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# Bis(tetraethylammonium) octabromotrimercurate(II), $(Et_4N)_2[Hg_3Br_8]$

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**Key indicators**

Single-crystal X-ray study
*T* = 293 K
Mean σ(C–C) = 0.015 Å
*R* factor = 0.034
*wR* factor = 0.088
Data-to-parameter ratio = 22.7

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

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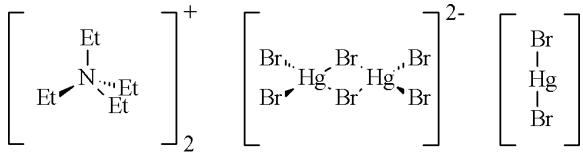
The structure of $(Et_4N)_2[Hg_3Br_8]$ contains isolated dinuclear $[Hg_2Br_6]^{2-}$ anions and neutral $HgBr_2$ molecules. Charge balance is achieved by ordered $[Et_4N]^+$ cations. The formula may therefore be written as $(Et_4N)_2[Hg_2Br_6][HgBr_2]$. The N atoms of the $(Et_4N)^+$ ions lie on a $\bar{4}$ axis along [001] and, whereas one of the mercury(II) ions is placed on a mirror plane perpendicular to the *c* axis, the second one is located on a special position of site symmetry 2/*m*.

## Comment

The crystal structures of several halogenomercurates(II) have been reported and show a wide variety of stereochemical arrangements, as listed in a recent overview (Serezhkin *et al.*, 2001). With simple cations, such as $NH_4^+$ or alkali metals, the 'characteristic' coordination of mercury (Grdenić, 1965) is usually digonal, with Br—Hg—Br quasi-molecules. The coordination of mercury is then often completed to an 'effective' [2+4] distorted octahedron, with two covalent bonds and four additional Br atoms which are significantly further away, but still within the sum of the van der Waals radii. A typical example is $(NH_4)_4HgBr_6$, with isolated [2+4] octahedra of $Br^-$ surrounding $Hg^{2+}$ (Nockemann & Meyer, 2001).



(I)

The crystal structure of $(Et_4N)_2[Hg_2Br_6]$ (Fig. 1) contains isolated bitetrahedral $[Hg_2Br_6]^{2-}$ units consisting of two tetrahedra sharing one common edge (Nockemann & Meyer, 2001, 2002). Another compound in the $(Et_4N)Br/HgBr_2$ system is $(Et_4N)_2[HgBr_4]$, which consists of isolated $[HgBr_4]^{2-}$ tetrahedra (Dean *et al.*, 1994).

The structure of $(Et_4N)_2[Hg_3Br_8]$, or $(Et_4N)_2[Hg_2Br_6]$-$[HgBr_2]$, (I), contain isolated bitetrahedral $[Hg_2Br_6]^{2-}$ units consisting of two tetrahedra sharing one common edge, and further contains molecular digonal Br—Hg—Br units. Each Hg centre of the bitetrahedral $[Hg_2Br_6]^{2-}$ units exhibits two short bonds of 2.5171 (16) and 2.5334 (17) Å, and two long bonds to the bridging $Br^-$ ions of 2.7553 (9) Å. The coordination sphere of the digonal Br—Hg—Br unit [Hg—Br 2.3885 (14) Å] is completed to a distorted octahedron with an 'effective' [2+2+2] coordination by two long Hg···Br contacts of approximately 3.458 Å, and two very long Hg···Br contacts of approximately 3.836 Å, as shown in Fig. 2. In

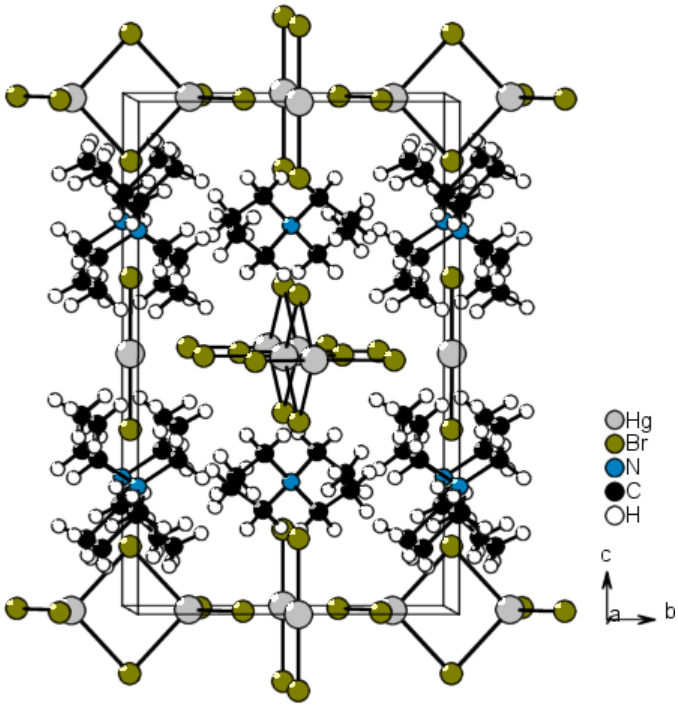



**Figure 1**
Packing diagram of $(Et_4N)_2[Hg_3Br_8]$, viewed down the *a* axis.

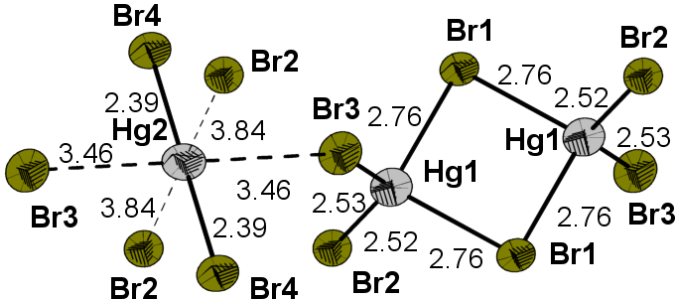



**Figure 2**
Bitetrahedral $[Hg_2Br_6]^{2-}$ units sharing one common edge and their distances to the $HgBr_2$ units.

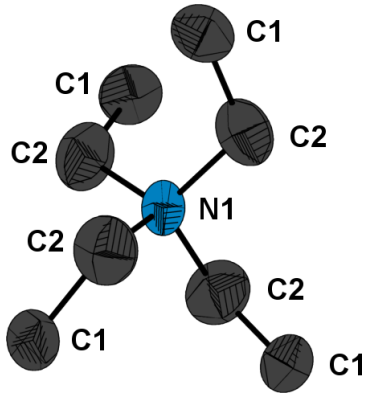



**Figure 3**
View of one of the $[Et_4N]^+$ cation.

$(Et_4N)_2[Hg_3Br_8]$ charge balance is achieved by ordered $[Et_4N]^+$ cations (Figs. 3 and 4), which are located between the $[Hg_2Br_6][HgBr_2]$ layers. The distance between these layers amounts to half of the *c* axis.

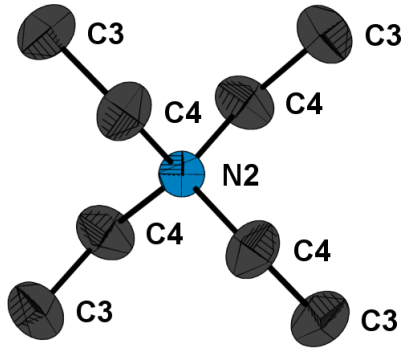



**Figure 4**
View of the other $[Et_4N]^+$ cation.

## Experimental

1 mmol (0.1717 g) of tetraethylammonium bromide, $(Et_4)NBr$, and 3 mmol (0.8145 g) of mercuric bromide, $HgBr_2$, were dissolved by stirring in 50 ml methanol at 323 K until a clear solution was obtained. Single crystals were obtained when the solution was allowed to stand at room temperature for 2 d.

*Crystal data*

| | |
|---|---|
| $(C_8H_{20}N)_2[Hg_2Br_6][HgBr_2]$ | Mo $K\alpha$ radiation |
| $M_r$ = 1501.55 | Cell parameters from 23650 reflections |
| Tetragonal, $P4_2/m$ | $\theta$ = 2.0–26.0° |
| $a$ = 10.0888 (11) Å | $\mu$ = 23.79 mm$^{-1}$ |
| $c$ = 16.094 (2) Å | $T$ = 293 (2) K |
| $V$ = 1638.1 (3) Å$^3$ | Prism, colourless |
| $Z$ = 2 | 0.20 × 0.15 × 0.10 mm |
| $D_x$ = 3.044 Mg m$^{-3}$ | |

*Data collection*

| | |
|---|---|
| Stoe Imaging Plate Diffraction System (IPDS-I) | 1681 independent reflections |
| $\varphi$ scans | 1114 reflections with $I > 2\sigma(I)$ |
| Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998) | $R_{int}$ = 0.116 |
| $T_{min}$ = 0.023, $T_{max}$ = 0.093 | $\theta_{max}$ = 26.0° |
| 23 650 measured reflections | $h = -12 \rightarrow 12$ |
| | $k = -12 \rightarrow 11$ |
| | $l = -19 \rightarrow 19$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0507P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)]$ = 0.035 | $(\Delta/\sigma)_{max} < 0.001$ |
| $wR(F^2)$ = 0.088 | $\Delta\rho_{max}$ = 1.33 e Å$^{-3}$ |
| $S$ = 0.91 | $\Delta\rho_{min}$ = −0.84 e Å$^{-3}$ |
| 1681 reflections | Extinction correction: *SHELXL97* |
| 74 parameters | Extinction coefficient: 0.0087 (4) |
| H-atom parameters constrained | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Hg1—Br2 | 2.5171 (16) | N1—C2 | 1.513 (10) |
| Hg1—Br3 | 2.5334 (17) | N2—C4 | 1.515 (8) |
| Hg1—Br1 | 2.7553 (9) | C1—C2 | 1.511 (16) |
| Hg2—Br4 | 2.3885 (14) | C3—C4 | 1.502 (13) |
| | | | |
| Br2—Hg1—Br3 | 128.79 (6) | C2—N1—C2$^{iii}$ | 112.1 (10) |
| Br2—Hg1—Br1 | 109.00 (3) | C2$^{iii}$—N1—C2$^{iv}$ | 108.2 (5) |
| Br3—Hg1—Br1 | 105.64 (3) | C4—N2—C4$^{v}$ | 106.2 (7) |
| Br1$^{i}$—Hg1—Br1 | 92.84 (4) | C4$^{v}$—N2—C4$^{vi}$ | 111.1 (4) |
| Br4$^{ii}$—Hg2—Br4 | 180.0 | C1—C2—N1 | 115.5 (9) |
| Hg1$^{i}$—Br1—Hg1 | 87.16 (4) | C3—C4—N2 | 115.3 (7) |

Symmetry codes: (i) $1-x, -y, -z$; (ii) $-x, 1-y, -z$; (iii) $-x, -y, z$; (iv) $y, -x, \frac{1}{2}-z$; (v) $1-x, 1-y, z$ (vi) $1-y, x, \frac{1}{2}-z$.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-STEP*32 (Stoe & Cie, 2000); data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

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