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Bis(tetraethylammonium) decachlorotetramercurate(II), $(Et_4N)_2[Hg_4Cl_{10}]$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.016 Å
R factor = 0.037
wR factor = 0.080
Data-to-parameter ratio = 25.5

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

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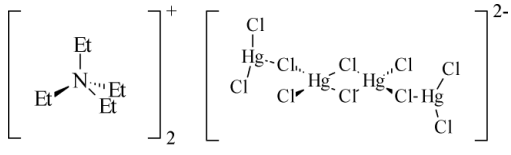
The structure of $(Et_4N)_2[Hg_4Cl_{10}]$ contains dinuclear $[Hg_2Cl_6]^{2-}$ anions and $HgCl_2$ molecules, with definite interactions so that the anion can also be formulated as $[Hg_4Cl_{10}]^{2-}$. Alternatively the compound can be written as $(Et_4N)_2[Hg_2Cl_6][HgCl_2]_2$. Charge balance is achieved by ordered $[Et_4N]^+$ cations. An inversion centre is situated at the centre of the $[Hg_2Cl_6]^{2-}$ anions.

Comment

Chloromercurate(II) anions show a wide variety of stereochemical arrangements, dependent on the charge and size of the counter cation and the stoichiometry (House *et al.*, 1994; Serezhkin *et al.*, 2001).

Three phases are reported for the system $(Et_4N)Cl$ / $HgCl_2$. $(Et_4N)[HgCl_3]$ exhibits a trigonal bipyramid around Hg(II), connected to give infinite chains (Sandström & Liem, 1978). The structure of $(Et_4N)_2[HgCl_4]$ contains isolated $[HgCl_4]^{2-}$ tetrahedra (Mahoui *et al.*, 1996). Finally, $(Et_4N)_2[Hg_3Cl_8]$ forms $[Hg_3Cl_8]^{2-}$ units with distorted trigonal bipyramids surrounding Hg(II) (Pabst *et al.*, 1995).

We have recently reported the structure of $(Et_4N)_2Hg_3Br_8$ with isolated bitetrahedral $[Hg_2Br_6]^{2-}$ units consisting of two tetrahedra sharing one common edge (Nockemann & Meyer, 2002). Additionally, the structure contains molecular digonal Br—Hg—Br units; there are no interactions between the anions and these linear units.



(I)

The crystal structure of $(Et_4N)_2[Hg_4Cl_{10}]$ or $(Et_4N)_2[Hg_2Cl_6][HgCl_2]_2$, (I), also contains bitetrahedral $[Hg_2Cl_6]^{2-}$ units consisting of two tetrahedra sharing one common edge. Two additional $HgCl_2$ units, with Cl—Hg—Cl angles around 170°, are found to interact with the $[Hg_2Cl_6]^{2-}$ units so that, in total, one could formulate the anion as $[Hg_4Cl_{10}]^{2-}$. The bitetrahedral $[Hg_2Cl_6]^{2-}$ units exhibit two short bonds of 2.450 (2) Å and two long bonds of 2.840 (2) Å to the bridging chloride ions. The distorted tetrahedral coordination sphere of Hg2 is completed by two Hg—Cl bonds of 2.414 (3) and 2.447 (3) Å, respectively. The angle to the bridging chloride ions is 85.30 (8)°, while the opposite angle, Cl3—Hg2—Cl5, has a value of 111.24 (9)°. Such a $[Hg_2Cl_6]^{2-}$ anion is quite unusual, because it can be derived from two interacting trigonal $[HgCl_3]^-$ units, while most other

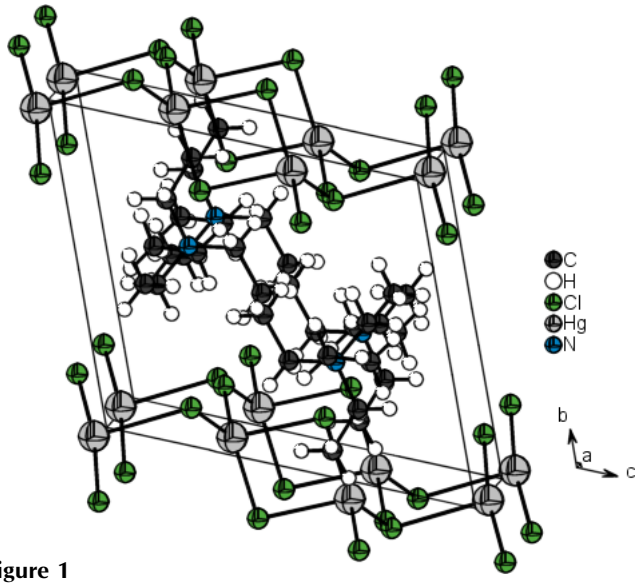


Figure 1
Packing diagram of $(Et_4N)_2[Hg_4Cl_{10}]$, viewed down the *a* axis.

known $[Hg_2Cl_6]^{2-}$ units need to be considered as $HgCl_2$ units bridged by Cl anions with long Hg···Cl contacts, *e.g.* as in $(Bu_4N)[HgCl_3]$ (Goggin *et al.*, 1982).

The $HgCl_2$ units within the $[Hg_4Cl_{10}]^{2-}$ anion exhibit short covalent Hg—Cl bonds [2.314 (2) Å and 2.327 (2) Å] and interact with the $[Hg_2Cl_6]^{2-}$ units by long Hg—Cl contacts of 2.939 (3) Å, which are only slightly longer than the bridging Hg2—Cl1 contacts of 2.840 (2) Å. The angle Cl2—Hg1—Cl4, with a value of 170.64 (9)°, is further evidence for this interaction: The coordination sphere of Hg2 is adjusted to T-shaped units. In $(Et_4N)_2[Hg_4Cl_{10}]$ charge balance is achieved by ordered $[Et_4N]^+$ cations, which are located between the $Hg_4Cl_{10}^{2-}$ layers.

Experimental

1 mmol (0.1657 g) of tetraethylammonium chloride, $(Et_4)NCl$, and 2 mmol (0.5430 g) of mercuric chloride $HgCl_2$, 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

$(C_8H_{20}N)_2[Hg_4Cl_{10}]$
M_r = 1417.36
Triclinic, $P\overline{1}$
a = 8.3409 (15) Å
b = 10.5043 (18) Å
c = 11.039 (2) Å
α = 105.537 (14)°
β = 96.467 (15)°
γ = 109.182 (14)°
V = 858.4 (3) Å^3
Z = 1
D_x = 2.742 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12624 reflections
θ = 2.7–27.0°
μ = 18.62 mm^{-1}
T = 293 (2) K
Prism, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Stoe IPDSI diffractometer
φ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
T_{min} = 0.047, T_{max} = 0.155
12624 measured reflections
3750 independent reflections
2408 reflections with $I > 2\sigma(I)$
R_{int} = 0.084
θ_{max} = 27.0°
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 12$
$l = -14 \rightarrow 14$

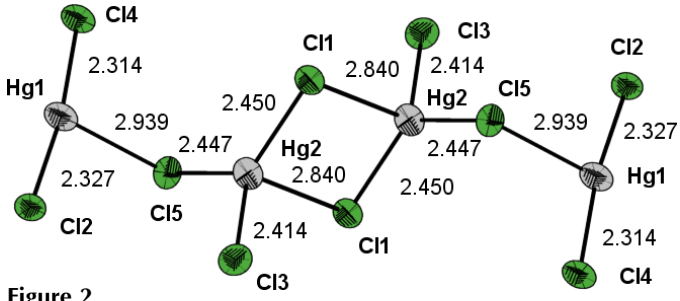


Figure 2
View of the $[Hg_4Cl_{10}]^{2-}$ anions, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

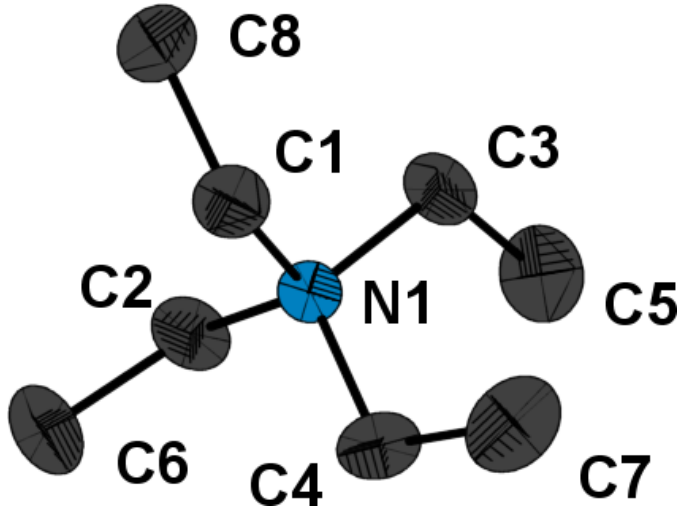


Figure 3
View fn the $[Et_4N]^+$ cation, showing 50% probability displacement ellipsoids.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.080
S = 0.82
3750 reflections
147 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.36 e Å^{-3}
$\Delta\rho_{min}$ = −1.61 e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0148 (5)

Table 1
Selected geometric parameters (Å, °).

Hg1—Cl4	2.314 (2)	N1—C4	1.521 (11)
Hg1—Cl2	2.327 (2)	N1—C1	1.512 (11)
Hg1—Cl5	2.939 (3)	N1—C3	1.526 (11)
Hg2—Cl3	2.414 (3)	C1—C8	1.505 (14)
Hg2—Cl5	2.447 (3)	C2—C6	1.526 (13)
Hg2—Cl1	2.450 (2)	C3—C5	1.504 (14)
Hg2—Cl1^{i}	2.840 (2)	C4—C7	1.508 (14)
N1—C2	1.514 (10)		
Cl4—Hg1—Cl2	170.64 (9)	C2—N1—C1	111.5 (7)
Cl4—Hg1—Cl5	94.59 (9)	C4—N1—C1	108.1 (7)
Cl2—Hg1—Cl5	94.76 (8)	C2—N1—C3	107.9 (7)
Cl3—Hg2—Cl5	111.24 (9)	C4—N1—C3	110.8 (7)
Cl3—Hg2—Cl1^{i}	102.17 (9)	C1—N1—C3	109.7 (6)
Cl5—Hg2—Cl1^{i}	98.23 (8)	C8—C1—N1	115.7 (8)
Cl1—Hg2—Cl1^{i}	85.30 (8)	N1—C2—C6	114.9 (8)
Hg2—Cl1—Hg2^{i}	94.70 (8)	C5—C3—N1	114.6 (8)
Hg2—Cl5—Hg1	103.59 (10)	N1—C4—C7	115.2 (8)
C2—N1—C4	108.7 (6)		

Symmetry code: (i) $2-x, -y, 1-z$.

H atoms were fixed at calculated positions using the AFIX23 and AFIX33 commands in *SHELXL*97 (Sheldrick, 1997). The highest peak is located 0.76 Å from Hg2 and the deepest hole 0.93 Å from Hg2.

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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