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Structure of Bis(tetraethylammonium) Hexaiododimercurate(II) Diiodomercury(II)

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Abstract. $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Hg}_2\text{I}_6] \cdot \text{HgI}_2$, $M_r = 1781.53$, tetragonal, $P4_2/m$, $a = 10.391(1)$, $c = 17.051(1)$ Å, $V = 1841.4$ Å³, $Z = 2$, $D_x = 3.386$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 195.23$ cm⁻¹, $F(000) = 1628$, $T = 293$ K, $R = 0.0468$ for 1201 observed reflections. The structure consists of two crystallographically independent tetraethylammonium cations, a linear centrosymmetric HgI_2 molecule [Hg—I bond length is $2.574(1)$ Å] and a dimeric anion $[\text{Hg}_2\text{I}_6]^{2-}$. There are two van der Waals contacts between the Hg atom of HgI_2 and two iodines from $[\text{Hg}_2\text{I}_6]^{2-}$ [$3.547(2)$ Å] and two I—I van der Waals contacts [$3.769(2)$ Å] between iodines of HgI_2 and $[\text{Hg}_2\text{I}_6]^{2-}$. The latter are considerably shorter than the van der Waals I...I distance (4.3 Å).

Introduction. Previous studies have shown that the characteristic coordination of mercury by I atoms (Grdenić, 1965), which is in most cases distorted, is digonal, (rarely) trigonal and tetrahedral. In addition, it has often been observed that Hg atoms tend to be surrounded by further more-distant iodines. These iodines together with those involved in the characteristic coordination usually surround Hg in the form of a distorted regular object, such as an octahedron or a trigonal bipyramid. Structures

which contain Hg which is tetrahedrally coordinated by iodine may be separated into three groups: (a) with isolated molecules HgI_4^- , (b) with dimeric molecules $\text{Hg}_2\text{I}_6^{2-}$ which consist of two edge-shared coordination tetrahedra and (c) Hg—I polymers with corner-shared tetrahedra. The aim of the present work was to establish the structure of the title compound and to compare it with related ones.

Experimental. The title compound was one of the products of the reaction of tetraethylammonium iodide with mercury(II) iodide in petroleum ether. Yellow crystals were prepared by subsequent recrystallization from propanone.

Sphere-ground crystal ($R = 0.162$ mm), $\mu R = 3.173$, Enraf–Nonius CAD-4F diffractometer, 50 kV/30 mA, graphite-monochromated Mo $K\alpha$. Lattice parameters from least-squares refinement of 25 reflections ($15.30 < \theta < 17.30^\circ$). $\omega/2\theta$ scan mode, $\omega = (1.30 + 1.05 \tan \theta)^\circ$, vertical aperture 4 mm. The intensity-standard reflection (068) was monitored ever 1800 s; intensity variation ($\pm 5\%$) during the data collection. The prescan speed was $10^\circ \text{ min}^{-1}$. The final scan was not applied for reflections where $\sigma(I)/I$, determined after the prescan, lay outside the interval (0.05, 1). The maximum final-scan measurement time was 30 s.

3057 reflections were measured up to $\theta = 30^\circ$ ($0 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 23$); *i.e.* 2776 unique

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reflections from which 1201 were considered observed [$I > 1.96\sigma(I)$].

Linear correction for the variance of the intensity checking reflection, and Lp and absorption corrections were applied (*International Tables for X-ray Crystallography*, 1959, Vol. II). The minimum and maximum transmission factors were 0.0227 and 0.0467, respectively.

The positions of Hg and I were determined by direct methods by the program package *AREN85* (Andrianov, 1987) and subsequent calculations were performed by the *SDS* programs (Petříček & Malý, 1988).

Scattering factors (including anomalous-dispersion corrections) were taken from Cromer & Mann (1968) and *International Tables for X-ray Crystallography* (1974, Vol. IV). After the localization and anisotropic refinement of all non-H atoms a secondary-extinction correction was applied. The refinement under the assumption of extinction type II (Becker & Coppens, 1974) resulted in a higher *R* factor than that of extinction type I, which gave practically the same results for Lorentzian as for Gaussian distribution, in both cases isotropic [$g_{\text{Lorentz}} = 0.16(2) \times 10^{-4}$, $g_{\text{Gauss}} = 0.13(1) \times 10^{-4}$]. (The differences between corresponding structure parameters for both distributions were less than their standard deviations.)

It was not possible to locate H atoms successfully and they were not considered further.

Finally, 74 parameters were refined, $w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = [\sigma^2(F_o) + (0.03|F_o|)^2]$ where $\sigma(F_o)$ is derived from counting statistics. The refinement resulted in $R = 0.1372$, $wR = 0.0833$ for reflections including unobserveds, and $R = 0.0468$,

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Hg(1)	0	5000	5000	6.00 (6)
Hg(2)	338 (1)	3145 (1)	0	4.11 (3)
I(1)	0	5000	1280 (1)	3.48 (4)
I(2)	0	5000	3491 (1)	3.80 (4)
I(3)	1480 (2)	1628 (2)	5000	3.79 (4)
I(4)	2898 (2)	2689 (2)	0	4.77 (5)
N(1)	0	0	2500	2.5 (4)
N(2)	5000	5000	2500	3.8 (7)
C(1)	835 (15)	835 (14)	1954 (10)	3.2 (4)
C(2)	1761 (17)	1745 (16)	2387 (11)	4.1 (5)
C(3)	4931 (23)	3779 (16)	2977 (17)	6.7 (8)
C(4)	3867 (21)	3796 (18)	3631 (14)	5.8 (7)

Table 2. Relevant intra- and intermolecular distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Hg(1)—I(2)	2.574 (1)	Hg(2)—I(1)	2.934 (1)
Hg(2)—I(3) ⁱⁱ	2.678 (2)	Hg(2)—I(4)	2.702 (2)
N(1)—C(1)	1.54 (2)	C(1)—C(2)	1.54 (2)
N(2)—C(3)	1.51 (2)	C(3)—C(4)	1.57 (4)
Hg(1)—I(4)	3.547 (2)	Hg(1)—I(3)	3.826 (2)
I(1)—I(2)	3.769 (2)	Hg(2)—Hg(2) ^{vi}	3.919 (2)
I(2)—Hg(1)—I(2) ^{viii}	180.00 (0)	I(1)—Hg(2)—I(1) ⁱ	96.19 (4)
I(1)—Hg(2)—I(3) ⁱⁱⁱ	109.46 (3)	Hg(2)—I(1)—Hg(2) ^{vi}	83.81 (4)
I(1)—Hg(2)—I(3) ⁱⁱ	109.46 (3)	I(1)—Hg(2)—I(4)	103.49 (4)
I(3) ⁱⁱ —Hg(2)—I(4)	129.63 (7)	I(1)—Hg(2)—I(4)	103.49 (4)
C(1)—N(1)—C(1) ⁱⁱⁱ	105.6 (8)	C(1)—N(1)—C(1) ⁱⁱⁱ	111.4 (8)
N(1)—C(1)—C(2)	114.1 (12)	N(2)—C(3)—C(4)	114.0 (15)
C(3)—N(2)—C(3) ^v	114.8 (14)	C(3)—N(2)—C(3) ^v	106.9 (13)
I(2)—Hg(1)—I(3)	90.00 (0)	I(2)—Hg(1)—I(4) ⁱⁱ	90.00 (0)
I(3)—Hg(1)—I(4) ⁱⁱ	75.68 (4)		

Symmetry code: (i) $x, y, -z$; (ii) $-y, x, (-z + 0.5)$; (iii) $-x, -y, z$; (iv) $y, (-x + 1), (-z + 0.5)$; (v) $(-x + 1), (-y + 1), z$; (vi) $-x, (-y + 1), z$; (vii) $y, -x, (-z + 0.5)$; (viii) $x, y, (-z + 1)$.

$wR = 0.0565$ for observed reflections only. $S = 1.074$, residual electron densities $\Delta\rho(\text{max.}) = 3.53$, $\Delta\rho(\text{min.}) = -3.90 \text{ e \AA}^{-3}$, $(\Delta/\sigma)_{\text{max}} < 0.01$.

Discussion. The structure is shown in Fig. 1. The coordinates and B_{eq} values are given in Table 1, the relevant intra- and intermolecular distances are given in Table 2.*

The most interesting feature of the linear centrosymmetric molecule HgI₂ is the short Hg—I bond length [2.574 (1) \AA] which is slightly longer than that observed in HgI₂ vapour [2.554 (3) \AA ; Spiridonov, Gershikov & Butayev, 1979). On the other hand the bond length observed in the present structure is considerably shorter than that found both in yellow HgI₂ (Jeffrey & Vlasse, 1967) where the average

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53286 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

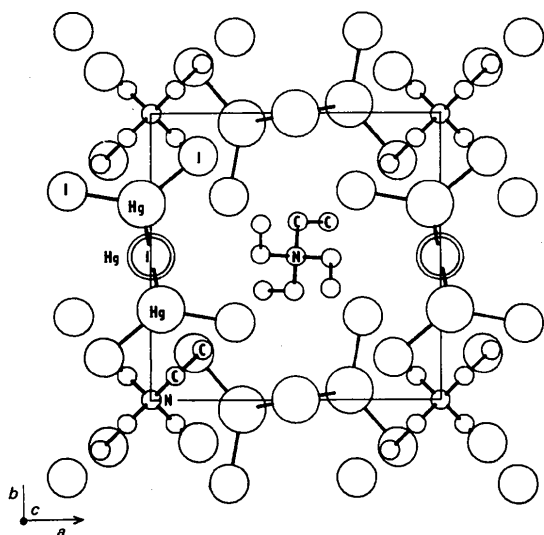


Fig. 1. A view of the structure along the *c* axis. H atoms omitted.

Hg—I bond length = 2.617 (6) Å and the angle I—Hg—I = 178.3°, and in the 1:1 complex between 18-crown-6 and HgI₂ (Pears, Fraser Stoddart, Crosby, Allwood & Williams, 1986a) which contains a linear HgI₂ molecule where the Hg—I bond length = 2.622 (1) Å.

The geometry of the dimeric anion [Hg₂I₆]²⁻ is very similar to that found previously: Pears, Fraser Stoddart, Crosby, Allwood & Williams (1986b), Shibaeva & Kaminskij (1984) and Zacharie, Wuest, Olivier & Beauchamps (1985). In these structures, however, the bridging iodines are not equidistant from the bonded Hg atoms (2.906 and 2.944, 2.819 and 2.957, 2.864 and 2.962 Å), contrary to the present case [2.934 (1) Å]. Correspondingly, the angle Hg—I_{bridge}—Hg in the present structure [83.81 (4)°] is somewhat smaller than that in the references listed above: 88.0 (1), 87.2 (2) and 85.7 (2)°.

There are two van der Waals contacts [3.769 (2) Å] – see Fig. 2 – between iodines of HgI₂ and [Hg₂I₆]²⁻ [*r*_w(I) = 2.15 Å; *CRC Handbook of Chemistry and Physics* (1979)] and two van der Waals contacts between Hg(1) and two equivalent I(4) atoms [*r*_w(Hg) = 1.50 Å; Grdenić, 1965]. However, there are also two further distances Hg(1)—I(3) [Hg(1) belongs to the HgI₂ molecule] which exceed the sum of van der Waals radii of Hg and I, just completing the environment of the Hg(1) atom to form a very deformed octahedron.

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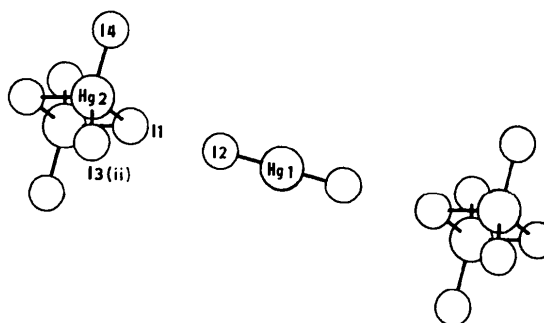


Fig. 2. A view of the [Hg₂I₆]²⁻ and HgI₂ molecules. The atoms Hg(1), I(2) and I(1) lie within a line parallel to the *c* axis.

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Structures of (β-Cyanoethyl)(3-ethylpyridine)bis(dimethylglyoximato)cobalt(III) (1) and (β-Cyanoethyl)(4-ethylpyridine)bis(dimethylglyoximato)cobalt(III) (2)

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Abstract. (1): [Co(C₃H₄N)(C₇H₉N)(C₄H₇N₂O₂)₂], *M*_r = 450.38, monoclinic, *P*2₁/*n*, *a* = 19.570 (2), *b* = 9.288 (2), *c* = 11.644 (2) Å, β = 92.37 (2)°, *V* =

2114.6 (6) Å³, *Z* = 4, *D*_x = 1.415 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 7.91 cm⁻¹, *F*(000) = 944, *T* = 298 K, *R* = 0.071 for 3079 independent reflections.