b (Å)	15.500(2)	13.126(1)
c (Å)	9.324(1)	12.998(2)
β (°)	97.96(1)	91.63(1)
U (Å^3)	1216.0(3)	1495.0(2)
Z	4	4
D_c/g cm^{-3}	3.596	3.112
Crystal size/mm	0.20×0.13×0.31	0.37×0.17×0.17
Temperature/°C	23	23
Radiation (graphite monochromator)/Å	Mo*K*α, 0.71069	Mo*K*α, 0.71069
θ interval/°	3–28	3–28
h, k, l range	±11, +20, +12	±11, +17, +17
ω − 2θ scan width, Δω/°	0.7+0.5 tan θ	1.0+0.3 tan θ
$\sigma(I)/I$ requested in a scan	0.028	0.028
Maximum recording time/s	120	120
μ/cm^{-1}	203.0	165.2
No. measured reflections	3086	3728
No. unique reflections	2878	3543
No. reflexions with $I>3\sigma(I)$	1619	1995
No. parameters refined	73	100
C1 in weighting function[a]	0.035	0.017
C2 in weighting function	4.00	2.00
$(\Delta/\sigma)_{max}$ (non-hydrogen atoms)	0.030	0.092
R_{int}	0.012	0.012
R	0.046	0.044
R_w	0.063	0.063
S	1.07	1.01
δR-plot, slope	1.00	1.18
δR-plot, intercept	−0.08	−0.09

[a] $w^{-1} = \sigma/4|F_o|^2 + (C1|F_o|)^2 + C2$.

Table 2. Fractional coordinates and isotropic thermal parameters for $(Me_3S)HgI_3$(s).

Atom	x/a	y/b	z/c	B_{eq} [a]
Hg	0.2567(1)	0.0221(1)	0.5668(1)	2.16(1)
I1	0.3638(1)	0.0916(1)	0.3319(1)	1.42(1)
I2	0.3193(1)	0.0885(1)	0.8341(1)	1.52(1)
I3	0.1066(1)	−0.1317(1)	0.5072(1)	1.34(1)
S	−0.1185(5)	0.1308(3)	0.0801(5)	1.55(1)
C1	−0.145(3)	0.113(2)	−0.114(3)	2.9(3)
C2	−0.298(2)	0.183(2)	0.098(2)	1.9(2)
C3	0.020(2)	0.217(1)	0.098(3)	2.1(2)

[a] $B_{eq}=(8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}(U_{ij}a_i^*a_j^*\boldsymbol{a}_i\boldsymbol{a}_j)$.

Table 3. Fractional coordinates and isotropic thermal parameters for $(Et_3S)HgI_3$(s).

Atom	x/a	y/b	z/c	B_{eq} [a]
Hg	0.1456(1)	0.1157(1)	0.0016(1)	1.45(1)
I1	0.4055(1)	0.1216(1)	−0.1043(1)	1.45(1)
I2	0.0934(1)	0.2838(1)	0.1186(1)	1.59(1)
I3	−0.1173(1)	0.0666(1)	−0.1278(1)	1.62(1)
S	0.1021(5)	0.3340(3)	−0.1951(3)	1.24(3)
C1	0.213(6)	0.438(4)	−0.167(5)	8.6(8)
C2	0.359(3)	0.429(2)	−0.112(2)	2.3(2)
C3	−0.070(4)	0.395(4)	−0.210(4)	9.2(9)
C4	−0.189(3)	0.392(2)	−0.133(2)	2.2(2)
C5	0.130(8)	0.319(2)	−0.325(2)	6.9(9)
C6	0.121(3)	0.222(2)	−0.370(2)	2.1(2)

[a] $B_{eq}=(8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}(U_{ij}a_i^*a_j^*\boldsymbol{a}_i\boldsymbol{a}_j)$.

anomalous dispersion were taken from Ref. 16. The final positional and thermal parameters are given in Tables 2 and 3.

$(Me_3S)HgI_3$. The structure was solved using the MULTAN 80 program with magic integers,[17] which revealed the positions of the mercury and all three iodine atoms. Subsequent difference Fourier calculations gave the positions of the S and C atoms. The absorption corrections of the values of I and $\sigma(I)$ were made according to the method of Walker and Stuart.[18] The corrections were in the ranges 0.81–1.20 for $A_{p,s}$ and 0.93–1.22 for A_{Θ}.[19] In the final difference Fourier map $(\Delta\rho)_{max}=1.6$ and $(\Delta\rho)_{min}=-2.4$ e Å^{-3}, respectively.

$(Et_3S)HgI_3$. The structure was solved by use of Patterson and difference Fourier methods. The absorption corrections were made as described above. The values of $A_{p,s}$ were in the range 0.84–1.25 and A_{Θ} in the range 0.89–1.10. The electron densities from the final difference Fourier map were $(\Delta\rho)_{max}=1.2$ and $(\Delta\rho)_{min}=-1.2$ e Å^{-3}, respectively.

Liquid X-ray scattering. The structure of a 0.4 M acetone solution of $(Et_3S)HgI_3$ (Table 4) was investigated at room temperature. A Θ-Θ large-angle GSD Seifert X-ray diffractometer was used to record the scattering of Mo$K\alpha$ radiation ($\lambda=0.7107$ Å) from the surface of the acetone solution, employing an EG&G ORTEC Ge solid-state detector, in which the energy discrimination is electronically controlled. The solution was kept in a calibrated thin-wall cylindrical glass container, in order to avoid evaporation. The scattering was registered at discrete angles in the region $7.52<2\Theta<120.84°$ collecting in total 8×10^4 counts at each angle. The increment between scattering angles were 0.0335 in s, as defined by $s=4\pi\lambda^{-1}\sin\Theta$. The scattering data below $2\Theta=7.52°$ were estimated by extrapolation.

Corrections and data treatment have been thoroughly described elsewhere.[20–24] The experimental data were normalised to a stoichiometric unit volume, V, containing one mercury atom. The factors for coherent and incoherent scattering were taken from the usual sources,[16,25,26] and the KURVLR and STEPLR programs were used to evaluate the liquid structure.[27,28]

Raman spectroscopy. The backscattering from the samples $(Me_3S)HgI_3$(s), $(Et_3S)HgI_3$(s) (at room temperature), $(Me_3S)HgI_3$(l), $(Et_3S)HgI_3$(l) (at 165 and 110 °C, respectively) and their 0.4 M acetone solutions (at room temperature) were recorded using the 1064 nm radiation of a low-power Nd:YAG laser of a Bruker IFS-66/FRA-106 FT Raman spectrometer with a Ge-diode detector. The resolution used was 4 cm^{-1}.

NMR spectroscopy. A Varian Unity 300 MHz spectrometer was used to record the ^{1}H, ^{13}C, ^{33}S, ^{199}Hg and ^{127}I spectra of acetone solutions of $(R_3S)HgI_3$, R = Me and Et. Only the ^{199}Hg spectra provide detailed information about the coordination chemistry of the triiodomercurate(II) ions in solution. The chemical shifts of ^{199}Hg spectra are given relative to Me_2Hg.

Results and discussion

Crystal structure. $(Me_3S)HgI_3$(s) consists of pyramidal Me_3S^+ cations and trigonal HgI_3^- units stacked into one-dimensional chains along the c-axis. $(Et_3S)HgI_3$(s) on the other hand consists of spider-like Et_3S^+ cations

Table 4. Composition and physical data for 0.4 M $(Et_3S)HgI_3$ in acetone.

C_{Hg} [a]	C_I [a]	C_S [a]	C_O [a]	C_C [a]	C_H [a]	V/Å^3 [b]	ρ/g cm^{-3}	μ/cm^{-1}
0.401	1.203	0.401	12.28	39.24	79.68	4141	0.994	15.8

[a] Concentrations in mol dm^{-3}. [b] Per mercury atom.

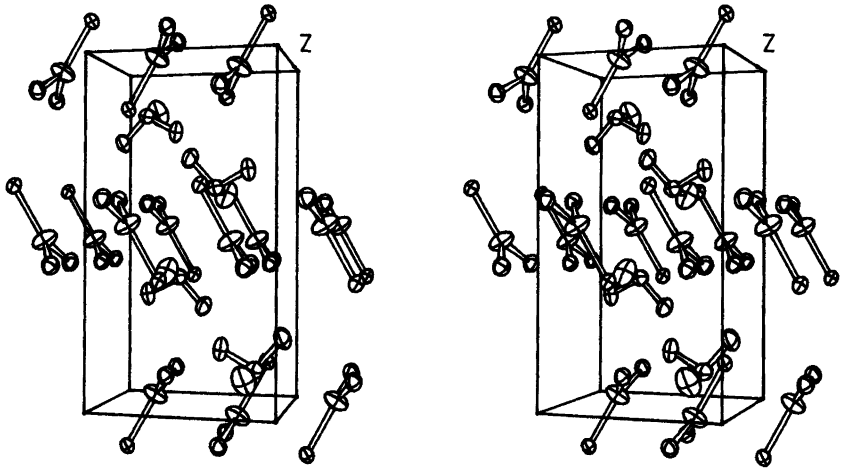

Fig. 1. A stereoscopic view of the crystal structure of $(Me_3S)HgI_3$(s).

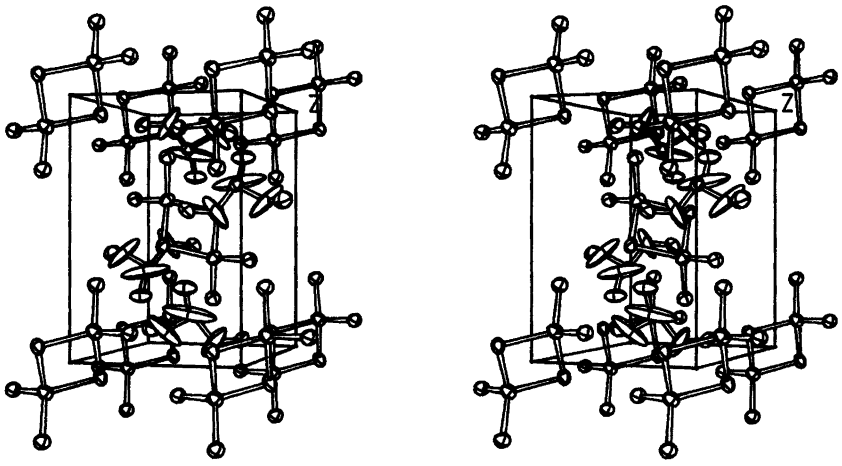

Fig. 2. A stereoscopic view of the crystal structure of $(Et_3S)HgI_3$(s).

and isolated $Hg_2I_6^{2-}$ dimers. Stereoscopic views of the unit cells are shown in Figs. 1 and 2.

The anion structure of the triethyl sulfonium compound can be visualised as being formed from the trimethyl sulfonium compound by a rearrangement of the HgI_3^- chains into $Hg_2I_6^{2-}$ dimers, followed by a twist of the dimers away from the *c*-axis direction. The structural relationship is shown in Fig. 3. It is noteworthy that the ellipsoids of the central mercury atom in the HgI_3^- anions exhibit a large, static or dynamic, disorder out of the HgI_3^- plane. The distances between the nearest neighbours of a single HgI_3^- unit in the chains are 4.42 and 4.53 Å, respectively. The mercury ellipsoids may indicate a tendency to dimerisation already in the trimethyl sulfonium salt. The mercury atom is, on average, 0.088(1) Å out of the plane defined by the iodines. The results obtained for $(Me_3S)HgI_3$ are indeed very similar to those originally reported by Fenn, although the precision and accuracy reported in the present work (merely reflecting the technological development over time) is significantly higher. The structure was redetermined in order to verify that the iodomercurate structures of the two trialkyl sulfonium compounds really are different.

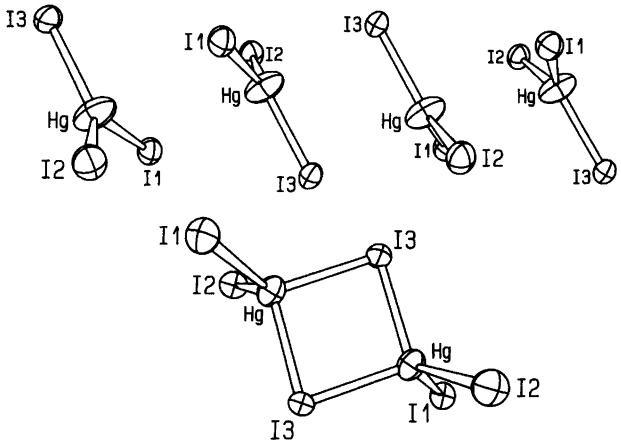

Fig. 3. The structural relationship between the one-dimensional chain of HgI_3^- units in $(Me_3S)HgI_3$(s) and the $Hg_2I_6^{2-}$ dimers in $(Et_3S)HgI_3$(s).

The HgI_3^- units in $(Me_3S)HgI_3$(s) are nearly perfectly trigonal with the mercury–iodide distances only ranging from 2.68 to 2.72 Å and the I–Hg–I angles from 113 to 124°. The shortest intermolecular mercury–iodide contact is 3.51 Å, and should therefore not be regarded as bonding. The sulfonium cations are positioned relative to the HgI_3^- anions at the I–I edges. The intermolecular I–S distances are between 3.84 and 4.88 Å, and the I–C distances between 3.74 and 4.61 Å. The S–C distances are 1.76–1.82 Å and the C–S–C angles 100–103°, which is slightly less than a perfect tetrahedral angle. The shortest intra- and intermolecular distances and angles are given in Table 5.

The centrosymmetric $Hg_2I_6^{2-}$ dimers in $(Et_3S)HgI_3$(s) consist of two tetrahedra joined at an edge. The bridging mercury–iodine distances are significantly longer, 2.89 and 2.92 Å, than the terminal ones, 2.70 and 2.73 Å.

The angles between the terminal and bridging iodines are about 112 and 94°, respectively. The Hg–Hg distance is as long as 3.97 Å, and no direct covalent Hg–Hg interaction is therefore inferred. The bridging $Hg_2I_2^{2+}$ unit is thus almost rectangular. The cations are positioned relative the $Hg_2I_6^{2-}$ anions over the triangular faces in the HgI_4^{2-} tetrahedra. The cation position is very similar to that found in $(Me_3S)HgI_3$ and also in the tetrahedra of $(Et_3S)_2CdI_4$(s) and $(Et_3S)_2HgI_4$(s).[13] The intermolecular I–S distances are between 4.01 and 4.13, and the I–C distances range from 3.95 to 4.75 Å, which is only slightly longer than in the trimethyl sulfonium compound and in the same range as in the trialkyl sulfonium polyiodides (3.91–5.25 Å).[1,29] The S–C distances in the cation are between 1.71 and 1.72 Å, and the angles are in the range 95–102°. The C–C bonds are between 1.41 and 1.48 Å and the S–C–C angles are in the range 120–123°. Table 6 contains some intra- and intermolecular distances and angles.

The structural motif of $Hg_2I_6^{2-}$ has also been observed in $(Et_3S)HgI_9$(s), which represents an I_2-containing analogue.[2] The dimeric structure is quite common among formal triiodomercurate(II) compounds of large cations, as is visualised in Table 7. The average terminal Hg–I bond length is 2.7 Å, whereas the bridging one is 2.9 Å. It seems that the formation of new Hg–I bonds at about 2.9 Å, going from more or less isolated HgI_3^- units to $Hg_2I_6^{2-}$ dimers, is energetically at least partly compensated for by the elongation of another Hg–I bond from 2.7 to 2.9 Å.

The results of *ab initio* theoretical calculations using local and extended model systems to compare the total energy between the HgI_3^- and $Hg_2I_6^{2-}$ conformations indicate that the state of 2 HgI_3^- is more stable than the

Table 5. Some intramolecular distances and angles and intermolecular distances below 5 Å in $(Me_3S)HgI_3$(s).

	Distance/Å		Angle/°
HgI_3^-			
Hg–I_1	2.709(1)	I_1–Hg–I_2	123.60(5)
Hg–I_2	2.680(1)	I_1–Hg–I_3	112.52(5)
Hg–I_3	2.724(1)	I_2–Hg–I_3	123.56(5)
I_1–I_2	4.604(2)		
	4.750(2)		
I_1–I_3	4.518(2)		
I_2–I_3	4.762(2)		
$(CH_3)_3S^+$			
S–C_1	1.82(3)	C_1–S–C_2	100(1)
S–C_2	1.76(2)	C_1–S–C_3	101(1)
S–C_3	1.77(2)	C_2–S–C_3	103(1)
Intermolecular distances below 5 Å			
Hg–I_1	3.682(2)	C_2–I_2	4.07(2)
Hg–I_3	3.507(2)		4.22(2)
Hg–Hg	4.421(2)		4.26(2)
	4.532(2)	C_2–I_3	3.90(2)
Hg–S	4.348(5)		3.92(2)
S–I_1	4.473(5)	C_3–I_1	3.91(2)
	4.877(5)		3.97(2)
S–I_2	3.936(5)	C_3–I_2	4.23(2)
	4.679(5)		4.26(2)
S–I_3	3.835(5)	C_3–I_3	4.17(2)
C_1–I_1	4.07(3)		4.19(2)
	4.61(3)		
C_1–I_2	4.06(3)		
	4.52(3)		
C_1–I_3	3.74(3)		
C_2–I_1	4.09(1)		
	4.60(2)		

Table 6. Some intramolecular distances and angles and intermolecular distances below 5 Å in $(Et_3S)HgI_3$(s).

	Distance/Å		Angle/°
$Hg_2I_6^{2-}$			
Hg–I_1	2.696(1)	I_1–Hg–I_2	114.77(5)
Hg–I_2	2.726(1)	I_1–Hg–I_3	112.39(4)
Hg–I_3	2.887(1)		113.42(4)
	2.916(1)	I_2–Hg–I_3	109.41(4)
I_1–I_2	4.567(2)		111.24(4)
I_1–I_3	4.266(2)	I_3–Hg–I_3	93.75(4)
	4.641(2)		
I_2–I_3	4.633(2)		
$(C_2H_5)_3S^+$			
S–C_1	1.71(5)	C_1–S–C_3	98(2)
S–C_3	1.71(4)	C_1–S–C_5	102(3)
S–C_5	1.72(3)	C_3–S–C_5	95(3)
C_1–C_2	1.45(6)	S–C_1–C_2	122(4)
C_3–C_4	1.48(5)	S–C_3–C_4	123(3)
C_5–C_6	1.41(4)	S–C_5–C_6	120(2)
Intermolecular distances below 5 Å			
Hg–Hg	3.967(2)	C_2–I_2	4.30(3)
Hg–S	3.852(4)	C_3–I_2	4.70(5)
S–I_1	4.007(4)	C_3–I_3	4.47(5)
S–I_2	4.132(4)	C_4–I_2	4.28(3)
S–I_3	4.108(5)	C_4–I_3	4.32(2)
C_1–I_1	3.95(6)	C_5–I_1	4.51(5)
	4.54(5)	C_5–I_3	4.75(4)
C_1–I_2	4.38(6)	C_6–I_1	4.40(2)
C_2–I_1	4.07(3)	C_6–I_3	4.34(2)

Table 7. Average Hg–I distances of some HgI_3^- and $L_2Hg_2I_4$ structural motifs.

Compound	$\langle Hg–I \rangle_{term}$/Å	$\langle Hg–I \rangle_{bridg}$/Å	Ref.
$[C_5H_8N_2]HgI_2$	2.65	3.23	38
$[C_{11}H_{22}N_2S_4]Hg_2I_4$	2.62	2.90	39
$[C_{36}H_{30}P_2]Hg_2I_4$	2.68	2.92	40
$[C_{18}H_{42}P_2]Hg_2I_4$	2.69	2.96	41
$[C_{14}H_{14}N_2S_2]Hg_2I_4$	2.67	3.01	42
$[C_{22}H_{30}N_2S_2]Hg_2I_4$	2.67	2.94	43
$[C_{46}H_{38}P_2]Hg_2I_4$	2.68	2.96	44
$[C_{14}H_{20}S_2]Hg_2I_4$	2.71	2.96	45
$[C_{60}H_{124}N_{18}Hg_3I_{11}O_{14}S_{12}]HgI_3$	2.66		46
$[KH_2O]HgI_3$	2.72	2.87	47
$[C_4H_{12}N]HgI_3$	2.68	2.92	48
$[C_4H_{16}N_4Hg_2I_3]HgI_3$	2.73		49
$[C_{33}H_{35}CoO_3P_3]HgI_3$	2.69		50
$[C_3H_9S]HgI_3$	2.68		7
$[C_{16}H_{36}N]HgI_3$	2.69		11
$[C_3H_9S]HgI_3$	2.70		[a]
$[C_{10}H_{20}N_2S_3]Hg_2I_6$	2.69	2.94	51
$[C_{16}H_{40}N_2HgI_2]Hg_2I_6$	2.70	2.92	52
$[C_{48}H_{40}P_2]Hg_2I_6$	2.70	2.91	53
$[C_{38}H_{50}O_6S_2]Hg_2I_6$	2.70	2.92	54
$[C_{24}H_{56}N_2]Hg_2I_6$	2.70	2.90	55
$[C_{16}H_{40}N_2HgI_2]Hg_2I_6$	2.69	2.93	56
$[C_{36}H_{16}Se_8]Hg_2I_6$	2.74	2.89	57
$[C_{16}H_{40}N_2]Hg_2I_6$	2.69	2.91	58
$[C_{12}H_{30}S_2I_{12}]Hg_2I_6$	2.72	2.85	2
$[C_{12}H_{30}S_2]Hg_2I_6$	2.71	2.90	[a]

[a] This work.

dimeric state by some 0.9 eV (about 90 kJ mol^{-1}).[30] The fact that HgI_3^- anions seem to predominate in melts and acetone solution, in which packing effects are absent (*vide infra*), supports the results of the quantum-chemical calculations.

The trialkylsulfonium cations do not seem to bond covalently to the mercury iodide anions, since the I–S distances are in the same range as those found in trialkyl sulfonium triiodides. The cation–anion contacts in such polyiodide systems were shown by X-ray absorption spectroscopy to have negligible electron density between the cation and anion.[1,29] A covalent cation–anion interaction is therefore unlikely. The interaction between the trialkyl sulfonium cations and the mercury halide anions is most likely of a Coulombic or van der Waals type. The shortest I–S distances observed in the structures are 3.84 Å in the HgI_3^- compound and 4.01 Å in the $Hg_2I_6^{2-}$ one. The difference in Coulombic energy only amounts to some 0.05 eV per $I^- – S^+$ contact, as estimated from an unscreened Coulombic potential. It therefore seems appropriate to attribute the driving force for dimer formation in the solid state either to van der Waals interactions between large cations and the anions enhanced by the formation of larger anion entities, i.e. dimers, or to packing effects in which the formation of dimers provides more space for the larger cations without dramatic changes of the crystal lattice. Structures such as that of $[(n\text{-}Bu)_4N]HgI_3$ (isolated HgI_3^-) show that the shape of the cations is indeed of importance.[11,31]

Large-angle X-ray scattering. The $(R_3S)HgI_3$ compounds decompose upon melting (approximate melting points are 160 and 105 °C for R = Me and R = Et, respectively) to give products such as R_2S and I_3^-. However, the triiodomercurates are readily soluble in acetone. The reduced intensity function and reduced radial distribution function (rRDF) of a 0.4 M acetone solution of $(Et_3S)HgI_3$ recorded at room temperature are shown in Fig. 4. The rRDF is totally dominated by two peaks at 2.72 and 4.57 Å. These peaks are in almost perfect agreement with previous results in more strongly coordinating solvents such as DMSO, water and DMF.[32–35]

The peak at 2.72 Å is identified as the Hg–I distance and the peak at 4.57 Å as the I–I distance in a pyramidal HgI_3^- ion. The mercury atom is 0.66 Å out of the plane defined by the iodides. The apex of the pyramid is most likely occupied by a solvent molecule to give a quasi-tetrahedral configuration, shown in Fig. 5, although the $Hg–OC(CH_3)_2$ distance cannot be directly determined. No distinct cation–anion contact can be identified, although they most likely give the main contributions to the broad peak between 4 and 5 Å. It is obvious that the planar trigonal HgI_3^- geometry does not persist in solution, in which solvent–solute interactions are of importance. The planar trigonal configuration appears easy to distort, since even such a weakly coordinating solvent molecule as acetone can reduce the symmetry from D_{3h} to C_{3v}.

The liquid X-ray structure of an acetone solution of

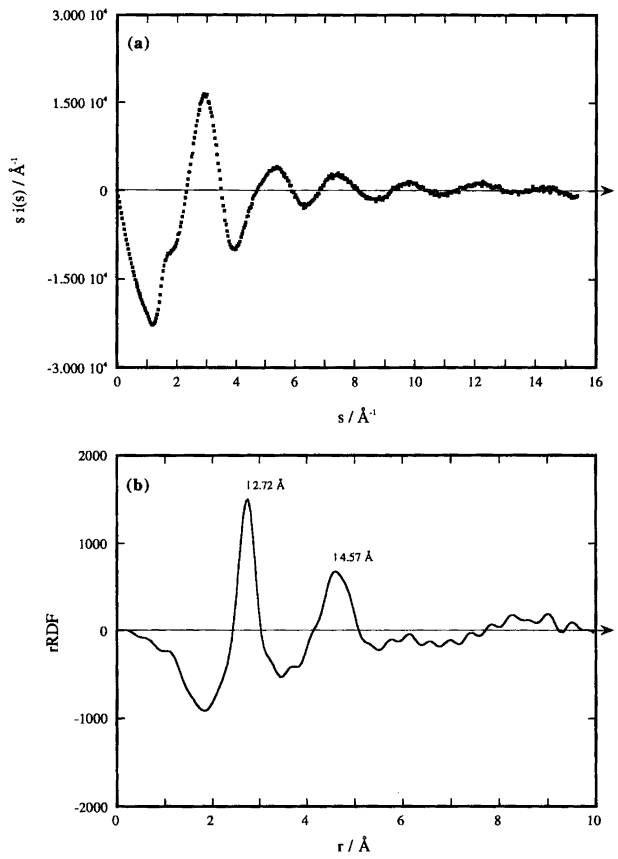

Fig. 4. Experimental data for a 0.4 M acetone solution of $(Et_3S)HgI_3$; **(a)** reduced intensity data; **(b)** experimental rRDF (———).

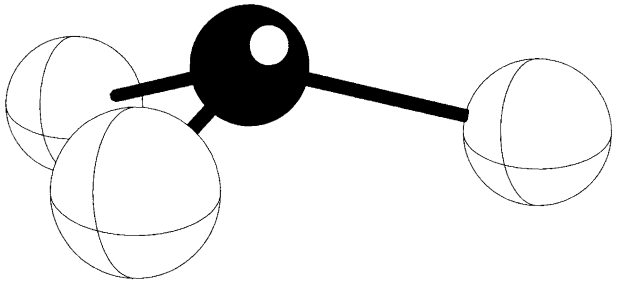

Fig. 5. The pyramidal structure of HgI_3^- in solution as determined by liquid X-ray scattering.

$(Me_3S)HgI_3$ was not determined, since the very similar Raman and NMR spectra (*vide infra*) clearly show that the structure must be identical to that of $(Et_3S)HgI_3$ in acetone.

Raman spectroscopy. Raman spectra were recorded for solid, molten and 0.4 M acetone solution of the two $(R_3S)HgI_3$ compounds. All spectra, apart from that of solid $(Et_3S)HgI_3$ where additional peaks appear, display a single strong peak at about 130–135 cm^{-1} in the low-frequency region. Such a peak has been shown to correspond to a three-coordinate mercury–iodide complex with C_{3v} or D_{3h} symmetry.[2,10,11,34] No detailed symmetry analysis can be done, since this single peak is the only significant spectral feature. A planar trigonal structure has been proposed for HgI_3^- in TBP solution, based on spectroscopic results.[36] Far-IR measurements could possibly give enough information to distinguish between the C_{3v} and D_{3h} symmetries in the melts and acetone solutions. However, such spectra often display overlapping bands which make accurate assignments difficult. Furthermore, the main information can already be extracted: the melts and acetone solutions contain isolated planar or pyramidal HgI_3^- units. The case of solid $(Et_3S)HgI_3$ is complicated by the presence of a mixture of compounds having an overall composition of $(Et_3S)HgI_3$ (see Experimental section).

NMR spectroscopy. The ^1H, ^{13}C, ^{33}S and ^{127}I spectra of the melts and acetone solutions of $(R_3S)HgI_3$, R = Me and Et, provide little information. Only small differences in the chemical shifts and coupling patterns are observed. This fact, however, indicates that the systems are structurally very similar. The NMR spectra of ^{199}Hg provide some further information about the composition of the mercury–iodide complex, though. The ^{199}Hg spectra of the 0.4 M acetone solutions exhibit a single peak at −3291 and −3346 ppm relative to Me_2Hg for the trimethyl and triethyl sulfonium compounds, respectively. A chemical shift at about −3000 ppm in a weakly coordinating solvent such as acetone is indicative of a three-coordinated mercury–iodide species in the solution.[37] The results thus further support those of liquid X-ray scattering and show together with the Raman spectroscopic data that the trimethyl and triethyl sulfonium triiodomercurate acetone solutions are analogous.

Concluding remarks

The structure of $(Et_3S)HgI_3$ consists of $Hg_2I_6^{2-}$ dimers and can be visualised as being formed from the trimethyl sulfonium compound by a condensation of the HgI_3^- chains into chains of discrete dimers (much like the condensation of a hypothetical one-dimensional chain of hydrogen atoms into a chain of H_2 molecules). The energetically favoured triiodomercurate(II) configuration is HgI_3^- with D_{3h} symmetry. In molecular solution the ideal trigonal geometry is distorted by the interaction with solvent molecules to give a quasi-tetrahedral HgI_3L^- moiety (L represents a solvent molecule). Isolated HgI_3^- units of D_{3h} or C_{3v} symmetry also prevail in the molten compounds. Since the energy difference between the monomeric and dimeric states is small, several effects can cause the observed structural difference between the two solid compounds. Because of the small difference in Coulombic cation–anion interaction it seems appropriate to attribute the structural difference to either van der Waals or packing effects, or both. The fact that monomeric triiodomercurate(II) ions predominate in solution and

melts, in which static packing effects are absent, indicates that the difference in solid-state structures is indeed the result of packing requirements. In relation to the structure of the iodine-containing analogue $(Et_3S)HgI_9$, it should be emphasized that the dimerisation is not apparently induced by the presence of I_2, since the dimers already exist in $(Et_3S)HgI_3$.

Supplementary Material

Supplementary data are available from the authors on request.

This work has been supported by the Swedish Natural Science Research Council and DFG (contract no. Stc 663) and the *Fonds der Chemischen Industrie*.

References

1. Bengtsson, L. A., Stegemann, H., Holmberg, B. and Füllbier, H. *Mol. Phys.* **73** (1991) 283.
2. Stegemann, H., Tebbe, K.-F. and Bengtsson, L. A. *Z. Anorg. Allgem. Chem. 621* (1995) 165.
3. Tebbe, K.-F. In Rheingold, A. L. (Ed.), *Polyhalogen Cations and Polyhalide Anions*, Elsevier, Amsterdam, 1977.
4. Marks, T. J. and Kalina, D. W. In Miller, J. S. (Ed.), *Highly Conductive Halogenated Low-Dimensional Materials*, Plenum Press, New York 1982.
5. Rabenau, A., Schulz, H. and Stoeger, W. *Naturwiss. 63* (1976) 245.
6. Fenn, R. H., Oldham, J. W. H. and Phillips, D. C. *Nature (London) 188* (1963) 381.
7. Fenn, R. H. *Acta Crystallogr. 20* (1966) 20.
8. Wells, A.F. *Structural Inorganic Chemistry*, Clarendon Press, Oxford 1984.
9. Grdenic', D. In Dodson, G., Glusker, J. P. and Sayre, D. (Ed.), *Connections in the Crystal Structures of Mercury Compounds*, Clarendon Press, Oxford 1981.
10. Barr, R. M. and Goldstein, M. *J. Chem. Soc., Dalton Trans.* (1976) 1593.
11. Goggin, P. L. *et al., J. Chem. Soc., Dalton Trans.* (1982) 875.
12. Ray, P. C. and Adhikary, N. *J. Indian Chem. Soc 7* (1930) 297.
13. Bengtsson, L. A., Berglund, J. and Stegemann, H. *To be published.*
14. Bengtsson, L. A., Svensson, P. and Stegemann, H. *To be published.*
15. Lundgren, J. O. *Crystallographic Computer Programs*, Report No. UUIC-B13-4-05, University of Uppsala, Uppsala, Sweden 1982.
16. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974.
17. Main, P. *et al., MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, Universities of York, England, and Louvain, Belgium 1980.
18. Walker, N. and Stuart, D. *Acta Crystallogr., Sect. A 39* (1983) 158.
19. Ugozzoli, F. *Comput. Chem. 11* (1987) 109.
20. Levy, H. A., Danford, M. D. and Narten, A. H. *Data Collection and Evaluation with an X-Ray Diffractometer Designed for the Study of Liquid Structure*, ORNL-3960, Oak Ridge National Laboratory, Oak Ridge, TN 1966.
21. Persson, I. and Sandström, M. *J. Chem. Soc., Dalton Trans.* (1985) 1597.
22. Sandström, M. and Johansson, G. *Acta Chem. Scand., Ser. A 35* (1977) 275.
23. Johansson, G. *Acta Chem. Scand. 20* (1966) 553.
24. Johansson, G. *Acta Chem. Scand. 25* (1971) 2787.
25. Compton, D. T. and Allison, J. W. *X-Rays in Theory and Experiment*, Van Nostrand, New York 1935.
26. Cromer, D. T. *J. Chem. Phys. 50* (1969) 4857.
27. Johansson, G. and Sandström, M. *Chem. Scr. 4* (1973) 195.
28. Molund, M. and Persson, I. *Chem. Scr. 25* (1985) 197.
29. Bengtsson, L.A., Oskarsson, Å., Stegemann, H. and Redeker, A. *Inorg. Chim. Acta. 215* (1994) 33.
30. Bengtsson, L. A. *Unpublished results.*
31. Mingos, D. M. P. and Rohl, A. L. *J. Chem. Soc., Dalton Trans.* (1991) 3419.
32. Gaizer, F. and Johansson, G. *Acta Chem. Scand. 22* (1968) 3013.
33. Sandström, M. and Johansson, G. *Acta Chem. Scand., Ser. A 31* (1977) 132.
34. Sandström, M. *Acta Chem Scand., Ser. A 32* (1978) 627.
35. Ahrland, S., Hansson, E., Iverfeldt, Å and Persson, I. *Acta Chem. Scand., Ser. A 35* (1981) 275.
36. Waters, D. N., Short, E. L., Tharwat, M. and Morris, D. F. C. *J. Mol. Struct. 17* (1973) 389.
37. Kidd, R. G. and Goodfellow, R. J. in Harris, R. K. and Mann, B. E. (Ed.), *The Transition Metals*, Academic Press, London 1978.
38. Battaglia, L. P., Corradi, A. B., Biddau, M. and Ponticelli, G. *J. Cryst. Spectrosc. Res. 16* (1986) 721.
39. Enckewort, W. J. P. V., Buerskens, P. T., Menger, E. M. and Bosman, W. P. *Cryst. Struct. Commun. 6* (1977) 417.
40. Bell, N. A., March, L. A. and Nowell, I. W. *Inorg. Chim. Acta 156* (1989) 201.
41. Bell, N. A., Chudley, N. A., March, L. A. and Nowell, I. A. *Inorg. Chim. Acta 141* (1988) 155.
42. Hiller, V. W., Castinieras, A., Arquero, A. and Masaguer, J. R. *Acta Crystalogr., Sect. C 42* (1986) 151.
43. Castiñeiras, A., Arquero, A., Masaguer, J. R., Martinez-Carrera, S. and Garcia-Blanco, S. *Z. Anorg. Allgem. Chem. 539* (1986) 219.
44. Baenziger, N. C., Flynn, R. M., Swenson, D. C. and Holy, N. L. *Acta Crystallogr., Sect. B 34* (1978) 2300.
45. Baenziger, N. C., Flynn, R. M. and Holy, N. L. *Acta Crystallogr., Sect. B 36* (1980) 1642.
46. Cramer, R. E. and Carrié, M. J. J. *Inorg. Chem. 29* (1990) 3902.
47. Nyqvist, L. and Johansson, G. *Acta Chem. Scand. 25* (1971) 1615.
48. Fedorov, P. M. and Pakhomov, V. I. *Koord. Khim. 1* (1975) 1140.
49. Grdenic', D., Sikirica, M. and Vicković, I. *Acta Crystallogr., Sect. B 33* (1977) 1630.
50. Sullivan, R. J., Bao, Q.-B., Landon, S. J., Rheingold, A. L. and Brill, T. B. *Inorg. Chim. Acta 111* (1986) 19.
51. Buerskens, P. T., Bosman, W. P. J. H. and Cras, J. A. *J. Cryst. Mol. Struct. 2* (1972) 183.
52. Csordás, L., Kratochvil, B., Novotny, J. and Belencsák, I. *Acta Chim. Hung. 128* (1991) 267.
53. Zacharie, B., Wuest, J. D., Olivier, M. J. and Beauchamp, A. L. *Acta Crystallogr., Sect. C 41* (1985) 369.
54. Pears, D. A., Stoddart, J. F., Crosby, J., Allwood, B. L. and Williams, D. J. *Acta Crystallogr., Sect. C 42* (1986) 804.
55. Contreras, J. G., Seguel, G. V. and Hönle, W. *J. Mol. Struct. 68* (1980) 1.
56. Fábry, J. and Maximov, B. A. *Acta Crystallogr., Sect. C 47* (1991) 51.
57. Shibaeva, R. P. and Kaminskii, V. F. *Kristallografiya 29* (1984) 606.
58. Belencsák, I., Csordás, L., Kratochvil, B. and Gál, M. *Acta Chim. Hung. 127* (1990) 247.

Received September 22, 1994.