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Bis(tetrabutylammonium) decaiodotetramercurate(II), $(Bu_4N)_2[Hg_4I_{10}]$

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$(Bu_4N)_2[Hg_4I_{10}]$ is the first compound for which tetranuclear anions $[Hg_4I_{10}]^{2-}$ are observed in its crystal structure. Charge balance is achieved by ordered $[Bu_4N]^+$ cations.

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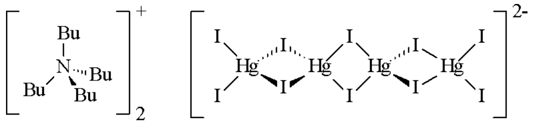
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.019 Å
R factor = 0.038
wR factor = 0.060
Data-to-parameter ratio = 26.8

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

Comment

Halogenomercurate(II) anions show a wide variety of steric arrangements, dependent upon the charge and size of the counter-cation(s) and the stoichiometry (Dean *et al.*, 1994; Grdenic *et al.* 1965; House *et al.*, 1994; Serezhkin *et al.*, 2001). Up to now, only one compound has been reported for the Bu_4NI/HgI_2 system, *viz*. $(Bu_4N)[HgI_3]$ contains trigonal planar $[HgI_3]^-$ units (Goggin *et al.*, 1982).



(I)

Other discrete iodomercurate(II) anions with different cations that have been reported are the tetrahedral $[HgI_4]^{2-}$ and the octahedral $[HgI_6]^{4-}$, as well as the dimeric $[Hg_2I_6]^{2-}$ and the trimeric $[Hg_3I_8]^{2-}$ units.

Recently, we have reported the structure of $(Et_4N)_2[Hg_4Cl_{10}]$ (Nockemann & Meyer, 2002). Bitetrahedral $[Hg_2Cl_6]^{2-}$ anions built from two tetrahedra sharing one common edge have two slightly bent $HgCl_2$ molecules, with Cl—Hg—Cl angles of about 170°, attached to either side so that, altogether, it may be considered as the tetrameric $[Hg_4Cl_{10}]^{2-}$ anion. The two terminal mercuric ions exhibit coordination number 2 + 1 in a T-shaped arrangement.

The tetrameric anion $[Hg_4I_{10}]^{2-}$ in the crystal structure of $(Bu_4N)_2[Hg_4I_{10}]$ may also be derived from bitetrahedral $[Hg_2I_6]^{2-}$ units to which two HgI_2 molecules are again attached on either side. The two central tetrahedra are only slightly distorted, with Hg–I distances ranging from 2.715 (1) to 2.910 (1) Å. The outer HgI_2 molecules show considerably shorter distances, ranging between 2.617 (1) and 2.647 (1) Å, with I—Hg—I angles of 149.09 (5) and 142.93 (4)°, but the distances to the iodide ions of the edges shared with the central $[Hg_2I_6]^{2-}$ are, in turn, much longer, 3.080 (1)–3.316 (1) Å. In summary, in the tetranuclear anion $[Hg_4I_{10}]^{2-}$, all mercuric ions may be considered as having coordination number 4, and all tetrahedra share common edges, in contrast to the situation in the tetranuclear $[Hg_4Cl_{10}]^{2-}$ where coordination numbers are 4 and 3 (twice each), respectively.

In $(Bu_4N)_2[Hg_4I_{10}]$, charge balance is achieved by two crystallographically independent, perfectly ordered tetrahedral $[Bu_4N]^+$ cations which are arranged in the crystal

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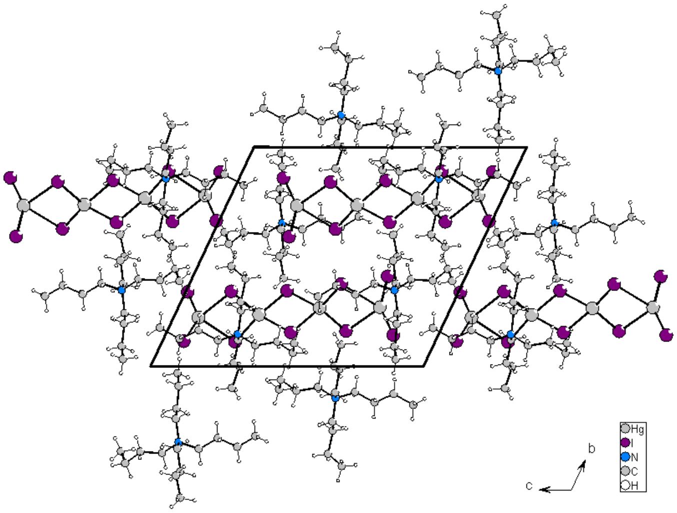

Figure 1
Packing diagram of $(Bu_4N)_2[Hg_4I_{10}]$, viewed down the *a* axis.

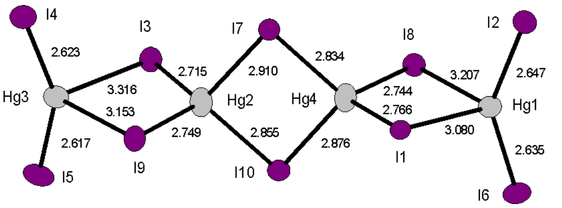

Figure 2
View of the $[Hg_4I_{10}]^{2-}$ anion, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

structure, together with the anions, in a 2:1 ratio, as Fig. 1 illustrates.

Experimental

1 mmol (0.369 g) of tetrabutylammonium iodide, $(Bu_4)NI$, and 2 mmol (0.454 g) of mercuric iodide HgI_2, were dissolved by stirring in 50 ml methanol at 323 K until a clear solution was obtained. Yellow single crystals were obtained when the solution was allowed to stand at room temperature for 2 d.

Crystal data

$(C_{16}H_{36}N)_2[Hg_4I_{10}]$
$M_r = 2556.28$
Triclinic, $P\bar{1}$
$a = 11.6809\ (13)$ Å
$b = 15.7701\ (19)$ Å
$c = 18.288\ (2)$ Å
$\alpha = 114.327\ (9)^\circ$
$\beta = 104.183\ (9)^\circ$
$\gamma = 90.178\ (9)^\circ$
$V = 2955.3\ (6)$ Å^3
$Z = 2$
$D_x = 2.873$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37776 reflections
$\theta = 3.6$–59.3°
$\mu = 15.60$ mm^{-1}
$T = 293\ (2)$ K
Prismatic needle, yellow
$0.30 \times 0.15 \times 0.10$ mm

Data collection

Stoe Imaging Plate Diffraction System, IPDS-I
φ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
$T_{min} = 0.075$, $T_{max} = 0.210$
37776 measured reflections
11615 independent reflections
5987 reflections with $I > 2\sigma(I)$
$R_{int} = 0.107$
$\theta_{max} = 26.0^\circ$
$h = -12 \rightarrow 14$
$k = -19 \rightarrow 19$
$l = -22 \rightarrow 22$

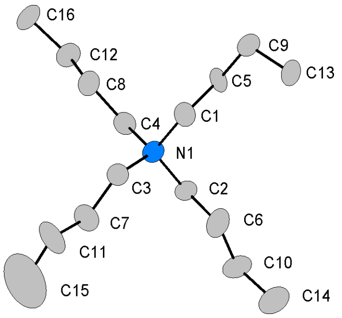

Figure 3
View of one $[Bu_4N]^+$ cation, showing 50% probability displacement ellipsoids.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.060$
$S = 0.75$
11615 reflections
434 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.23$ e Å^{-3}
$\Delta\rho_{min} = -1.22$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.001058 (11)

Table 1
Selected geometric parameters (Å, °).

Hg1—I6	2.6347 (11)	Hg4—I8	2.7435 (10)
Hg1—I2	2.6476 (10)	Hg4—I1	2.7659 (9)
Hg1—I1	3.0800 (9)	Hg4—I7	2.8346 (9)
Hg1—I8	3.2065 (10)	Hg4—I10	2.8759 (11)
Hg2—I3	2.7152 (9)	N1—C3	1.508 (13)
Hg2—I9	2.7489 (10)	N1—C2	1.514 (13)
Hg2—I10	2.8554 (9)	N1—C1	1.534 (12)
Hg2—I7	2.9103 (10)	N1—C4	1.548 (14)
Hg3—I5	2.6167 (11)	N2—C19	1.497 (13)
Hg3—I4	2.6231 (11)	N2—C17	1.519 (12)
Hg3—I9	3.1534 (9)	N2—C20	1.535 (12)
Hg3—I3	3.3150 (10)	N2—C18	1.541 (12)
I6—Hg1—I2	142.91 (4)	I8—Hg4—I10	113.95 (3)
I6—Hg1—I1	104.66 (3)	I1—Hg4—I10	114.20 (3)
I2—Hg1—I1	104.76 (3)	I7—Hg4—I10	93.49 (3)
I6—Hg1—I8	104.08 (3)	Hg4—I1—Hg1	84.53 (2)
I2—Hg1—I8	99.08 (3)	Hg2—I3—Hg3	80.86 (3)
I1—Hg1—I8	87.89 (2)	Hg4—I7—Hg2	86.95 (3)
I3—Hg2—I9	108.93 (3)	Hg4—I8—Hg1	82.50 (3)
I3—Hg2—I10	120.18 (3)	Hg2—I9—Hg3	83.38 (2)
I9—Hg2—I10	112.23 (3)	Hg2—I10—Hg4	87.22 (3)
I3—Hg2—I7	108.25 (3)	C3—N1—C2	113.0 (9)
I9—Hg2—I7	114.09 (3)	C3—N1—C1	104.9 (8)
I10—Hg2—I7	92.33 (3)	C2—N1—C1	111.6 (8)
I5—Hg3—I4	149.08 (4)	C3—N1—C4	111.6 (8)
I5—Hg3—I9	101.10 (3)	C2—N1—C4	106.7 (8)
I4—Hg3—I9	103.60 (3)	C1—N1—C4	109.1 (8)
I5—Hg3—I3	94.43 (3)	C19—N2—C17	108.2 (8)
I4—Hg3—I3	105.20 (3)	C19—N2—C20	111.1 (7)
I9—Hg3—I3	86.82 (2)	C17—N2—C20	109.4 (7)
I8—Hg4—I1	104.75 (3)	C19—N2—C18	111.5 (8)
I8—Hg4—I7	114.82 (3)	C17—N2—C18	110.9 (8)
I1—Hg4—I7	115.92 (3)	C20—N2—C18	105.7 (7)

H atoms were fixed at calculated positions using the AFIX23 and AFIX33 commands in *SHELXL*97. The highest peak and deepest hole were located 0.89 Å from I1 and 0.97 Å from I4, respectively.

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,

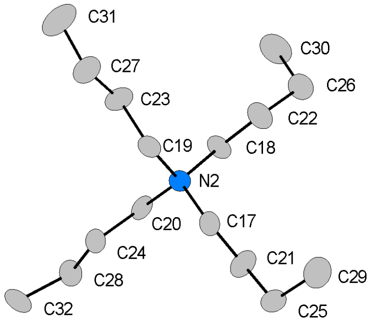

Figure 4
View of the second $[Bu_4N]^+$ cation, showing 50% probability displacement ellipsoids.

1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

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