Crystal and molecular structure of
3,5-bis(N,N-diethylimonium)-1,2,4-trithiolanetetraiododi-μ-iododimercurate(II)

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Abstract
The crystal and molecular structure of 3,5-bis(N,N-diethylimonium)-1,2,4-trithiolane-tetraiododi-μ-iododimercurate(II), \( (S_3C_2N_2(C_2H_5)_4)Hg_2I_6 \), has been determined from a single-crystal X-ray diffraction study. The monoclinic unit cell, space group \( P2_1/c \), with \( a = 12.574(3) \), \( b = 15.777(4) \), \( c = 14.560(4) \) Å, and \( β = 90.83(4)° \), contains four formula-units. Three-dimensional intensity data were collected on an automatic diffractometer. Atomic parameters were refined by full-matrix least-squares methods to a conventional \( R \) value of 0.05 for 1380 independent non-zero reflexions. The structure consists of (3,5-bis(N,N-diethylimonium)-1,2,4-trithiolane)\( ^2+ \) and \( Hg_2I_6^- \) ions. The cation contains a five-membered ring, \( S—S—C—S—C \), which can be formed by oxidation of dithiocarbamato and thiuramdisulfide complexes.

Introduction
During the work in our laboratory on the redox properties of dithiocarbamato (dtc, fig. 1a) complexes of transition metals, it was observed that the (dtc) ligands in some complexes could be oxidized to the ligand tetraalkylthiuramdisulfide (tds, fig. 1b) (Brinkhoff et al., 1969), which could be oxidized further to a positive ion, denoted by \( (dtc)_2^{2+} \) (Willemse & Steggerda, 1969). In previous communications, the syntheses and the crystal structure determinations of \( HgI_2(tds) \) complexes were reported (Brinkhoff, 1970; Beurskens et al., 1971). Brinkhoff (1970)
obtained yellow needle-shaped crystals by treating a concentrated solution of one mole of $\text{HgI}_2(\text{tds})$ in nitrobenzene with a solution of three times this molar concentration of iodine in the same solvent. This compound was denoted by the formula $(\text{dtc}_2)^{2+}\text{Hg}_2\text{I}_6^{-}$. Elemental analyses of this compound showed a deficiency of sulfur. To elucidate the nature of the positive ion, we performed an X-ray analysis of this compound. It was found that the positive ion is the 3,5-bis($N,N$-diethylamonium)-1,2,4-trithiolane cation = $(\text{bitt})^{2+}$ (fig. 1d). This ion can be considered as an oxidized form of tetraalkythiurammonosulfide (fig. 1c).

The present compound is formulated as $(\text{bitt})^{2+}\text{Hg}_2\text{I}_6^{-}$. Its infrared spectra in the region 4000–700 cm$^{-1}$ agree completely with those found by Willemse & Steggerda (1969) for the compound $\text{FeCl}_4(\text{dtc})$, for which the authors give strong evidence for the presence of a dipositive ion. It may now be concluded that this compound is of ionic composition $(\text{bitt})^{2+}(\text{FeCl}_4)^{2-}$.

Fig. 1. (a) dtc = $N,N$-dialkylthiocarbamato ion; (b) tds = $N,N,N',N'$-tetraalkylthiuramdisulfide; (c) tms = $N,N,N',N'$-tetraalkylthiurammonosulfide; (d) $(\text{bitt})^{2+} = 3,5$-bis($N,N$-dialkylamonium)-1,2,4-trithiolane ion.
Crystal data
The compound 3,5-bis(N,N-diethylimonium)-1,2,4-trithiolane-tetraiododi-μ-
iododimercurate(II), (S₃C₂N₂(C₂H₅))Hg₂I₆ (= (bitt)²⁺Hg₂I₆⁻), \(FW = 1427-06\),
crystallizes as yellow needles, elongated along c. Weissenberg photographs showed
the crystals to be monoclinic, with space group \(P2_1/c\) (no. 14). From platinum-
calibrated Weissenberg photographs, using CuK\(\alpha\) radiation (\(\lambda = 1-5418\ \text{Å}\)),
application of a least-squares procedure yielded the unit cell dimensions \(a = 12-574(3)\),
\(b = 15-777(4)\), \(c = 14-560(4)\ \text{Å}\), \(\beta = 90-83(4)°\) and \(V_c = 2888-2(5)\ \text{Å}^3\).
The calculated density is 3-28 g cm\(^{-3}\) with \(Z = 4\).

A crystal of approximate dimensions, 0-1, 0-1, 0-2, mm was mounted with the
c axis along the \(\phi\) axis of a Nonius automatic diffractometer. Intensity data were
measured with Zr-filtered Mo radiation, (linear absorption coefficient \(\mu = 175-3\ \text{cm}^{-1}\)) using the moving-counter moving-crystal method with a scan speed of
0-6°/min. After every 20 reflexions, a reference reflection was measured to detect
and allow correction to be made for slow fluctuations in the measuring apparatus.

The presumed standard deviation \(\sigma(I)\) of a measurement was calculated accord-
ing to \(\sigma^2(I) = \sigma_c^2 + (\frac{1}{4}I_B)^2\), where \(\sigma_c\) is the counting statistical error and \(I_B\) is the
number of background counts. Reflections with \(I < 3\sigma(I)\) were considered as
unobserved reflexions and were not used in the structure determination.

Absorption corrections were calculated according to the Busing & Levy (1957)
procedure, using \(8 \times 10 \times 12\) volume components and 10 accurately-located
boundary planes. Lorentz and polarization corrections were performed in the
usual way, and the presumed standard deviation \(\sigma(F_o)\) of the structure amplitudes
were derived from \(\sigma(I)\).

Of the 2685 independent reflexions theoretically attainable within the limit
\(\theta < 20°\), 1380 reflexions were observed.

Structure determination
The positions of the mercury and iodine atoms were determined from a three-
dimensional sharpened Patterson function.

Two subsequent difference Fourier syntheses gave the positions of the remaining
non-hydrogen atoms. The positional and vibrational parameters and the scale
factor were refined by full-matrix least-squares calculations, allowing anisotropic
vibration of the mercury and iodine atoms. The function that was minimized was
\[\sum w(|F_o| - |F_c|)^2,\] with weight \(w = (\sigma^2(F_o) + (0.05|F_o|)^2)^{-1}\) (Wijnhoven \textit{et al.},
1972). The atomic scattering factor of Hg, I, S, C and N were corrected for the
anomalous scattering component (\(\Delta F\)) using data from the International Tables
(1962). The final conventional \(R\) factor is 0-048.

Calculations were performed on an IBM 370/155 computer, using programs
written by Busing, Martin & Levy (1962), Ahmed & Pippy (1968), Johnson (1965)
and several programs written in the laboratory.
Table 1. Atomic parameters for \((\text{bilih})^{2+} \cdot \text{Hg}_2 \text{I}_6^2-\). The esd’s (in parentheses) result from the least-squares refinement. The expression for the anisotropic temperature factor is:

\[
\exp \left(- \left( \beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + 2\beta_{12} hk + 2\beta_{13} hl + 2\beta_{23} kl \right) \right).
\]

<table>
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<tr>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(\beta_{11})</th>
<th>(\beta_{22})</th>
<th>(\beta_{33})</th>
<th>(\beta_{12})</th>
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<td>Hg(1)</td>
<td>0.1516(2)</td>
<td>-0.0309(2)</td>
<td>0.0269(2)</td>
<td>0.0049(2)</td>
<td>0.0079(2)</td>
<td>0.0037(2)</td>
<td>0.0002(1)</td>
<td>-0.0008(1)</td>
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<td>0.0000(2)</td>
<td>0.4772(2)</td>
<td>0.0065(2)</td>
<td>0.0041(1)</td>
<td>0.0099(2)</td>
<td>0.0007(2)</td>
<td>-0.0005(1)</td>
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<tr>
<td>I(1)</td>
<td>0.2383(2)</td>
<td>-0.0055(2)</td>
<td>0.1955(2)</td>
<td>0.0058(2)</td>
<td>0.0044(2)</td>
<td>0.0046(2)</td>
<td>-0.0004(2)</td>
<td>-0.0018(2)</td>
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<tr>
<td>I(2)</td>
<td>0.2768(2)</td>
<td>-0.0887(2)</td>
<td>-0.1069(2)</td>
<td>0.0073(3)</td>
<td>0.0039(2)</td>
<td>0.0068(2)</td>
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<td>0.0016(2)</td>
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<tr>
<td>I(3)</td>
<td>0.0436(2)</td>
<td>-0.1285(2)</td>
<td>-0.0244(2)</td>
<td>0.0053(3)</td>
<td>0.0036(2)</td>
<td>0.0041(2)</td>
<td>-0.0006(2)</td>
<td>-0.0010(2)</td>
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<td>I(4)</td>
<td>0.4839(2)</td>
<td>0.0088(2)</td>
<td>0.6472(2)</td>
<td>0.0060(2)</td>
<td>0.0065(2)</td>
<td>0.0041(2)</td>
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<td>-0.0008(2)</td>
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<tr>
<td>I(5)</td>
<td>0.2440(3)</td>
<td>0.1526(2)</td>
<td>0.4784(2)</td>
<td>0.0111(4)</td>
<td>0.0044(2)</td>
<td>0.0059(2)</td>
<td>0.0022(2)</td>
<td>0.0030(2)</td>
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<tr>
<td>I(6)</td>
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<td>-0.1512(2)</td>
<td>0.4868(3)</td>
<td>0.0096(4)</td>
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<td>0.0107(3)</td>
<td>-0.0008(2)</td>
<td>-0.0058(2)</td>
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| \(S(1)\) | 0.1901(9) | 0.2116(7) | 0.2037(7) | 3.53(25) |
| \(S(2)\) | 0.3499(8) | 0.2004(7) | 0.2375(7) | 3.62(26) |
| \(S(4)\) | 0.2715(9) | 0.3729(7) | 0.2885(7) | 3.54(25) |
| \(C(3)\) | 0.3650(32) | 0.2934(24) | 0.2926(25) | 3.5(9) |
| \(N(3)\) | 0.4534(22) | 0.3082(17) | 0.3425(20) | 2.3(7) |
| \(C(31)\) | 0.4728(32) | 0.3869(25) | 0.3699(23) | 4.3(10) |
| \(C(32)\) | 0.4177(35) | 0.3756(26) | 0.4945(29) | 5.2(1-1) |
| \(C(33)\) | 0.5379(31) | 0.2394(23) | 0.3582(26) | 3.4(9) |
| \(C(34)\) | 0.6169(38) | 0.2542(30) | 0.2798(33) | 6.2(1-3) |
| \(C(5)\) | 0.1730(30) | 0.3164(22) | 0.2258(24) | 2.7(9) |
| \(N(5)\) | 0.0831(25) | 0.3564(20) | 0.2095(20) | 3.7(7) |
| \(C(51)\) | 0.0652(36) | 0.4442(30) | 0.2335(31) | 5.1(1-1) |
| \(C(52)\) | 0.0586(47) | 0.5027(38) | 0.1476(40) | 9.7(1-6) |
| \(C(53)\) | -0.0102(34) | 0.3072(25) | 0.1607(28) | 4.3(1-0) |
| \(C(54)\) | -0.0679(37) | 0.2640(27) | 0.2337(31) | 5.3(1-5) |
Fig. 2. Projection of the structure along b. The (bitt)\(^{2+}\) ion is represented by black bond lines; the ethyl groups are omitted, except for the upper-left cation. The Hg\(_2\)I\(^6^-\) ions are represented by open bond lines.

Fig. 3. Bond distances (Å) and angles (degrees), with esd’s, of the (bitt)\(^{2+}\) ion and of the two symmetry-independent centrosymmetric Hg\(_2\)I\(^6^-\) ions. The following angles are not given in the figure:

- I(1)'—Hg(1)'—I(3)' = 106·4°  I(2)—Hg(1)'—I(3)' = 108·4°,
- I(4)—Hg(2)'—I(5)' = 113·4°  I(4)'—Hg(2)'—I(6)' = 104·9°,

all ±0·2°.
Description of the structure

The atomic parameters are given in table 1 and the structure is illustrated in fig. 2. Bond distances and angles are given in fig. 3. The crystal structure analysis revealed the compound to be composed of two distinct ionic units, the 3,5-bis(N,N-diethyl-immonium)-1,2,4-trithiolane cation, \(\text{(bitt)}^{2+}\), and the tetraiododi-\(\mu\)-iodomercurate(II) anion.

The cation is situated at a general position, whereas two non-equivalent \(\text{Hg}_2\text{I}_6^-\) ions are found at centers of symmetry. The cation consists of two planar dithiocarbamate groups sharing one common sulfur atom \(\text{S}(4)\). The dithiocarbamate groups are planar within the accuracy of the structure determination. The dihedral angle calculated from the least-squares planes through these groups is 9-5°. The five-membered ring has a chair conformation; \(\text{S}(1)\) is 0.49 Å below the \(\text{S}(2), \text{S}(4), \text{C}(3), \text{N}(3), \text{C}(31), \text{C}(33)\) plane and \(\text{S}(2)\) is 0.27 Å above the \(\text{S}(1), \text{S}(4), \text{C}(5), \text{N}(5), \text{C}(51), \text{C}(53)\) plane.

The \(\text{Hg}_4\text{I}_8^-\) ions can be described as slightly-distorted edge-condensed bi-tetrahedrons. The terminal \(\text{Hg-I}\) bond lengths are the same as those found in \(\text{HgL}_{2}(\text{tds})\) (Beurskens et al., 1971) and in \([\text{S(CH}_3)_3]_2\text{HgL}\) (Fenn, 1966). The bridging bond lengths are significantly longer, as is to be expected. The statistically significant differences in the geometry of the two independent \(\text{Hg}_4\text{I}_8^-\) ions are probably not of chemical importance, and may be due to different environment.

All interatomic contacts are in the expected range; the shortest interactions are \(\text{I}(1)-\text{S}(1) = 3.48 \pm 0.01\) Å and \(\text{I}(1)-\text{S}(2) = 3.59 \pm 0.01\) Å.

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References


National Lending Library Supplementary Publication No. 60051 contains 11 pages of structure factor tables on 1 microfiche.