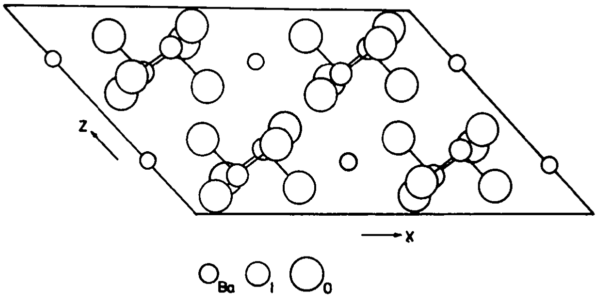

Fig. 2. Projection of the structure of $Ba(IO_3)_2$ on to the xz plane.

1·833, 2·600, 2·600 Å) and $3Cu(IO_3)_2.2H_2O$ (I—O 1·795, 1·801, 1·823, 2·771, 2·873 Å), shows there are no significant differences except a small expansion of the bonds in $Ba(IO_3)_2$.

Among the known structures of divalent metal iodates, $Ba(IO_3)_2$ contains the largest cation ($r_{Ba^{2+}}$ = 1·66 Å, Shannon, 1976). As a consequence, the coordination number of Ba^{2+} is ten, with an irregular arrangement of the O neighbours. The projection of the structure on to the xz plane is in Fig. 2.

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Mercuric Chloride, a Redetermination

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Abstract. $HgCl_2$, orthorhombic, $Pnma$, at 298 K a = 12·765 (6), b = 5·972 (3), c = 4·330 (2) Å, D_o = 5·44 (1), D_c = 5·464 Mg m^{-3}, Z = 4; at 303 K a = 12·776 (4), b = 5·986 (3), c = 4·333 (2) Å. Using all data, the Cl—Hg—Cl angle is 178·6 (4)° and the two Hg—Cl distances [2·292 (10), 2·274 (10) Å] average to 2·283 (9) Å. A refinement using only those data for which $(\sin\theta)/\lambda$ > 0·5 $Å^{-1}$ led to Cl—Hg—Cl = 178·9 (5)° and Hg—Cl (mean) = 2·291 (9) Å. The shortest non-bonded interactions are Hg—Cl = 3·37 and Cl—Cl = 3·33 Å. (The final R_1 value is 0·064.)

Introduction. Initially, crystals were grown by slowly evaporating a saturated solution of $HgCl_2$ in 95% ethanol. A single crystal of extreme dimensions 0·44 × 0·29 × 0·21 mm was selected and studied as described below. Full-matrix anisotropic least-squares refinement (Busing, Martin & Levy, 1962) converged at $R_1 = \sum(|F_o - |F_c||)/\sum F_o$ = 0·23 and $R_2 = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}$ = 0·25. The Cl—Hg—Cl bond angle and lengths were found to be 178·7 (1·1)°, 2·28 (3) and 2·31 (3) Å. However, the transmission coefficients in the absorption correction were very small and unreliable, ranging from 0·008 to 0·113, approximately. Furthermore, the slightly hygroscopic crystal decayed steadily by about 20% and lost its clarity during the data-collection process. To minimize these problems, the work was repeated as follows.

Very small single crystals of $HgCl_2$ were prepared by cooling a warm saturated toluene solution of $HgCl_2$. Crystals formed as needles elongated along a with lateral (001) and (00$\bar{1}$) faces, as before. A single crystal of extreme dimensions 0·20 × 0·07 × 0·05 mm was selected under paraffin oil and sealed in a fine glass capillary. X-ray diffraction data collected with this crystal were corrected for absorption and refined to give Cl—Hg—Cl = 179·5(4)° and Hg—Cl = 2·272 (13) and 2·262 (13) Å, but the error indices remained relatively high: R_1 = 0·11 and R_2 = 0·14. It is probable that available moisture attacked the fine hygroscopic

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crystal during the mounting process, and that the surviving single crystal was coated with wet non-crystalline $HgCl_2$. It follows that the absorption correction could not have been accurately performed, and this is judged to be largely responsible for the high final error indices. Accordingly, the work was repeated yet again as follows.

Fine crystals of $HgCl_2$ were recrystallized from warm toluene. One was transferred with minimal exposure to the atmosphere into a thin-walled Pyrex capillary and was dehydrated, annealed, and partially sublimed at 323 K for 1 h at 10^{-2} Pa. It was then sealed off under vacuum by torch. Microscopic examination revealed that the evacuation procedure had substantially diminished the crystal volume. The extreme dimensions of this relatively clear crystal, which was used in subsequent data collection, were 0·08 × 0·04 × 0·03 mm.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, λ 0·70930 Å; $K\alpha_2$, λ 0·71359 Å) and a pulse-height analyzer was used for preliminary experiments and for the measurement of intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 29°. The temperature was maintained between 302 and 304 K for this crystal. The θ–2θ scan mode was used with a scan rate (ω) in 2θ of 1° min^{-1}. The total background counting time, equal to the scan time, was equally spent at each end of the scan range, which varied from 1·7° at low 2θ to 2·1° at 70°, the upper limit of data collection. No systematic variations were observed in the intensities of three check reflections, which were measured after every 100 reflections during data collection.

Standard deviations were assigned to the individual reflections according to the formula $\sigma(I) = [\omega^2(\text{CT} + B_1 + B_2) + (pI)^2]^{1/2}$ where CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\text{CT} - B_1 - B_2)$. A value of 0·02 was assigned to the empirical parameter p to account for instrumental inaccuracies. The weights (w) used in the least-squares refinement of the structural parameters were the reciprocal squares of $\sigma(F_o)$. Of the 764 symmetry-independent reflections measured, 360 had intensities greater than three times their standard deviations, and only these were used in the subsequent calculations. The intensities were corrected for Lorentz and polarization effects (Ottersen, 1974*a*). The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction. An absorption correction (Busing & Levy, 1957) (μ = 48·9 mm^{-1}) was applied which approximated the crystal shape by a 14 × 14 × 14 grid (Ottersen, 1974*b*); the calculated transmission coefficients ranged from 0·157 to 0·329. The atomic scattering factors (*International Tables for X-ray Crystallography*, 1974*a*) used for Hg^0 and Cl^0 were modified to account for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974*b*).

The systematic absences $k + l$ odd for $0kl$, and h odd for $hk0$, are indicative of the space groups *Pnma* and $Pn2_1a$ (equivalent to $Pna2_1$). The Hg atom was located by Patterson methods at a general position in $Pna2_1$, and the Cl atoms were found on a subsequent Fourier function prepared using the fast-Fourier algorithm (Hubbard, Quicksall & Jacobson, 1971). Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1976), with anisotropic thermal parameters for all atoms, led to a structure with *Pnma* symmetry. Convergence at R_1 = 0·064 and R_2 = 0·060 was achieved using *Pnma*. The goodness of fit, $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$, is 2·6. The number of observations used in the least squares is m (360), and the total number of parameters varied is s (19). The over-determination ratio (m/s) is therefore 18·9.

The final positional and thermal parameters, together with their standard deviations, are presented in Table 1.* The final difference function (e.s.d. = 0·7 e Å^{-3})

Table 1. *Fractional atomic coordinates and thermal parameters* (×10^4)

For all atoms, $y = \frac{1}{4}$ and $\beta_{12} = \beta_{23}$ = 0·0. See Fig. 1 for the identities of the atoms. The estimated standard deviation is in the units of the least significant digit for the corresponding parameter. The temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hl\beta_{13})]$.

	$0 < (\sin\theta)/\lambda < 0{\cdot}8$ Å^{-1}	$0{\cdot}5 < (\sin\theta)/\lambda < 0{\cdot}8$ Å^{-1}
Hg		
x	1263 (2)	1264 (2)
z	468 (5)	461 (6)
β_{11}	38 (1)	36 (1)
β_{22}	201 (5)	190 (7)
β_{33}	503 (9)	435 (13)
β_{13}	−57 (6)	−67 (7)
Cl(1)		
x	2683 (8)	2674 (10)
z	3698 (23)	3700 (31)
β_{11}	51 (7)	35 (6)
β_{22}	190 (33)	200 (36)
β_{33}	642 (62)	576 (80)
β_{13}	−73 (35)	−110 (29)
Cl(2)		
x	−119 (8)	−136 (12)
z	−2837 (20)	−2881 (31)
β_{11}	40 (6)	51 (8)
β_{22}	295 (40)	299 (49)
β_{33}	431 (52)	364 (56)
β_{13}	−31 (29)	−52 (30)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35312 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Least-squares-refinement results*

	$0 < (\sin\theta)/\lambda < 0{\cdot}8$ Å^{-1}	$0{\cdot}5 < (\sin\theta)/\lambda < 0{\cdot}8$ Å^{-1}
Number of reflections	360	190
R_1	0·064	0·075
R_2	0·061	0·066
Goodness-of-fit	2·64	1·41
Hg–Cl(1)	2·292 (10) Å	2·284 (12) Å
Hg–Cl(2)	2·274 (10)	2·301 (14)
Cl–Hg–Cl	178·6 (4)°	178·9 (5)°

was essentially featureless except for two peaks, each 5 e Å^{-3} in height and 0·85 Å from Hg along *c*.

To determine the geometry of $HgCl_2$ more accurately using the available data, a refinement was carried out using only those reflections for which $(\sin\theta)/\lambda$ exceeded 0·5 Å^{-1}. These results are summarized in Tables 1 and 2.

Discussion. Electronic (Sponer & Teller, 1941) and vibrational (Braunne & Engelbrecht, 1932; Klemperer & Lindemann, 1956; Klemperer, 1963) spectra measured in the gas phase, and mass spectrometric (molecular beam) observations (Büchler, Stauffer & Klemperer, 1964), all indicate that $HgCl_2$ is linear. $HgCl_2$ has been reported (Akishin, Spiridonov & Khodchenkov, 1959) to be linear, with Hg—Cl = 2·29 (2) Å, but the precision of the determination of the Cl—Hg—Cl angle was low; it was judged by a secondary source (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965) to be 180 ± 40°. More recently, the angle was found (Kashiwabara, Konara & Kimura, 1973) to be 180 ± 16°, with a Hg—Cl distance of 2·252 (5) Å.

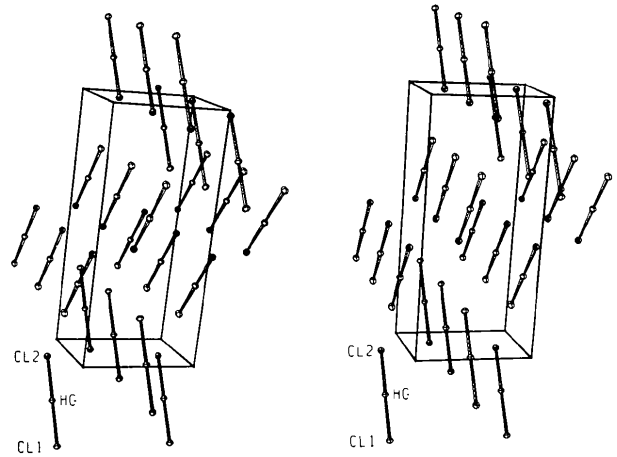

Fig. 1. A stereoview (Johnson, 1965) of the structure. Ellipsoids of 10% probability are used. The view is approximately along the *c* axis with *a* vertical and *b* horizontal in the plane of the page. The Cl(2) atoms are shaded so that they can be readily identified.

The structures of many complexes of $HgCl_2$ have been determined and reviewed (Bränden, 1964; Grdenić, 1965; Hursthouse, 1973, 1974, 1975, 1976, 1977) in recent years. They show various irregular arrangements of ligand atoms about Hg^{II}, with Cl—Hg—Cl angles ranging widely, from 85° in the adduct with collidine (Kulpe, 1967) to 180° in the $HgCl_2$–thiourea complex (Brotherton & White, 1973). Unfortunately, a relatively precise determination of the solid-state structure of $HgCl_2$ itself has not been available, and appropriate comparisons of the crystal structures of these complexes with that of $HgCl_2$ could not be made. This work was undertaken to remove that deficiency.

The Cl(1)—Hg—Cl(2) angle is found to be 178·9 (5)°. This does not differ significantly from 180°, so $HgCl_2$ may be considered linear. The two crystallographically non-equivalent Hg—Cl distances are Hg—Cl(1) = 2·284 (12) Å and Hg—Cl(2) − 2·301 (14) Å, which average 2·291 (9) Å. This is in agreement with Grdenić's (1950) result by two-dimensional crystallographic methods, that Hg—Cl = 2·25 Å. These results also agree with 2·32 (2) Å and 180·0° found for the discrete (uncomplexed) $HgCl_2$ molecules which exist at an inversion center in the crystal structure of the $HgCl_2$–thiourea complex (Brotherton & White, 1973).

A 3·33 Å intermolecular interaction is found between Cl(1) and Cl(2). This distance is short, considering the van der Waals radius (Pauling, 1960) of Cl, 1·80 Å. Each Hg atom participates in four non-bonded interactions (see Fig. 1), two to Cl(1) (3·37 and 3·44 Å) and two to Cl(2) (3·39 and 3·48 Å).

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