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# Crystal and molecular structure of 3,5-bis(*N*,*N*-diethylimonium)-1,2,4-trithiolane-tetraiododi-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 $a = 12{\cdot}574(3)$, $b = 15{\cdot}777(4)$, $c = 14{\cdot}560(4)$ Å, and $\beta = 90{\cdot}83(4)°$, 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 $Hg_2I_6^{2-}$ 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 $HgI_2$(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 $(dtc_2)^{2+}Hg_2I_6^{2-}$. 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*-diethylimonium)-1,2,4-trithiolane cation = $(bitt)^{2+}$ (fig. 1d). This ion can be considered as an oxidized form of tetraalkylthiurammonosulfide (fig. 1c).

The present compound is formulated as $(bitt)^{2+}$ $Hg_2I_6^{2-}$. Its infrared spectra in the region 4000–700 $cm^{-1}$ agree completely with those found by Willemse & Steggerda (1969) for the compound $FeCl_4$(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 $(bitt)^{2+}(FeCl_4)^{2-}$.

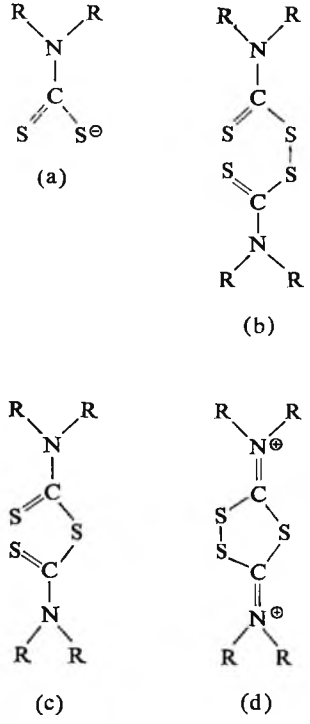


Fig. 1. (a) dtc = *N*,*N*-dialkyldithiocarbamato ion; (b) tds = *N*,*N*,*N*′,*N*′-tetraalkylthiuramdisulfide; (c) tms = *N*,*N*,*N*′,*N*′-tetraalkylthiurammonosulfide; (d) $(bitt)^{2+}$ = 3,5-bis(*N*,*N*-dialkylimonium)-1,2,4-trithiolane ion.

*Crystal data*

The compound 3,5-bis(*N*,*N*-diethylimonium)-1,2,4-trithiolane-tetraiododi-$\mu$-iododimercurate(II), $(S_3C_2N_2(C_2H_5))Hg_2I_6$ (= $(bitt)^{2+}Hg_2I_6^{2-}$), $FW = 1427{\cdot}06$, 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 Cu$K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), application of a least-squares procedure yielded the unit cell dimensions $a = 12{\cdot}574(3)$, $b = 15{\cdot}777(4)$, $c = 14{\cdot}560(4)$ Å, $\beta = 90{\cdot}83(4)°$ and $V_c = 2888{\cdot}2(5)$ 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 $\mu = 175{\cdot}3$ 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 according to $\sigma^2(I) = \sigma_c^2 + (\frac{1}{3}I_B)^2$, 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 $w = (\sigma^2(F_o) + (0{\cdot}05|F_o|)^2)^{-1}$ (Wijnhoven *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* $(bitt)^{2+}$ $Hg_2I_6^{2-}$. *The esd's (in parentheses) result from the least-squares refinement. The expression for the anisotropic temperature factor is:*

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

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Hg(1) | 0·1516(2) | −0·0309(2) | 0·0269(2) | 0·0049(2) | 0·0079(2) | 0·0037(2) | 0·0002(1) | −0·0008(1) | −0·0008(1) |
| Hg(2) | 0·3405(2) | 0·0000(2) | 0·4772(2) | 0·0065(2) | 0·0041(1) | 0·0099(2) | 0·0007(2) | −0·0005(1) | −0·0008(2) |
| I(1) | 0·2383(2) | −0·0055(2) | 0·1955(2) | 0·0058(2) | 0·0044(2) | 0·0046(2) | −0·0004(2) | −0·0018(2) | −0·0000(2) |
| I(2) | 0·2768(2) | −0·0887(2) | −0·1069(2) | 0·0073(3) | 0·0039(2) | 0·0068(2) | 0·0002(2) | 0·0016(2) | −0·0005(2) |
| I(3) | 0·0436(2) | 0·1285(2) | −0·0244(2) | 0·0053(3) | 0·0036(2) | 0·0041(2) | −0·0006(2) | −0·0010(2) | −0·0002(2) |
| I(4) | 0·4839(2) | 0·0088(2) | 0·6472(2) | 0·0060(2) | 0·0065(2) | 0·0041(2) | 0·0013(2) | −0·0008(2) | −0·0019(2) |
| I(5) | 0·2440(3) | 0·1526(2) | 0·4784(2) | 0·0111(4) | 0·0044(2) | 0·0059(2) | 0·0022(2) | 0·0030(2) | 0·0008(2) |
| I(6) | 0·2462(3) | −0·1512(2) | 0·4868(3) | 0·0096(4) | 0·0053(2) | 0·0107(3) | −0·0008(2) | −0·0058(2) | 0·0002(2) |
| | | | | $B$, Å² | | | | | |
| 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(1·0) | | | | | |
| 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) | | | | | |

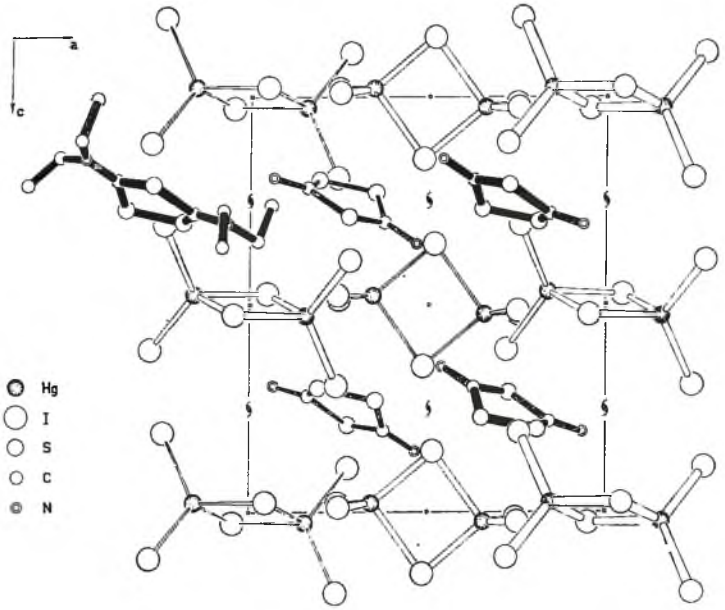


Fig. 2. Projection of the structure along *b*. The $(bitt)^{2+}$ ion is represented by black bond lines; the ethyl groups are omitted, except for the upper-left cation. The $Hg_2I_6^{2-}$ ions are represented by open bond lines.

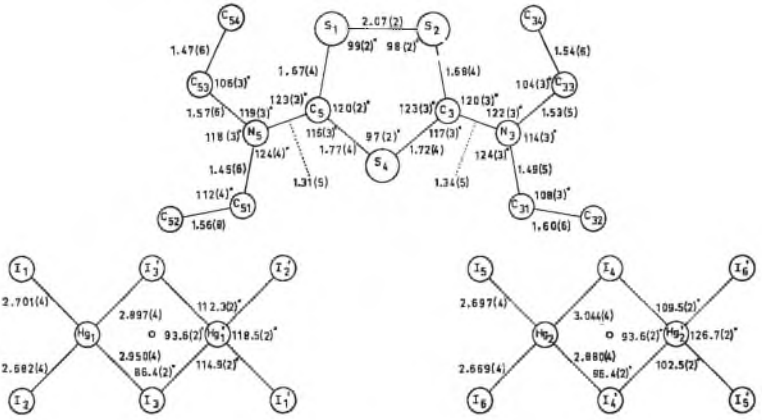


Fig. 3. Bond distances (Å) and angles (degrees), with esd's, of the $(bitt)^{2+}$ ion and of the two symmetry-independent centrosymmetric $Hg_2I_6^{2-}$ ions. The following angles are not given in the figure:

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*-diethylimonium)-1,2,4-trithiolane cation, $(bitt)^{2+}$, and the tetraiododi-$\mu$-iodomercurate(II) anion.

The cation is situated at a general position, whereas two non-equivalent $Hg_2I_6^{2-}$ ions are found at centers of symmetry. The cation consists of two planar dithiocarbamate groups sharing one common sulfur atom 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; S(1) is 0·49 Å below the S(2), S(4), C(3), N(3), C(31), C(33) plane and S(2) is 0·27 Å above the S(1), S(4), C(5), N(5), C(51), C(53) plane.

The $Hg_1I_6^{2-}$ ions can be described as slightly-distorted edge-condensed bitetrahedrons. The terminal Hg—I bond lengths are the same as those found in $HgI_2$(tds) (Beurskens *et al.*, 1971) and in $[S(CH_3)_3]_2HgI_4$ (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 $Hg_2I_6^{2-}$ 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 I(1)—S(1) = 3·48 ± 0·01 Å and I(1)—S(2) = 3·59 ± 0·01 Å.

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