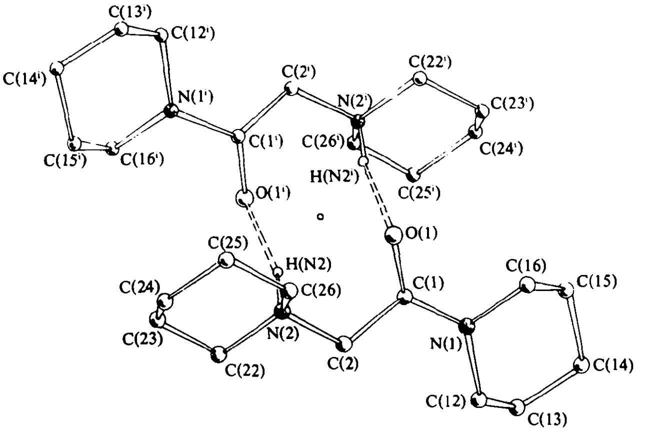

Fig. 2. Arrangement of hydrogen-bonded cations. All H atoms attached to C atoms have been omitted.

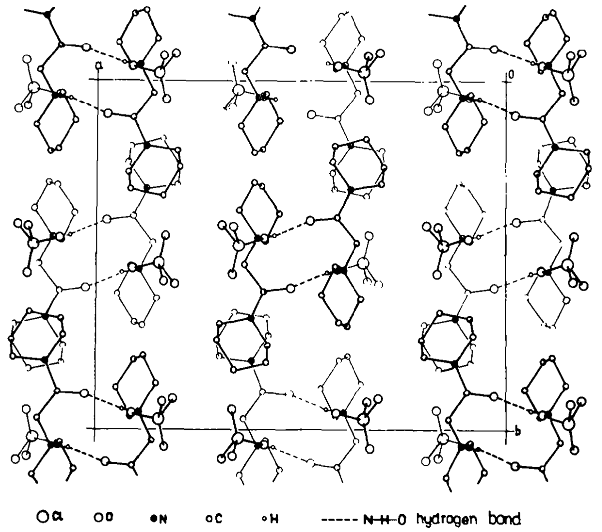

Fig. 3. Projection of the structure down the *c* axis. All H atoms attached to C atoms have been omitted.

the fact that the angle N(2)–H(N2)···O(1) of 101 (4)° is very unfavorable for hydrogen-bond formation lead to the conclusion that this short contact is probably better classified as a short van der Waals contact rather than a very weak hydrogen bond.

There are no short contacts between the perchlorate O atoms and atoms of the cation. All intermolecular distances are greater than the sums of the appropriate van der Waals radii.

We thank Professor M. Wiewiórowski for supplying excellent crystals.

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Bis(ethylenediamine)triiododimercury(II) Triiodomercurate(II)

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Abstract. $Hg_3I_6(en)_2$ (en = ethylenediamine, $C_2H_8N_2$), triclinic, $P\bar{1}$, a = 15·170 (6), b = 8·999 (3), c = 8·561 (4) Å, α = 83·52 (5), β = 84·12 (5), γ = 78·69 (4)°, V = 1134·8 Å^3. M_r = 1483·4, μ(Mo $K\alpha$) = 289 cm^{-1}, D_m = 4·213 (pycnometrically), D_x = 4·341 g cm^{-3}, Z = 2. The structure is built up of trigonal

planar [HgI(en)] cations and [HgI$_3$] anions, together with tetrahedral [HgI$_2$(en)] neutral complexes in a 1:1:1 ratio, so that the correct formulation of the compound is HgI(en)(HgI$_3$).HgI$_2$(en). The trigonal coordination of mercury in the cation is completed to a bipyramidal one by two I atoms, one from the anion, the other from the neutral complex, at the distances 3·48 and 3·29 Å respectively. In the columns formed by the anions the effective coordination of Hg is also bipyramidal with two additional Hg···I contacts at distances less than the sum of the conventional van der Waals radii.

Introduction. Yellow prismatic crystals were prepared by the reaction of ethylenediamine with mercury(II) iodide dissolved in an aqueous solution of potassium iodide and recrystallized from methanol as described for the preparation of HgI$_2$(en) (Straumanis & Cirulis, 1936). The crystallographic and intensity data were collected on a Philips PW 1100 automatic four-circle diffractometer (graphite-monochromatized Mo $K\alpha$ radiation, λ = 0·7107 Å) from a thin needle-shaped specimen (0·08 × 0·09 × 0·23 mm) by ω–2θ scans (scan speed 0·03 ° s^{-1}, scan range 1·2 °). The intensities of 2505 independent reflexions with $I > 3\sigma(I)$ were measured (θ < 30°) and were corrected for Lorentz–polarization effects but not for absorption since the crystals were not suitable for grinding to a spherical shape. Thus the e.s.d.'s are as obtained from the refinement procedure (see Gilli, Cano & García-Blanco, 1976). Four of the strongest reflexions ($\bar{1}10$, $\bar{2}20$, 002, 102) were severely affected by extinction and were omitted from the subsequent calculations. The structure analysis started from the Hg and I atom positions determined by direct methods using *MULTAN* (Declercq, Germain, Main & Woolfson, 1973).

Table 1. *Final positional parameters with their e.s.d.'s*

(*a*) Hg and I atoms. All values are × 10^4.

	x	*y*	*z*
Hg(1)	−694 (1)	5616 (2)	7682 (2)
Hg(2)	2115 (1)	7857 (2)	6914 (2)
Hg(3)	5227 (1)	9320 (2)	7681 (3)
I(11)	−1430 (2)	3138 (3)	8443 (3)
I(12)	1085 (2)	4994 (3)	6749 (3)
I(21)	773 (2)	10077 (3)	7198 (3)
I(31)	3630 (2)	10355 (3)	6253 (3)
I(32)	5916 (2)	11595 (3)	8686 (3)
I(33)	6106 (2)	6435 (3)	7980 (3)

(*b*) C, N and H atoms. All values are × 10^3.

	x	*y*	*z*
C(11)	−175 (2)	855 (4)	900 (4)
C(12)	−173 (3)	907 (5)	718 (5)
C(21)	385 (3)	585 (5)	569 (5)
C(22)	367 (3)	506 (5)	733 (5)
N(11)	−89 (2)	751 (4)	945 (4)
N(12)	−166 (2)	758 (4)	640 (4)
N(21)	299 (2)	666 (3)	501 (4)
N(22)	320 (2)	620 (4)	830 (4)
H(C11*A*)	−228	808	941
H(C11*B*)	−181	953	964
H(C12*A*)	−120	958	675
H(C12*B*)	−229	984	686
H(C21*A*)	416	507	488
H(C21*B*)	425	664	559
H(C22*A*)	333	426	732
H(C22*B*)	427	463	777
H(N11*A*)	−93	700	1063
H(N11*B*)	−34	801	938
H(N12*A*)	−143	769	521
H(N12*B*)	−228	729	640
H(N21*A*)	310	738	405
H(N21*B*)	267	586	462
H(N22*A*)	287	565	932
H(N22*B*)	360	676	880

Table 2. *Bond lengths and angles*

Neutral complex			
Hg(1)–I(11)	2·673 (3)	I(11)–Hg(1)–I(12)	113·8 (1)
Hg(1)–I(12)	2·702 (3)	I(11)–Hg(1)–N(11)	120·2 (7)
Hg(1)–N(11)	2·37 (3)	I(11)–Hg(1)–N(12)	112·0 (8)
Hg(1)–N(12)	2·32 (3)	I(12)–Hg(1)–N(11)	106·5 (7)
N(11)–C(11)	1·52 (4)	I(12)–Hg(1)–N(12)	121·3 (7)
C(11)–C(12)	1·57 (5)	N(11)–Hg(1)–N(12)	78·9 (10)
C(12)–N(12)	1·55 (5)	Hg(1)–N(11)–C(11)	102 (2)
		N(11)–C(11)–C(12)	113 (3)
		C(11)–C(12)–N(12)	105 (3)
		C(12)–N(12)–Hg(1)	110 (2)
Cation			
Hg(2)–I(21)	2·571 (3)	N(21)–Hg(2)–N(22)	77·1 (11)
Hg(2)–N(21)	2·22 (3)	I(21)–Hg(2)–N(21)	139·1 (7)
Hg(2)–N(22)	2·31 (3)	I(21)–Hg(2)–N(22)	143·5 (8)
Hg(2)–I(12)	3·288 (3)	I(21)–Hg(2)–I(12)	101·5 (1)
Hg(2)–I(31)	3·482 (4)	I(21)–Hg(2)–I(31)	91·4 (1)
N(21)–C(21)	1·50 (5)	I(12)–Hg(2)–I(31)	163·3 (1)
C(21)–C(22)	1·52 (6)	I(12)–Hg(2)–N(21)	79·7 (8)
C(22)–N(22)	1·43 (5)	I(12)–Hg(2)–N(22)	88·4 (9)
		I(31)–Hg(2)–N(21)	83·7 (8)
		I(31)–Hg(2)–N(22)	87·4 (9)
		Hg(2)–N(21)–C(21)	108 (2)
		N(21)–C(21)–C(22)	112 (3)
		C(21)–C(22)–N(22)	107 (3)
		C(22)–N(22)–Hg(2)	110 (2)
Anion			
Hg(3)–I(31)	2·775 (3)	I(31)–Hg(3)–I(32)	113·3 (1)
Hg(3)–I(32)	2·728 (4)	I(32)–Hg(3)–I(33)	120·9 (1)
Hg(3)–I(33)	2·673 (3)	I(33)–Hg(3)–I(31)	125·7 (1)
Hg(3$^{\mathrm{i}}$)–I(31)	3·633 (4)		
Hg(3$^{\mathrm{i}}$)–I(32$^{\mathrm{ii}}$)	3·500 (4)		

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

The positions of the C and N atoms were obtained by subsequent Fourier syntheses and the structure, with all non-hydrogen atoms, was refined by the full-matrix least-squares method with anisotropic temperature factors for the Hg and I atoms to an R value of 0·074.

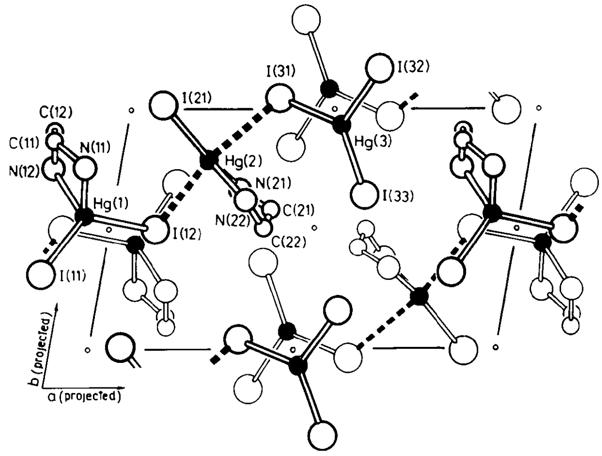

Fig. 1. The crystal structure of $Hg_3I_6(en)_2$ viewed along the c axis.

More than half the H atoms could be located from a Fourier difference synthesis; the positions of the others were calculated on the basis of the ideal bond lengths and angles. In the final refinement the H atoms were also included in the structure factor calculations with the isotropic thermal parameters of the bonded C and N atoms, but they were not allowed to refine. The final R value was 0·062.*

The atomic scattering factors were those of Cromer & Mann (1968) with corrections from Cromer & Liberman (1970) for the anomalous scattering for the non-hydrogen atoms.

Discussion. The final atomic coordinates with e.s.d.'s are given in Table 1. The crystal structure of $Hg_3I_6(en)_2$ consists of three distinct species, the [HgI(en)] cation, the $[HgI_3]$ anion, both planar and trigonal, and the neutral $[HgI_2(en)]$ molecule with Hg in tetrahedral coordination (Fig. 1). Their stereochemical parameters, defined by the bond lengths and angles (Table 2), are as expected from the known structural data (Wells, 1975). As a rule the characteristic trigonal coordination of Hg is completed in the crystal structure to effective tetrahedral or bipyramidal coordination by additional intermolecular contacts which are closer than the sum of the van der Waals radii (Grdenić, 1965). In the present structure Hg(2) in the cation as well as Hg(3) in the anion have effective bipyramidal coordination. For the cation these additional Hg···I contacts are at distances of 3·288 and 3·482 Å from I(12) of the neutral complex and I(31) of the anion respectively. Such contacts to Hg(3) are realized by stacking anions through the centre-of-symmetry operation at distances of 3·500 and 3·633 Å so that columns along the c axis are formed in which trigonal bipyramids share their two edges. The tetrahedral $[HgI_2(en)]$ complex is built up in the same way as the analogous $[Hg(SCN)_2(en)]$ complex (Duplančić, Grdenić, Kamenar, Matković & Sikirica, 1976). This is true also for the stereochemistry of the ethylenediamine ligand in the neutral complex as well as in the cation.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32440 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.