657. *The Polonium Halides. Part III.* Polonium Tetraiodide.*

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Polonium tetraiodide and cæsium hexaiodopolonite have been prepared and evidence for the existence of hexaiodopolonous acid has been obtained. The crystal structures of the cæsium salt and its tellurium analogue have been determined.

BURBAGE [1] reported that the attempted preparation of a polonium iodide from the elements was unsuccessful. By analogy with tellurium, a tetraiodide, and complex salts derived from it, would be expected to exist.

Polonium Tetraiodide.—Polonium tetraiodide is obtained as a black solid by the reaction of the elements at 1 mm. pressure at 40°, by treating polonium " hydroxide " or dioxide with 0·1N-hydriodic acid, by precipitation from solutions of polonium tetrachloride in dilute hydrochloric acid by 0·1N-hydriodic acid, or, as a black sublimate, when polonium dioxide is heated in dry hydrogen iodide at 200—250°. With dry hydrogen iodide in the cold polonium dioxide gives a black solid, which is probably an addition compound (PoO_2,xHI); this decomposes, when heated, into polonium tetraiodide and dioxide, and its *X*-ray powder photographs show no resemblance to those of the tetraiodide. Metallic polonium does not react with iodine in carbon tetrachloride, but an unidentified black solid is formed by the reaction of the metal with iodine in benzene.

The tetraiodide is slightly soluble in ethyl alcohol (1 g./l.) and in acetone, and is slowly hydrolysed to a white solid of indefinite composition in water. The hydrolysis products eventually become brown, probably owing to adsorbed iodine. The tetraiodide is insoluble in 2N-hydrochloric acid, N- or 2N-nitric acid, acetic acid, chloroform, benzene, carbon tetrachloride, and diethyl and dibutyl ether. It is decomposed by hot concentrated nitric acid or sodium hypochlorite solution, or slowly by concentrated potassium hydroxide solution. It is soluble in 2N-hydriodic acid, giving a solution which is red-brown at 20° and dark green at 0°; addition of a solution of cæsium iodide in 0·1N-hydriodic acid then yields an immediate precipitate of black cæsium hexaiodopolonite which is readily hydrolysed by water; the potassium and the rubidium salt are soluble.

Cæsium hexaiodopolonite decomposes at 200° *in vacuo*, yielding a black sublimate of polonium tetraiodide. Owing to the high volatility of the tetraiodide the vacuum thermal degradation technique used for the preparation of polonium dichloride and dibromide was unsuccessful.

The tetraiodide is reduced to the metal in warm gaseous hydrogen sulphide, and partly when sublimed in an *X*-ray capillary tube in a stream of nitrogen: as the sublimation proceeds,

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* Part II, *J.*, 1955, 3959.

[1] Burbage, *Record Chem. Progr.*, 1953, **4**, 167.

a trail of the relatively involatile metallic polonium remains behind. There does not appear to be any reaction in hot gaseous ammonia.

Suspensions of the tetraiodide in 0·1N-hydriodic acid are not reduced by hydrazine or sulphur dioxide, even at the b. p., and no precipitate is obtained when dilute solutions of hydriodic acid or potassium iodide are added to solutions of polonium dichloride in hydrochloric acid.

Handling.—The techniques and hazards involved in handling curie amounts of polonium have been described in previous papers.[2] Preparations and reactions were carried out in *X*-ray capillaries.

Analysis.—The preliminary analyses were made by labelling specimens of the tetraiodide with ^{131}I of known specific activity. For example, a solution of potassium iodide (326 μg. of potassium iodide; 4 μc of ^{131}I/ml.) was added to polonium tetrachloride (100 μg.) in N-hydrochloric acid (0·5 ml.) in a micro-centrifuge cone. The precipitated polonium tetraiodide was washed with distilled water (4 × 0·1 ml.) and acetone (2 × 0·1 ml.), and the precipitate was made into a slurry with acetone on a glass counting-tray and allowed to dry. The polonium was then estimated by α-counting and the iodine by β-counting, due allowance being made for the decay of ^{131}I and for the γ-emission from the polonium. Owing to the volatility of polonium tetraiodide, the counting equipment became badly contaminated and was out of use for a prolonged period. The results were unsatisfactory (atomic ratio, I : Po, 3·3—5·6 : 1). A similar procedure was used for a set of tracer experiments in which about 10^{-8} g. of the tetraiodide was sublimed before α- and β-counting (I : Po, 1·7—1·95 : 1).

FIG. 1. *Solubility of* $\mathrm{PoI_4}$ *in aq.* HI *at* □ 0°; ○ 22°; △ 50°.

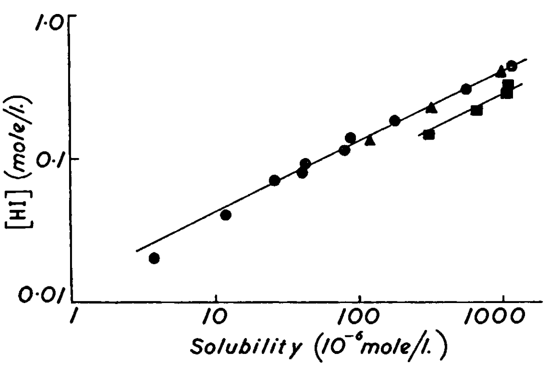
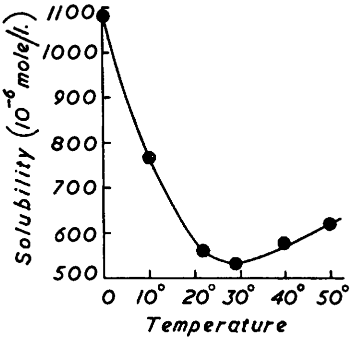


FIG. 2. *Solubility of* $\mathrm{PoI_4}$ *in* 0·3N-HI.



Attempted liberation of iodine from the tetraiodide by chromic–sulphuric acid, acidified sodium nitrite, and oxygen at 150—200° was unsuccessful. In the first two reactions the tetraiodide is decomposed but the amount of iodine found was always low. The third resulted in formation of a white solid containing all the polonium and a variable proportion of the iodine : the composition of this product is unknown and *X*-ray powder photographs were complex.

Better results were obtained by suspending the tetraiodide in 20-vol. hydrogen peroxide (1 ml.), acidified with N-hydrochloric acid (1 ml.). After 10 min. the tetraiodide was completely converted into tetrachloride, and the iodine was extracted with carbon tetrachloride (3 × 2 ml.) and titrated against N/500-sodium thiosulphate; the polonium remaining in the aqueous phase was estimated by α-counting. The cæsium salt was identified by *X*-ray powder photography.

Solubility of Polonium Tetraiodide in Hydriodic Acid Solutions.—The solubility of polonium tetraiodide in 0·02—0·5N-hydriodic acid was determined from 0° to 50°. Fig. 1 shows the dependence of the solubility on acid concentration, from which it has been found that the solubility is proportional to the square of the acid concentration (the observed slopes are 1·99 at 20° and 1·96 at 50°).

The solubility was also determined in hydriodic acid–lithium iodide solutions of constant total iodide-ion concentration and varying hydrogen-ion concentration; the results show that the solubility is independent of the hydrogen-ion concentration and the reaction involved must therefore be

$$\mathrm{PoI_4 + 2I^- \rightleftharpoons PoI_6^{2-}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

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[2] Bagnall, D'Eye, and Freeman, *J.*, 1955, 2320, 3959.

for which the equilibrium constant, $K_c = [PoI_6^{2-}]/[I^-]^2$, is $5{\cdot}9 \pm 0{\cdot}2 \times 10^{-3}$ at 22°. This relation does not hold for [HI] $< 0{\cdot}02$N and it is possible that the deviations at low acid concentrations are due to the reaction

$$PoI_4 + I^- \rightleftharpoons PoI_5^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The equilibrium constant, $K'_c = [PoI_5^-]/[I^-]$, can be estimated by calculating the contribution to the solubility due to reaction (1) and subtracting the result from the observed value. This gives $K'_c = 6{\cdot}7 \pm 0{\cdot}5 \times 10^{-5}$ at 22°. A very large number of determinations of the solubility in very dilute ($<0{\cdot}01$N) hydriodic acid were made using small ($\sim$10 μg.) amounts of the tetraiodide but the results were very inconsistent, presumably owing to hydrolysis of the tetraiodide as well as to radiolysis of the hydriodic acid.

The variation of the solubility with temperature is shown in Fig. 2; at 0°, 22°, and 50° the relation of solubility to acid concentration was found to be the same, so that the same complex ion is involved throughout.

Technique of solubility determinations. The polonium tetraiodide for these experiments was prepared by treating solid polonium tetrachloride (200 μg.) or freshly prepared polonium " hydroxide " with hydriodic acid (0·5 ml.) of the required concentration. The hydrochloric acid ($\sim 3 \times 10^{-6}$ mole) liberated in the first reaction did not affect the solubility determinations. The resulting suspension of polonium tetraiodide in hydriodic acid was stirred in a small constant-temperature bath for 15 min. (experiments had shown that equilibrium was attained in this time), then transferred to a micro-filter-stick [2] (for determinations at 22°) or to a 1 cm. diameter, no. 4 filter-stick (for determinations at other temperatures) mounted in a 15 ml. centrifuge tube. The centrifuge tubes and filter sticks were kept in the thermostat until required. The temperature was maintained only within ±1°, since the heat contributions from the polonium invalidate precise control.

Hydriodic acid is rapidly oxidised by the intense α-bombardment and quantitative experiments with 400 mc samples of polonium gave a *G* value of 2·25 for the oxidation of this acid. Hence, in 15 minutes' contact time, 1 curie of polonium will oxidise 4×10^{18} molecules of hydriodic acid, equivalent to 13½% of the acid in 0·5 ml. of 0·1N-acid. Determinations of the solubility in more dilute acid could not therefore be made by this procedure.

In an alternative method the contact time was reduced as follows. About 100 μg. of polonium tetraiodide were precipitated in a micro-filter-stick and brought to the required temperature in the thermostat. Hydriodic acid of known concentration, and at the same temperature, was centrifuged through the pad of polonium tetraiodide, and the solution assayed for dissolved polonium. The procedure was repeated until the concentration of polonium in the acid solution became constant, which generally occurred after 6 centrifugations, each of which involved a contact time of about ½ min.

Interhalogen Compounds.—Polonium dichloride with iodine in carbon tetrachloride gives a black solid which was shown by *X*-ray powder photography to contain polonium tetraiodide, presumably formed by the disproportionation of an intermediate interhalogen compound. Polonium dibromide, under similar conditions, gives a black solid which may be polonium dibromodiodide; the *X*-ray powder photographs indicated the presence of a new compound of low symmetry.

X-*Ray Crystallography.*—In previous work [2] crystallography of polonium compounds was complicated by the poor quality of the *X*-ray diffraction photographs. The same trouble has been experienced in the present work, and in general the diffraction photographs of the polonium–iodine compounds were of poorer quality than those of the chlorides and bromides.

Polonium tetraiodide. The diffraction pattern could not be indexed, owing to the apparent low symmetry of this compound and the poor quality of the photographs. The $\sin^2\theta$ values and the observed intensities are given below for identification.

$\sin^2\theta$ ...	0·0142	0·0387	0·0444	0·0600	0·0641	0·0810	0·1022	0·1106	0·1223	0·1331
I_0	vw	w	w+	w−	m−	vw	vvw	vw	vvw	vvw

Cæsium hexaiodopolonite and hexaiodotellurite. The diffraction pattern of cæsium hexaiodopolonite was indexed on the basis of a face-centred cubic cell with $a = 5{\cdot}89 \pm 0{\cdot}01$ kX. This cell is too small to contain even one molecule of Cs_2PoI_6. The true unit cell edge is therefore probably $a = 11{\cdot}77 \pm 0{\cdot}05$ kX. With 4 molecules of Cs_2PoI_6 in this larger unit cell, the calculated density is 5·00 g./c.c. The cæsium, polonium, and iodine atoms were placed in the special positions 8(c), 4(a), and 24(e) respectively of the space group O^5_h–Fm3m. The variable parameter for the iodine atoms was found from the intensity calculations to be $x = 0{\cdot}24$. This would give a Po–I distance of 2·82 kX. The agreement between the observed (I_0) and calculated (I_c) intensities is seen from Table 1 to be fair. The intensity calculations show that the diffraction lines due to the true cell have low structure factors and thus are not observed since the films all had high backgrounds due to the γ-radiation from the sample.

TABLE 1.

hkl	$\sin^2\theta_0$	$\sin^2\theta_c$	I_0	I_c *
111	—	0·0128	—	29·1
200	—	0·0171	—	10·9
220	—	0·0342	—	15·6
311	—	0·0470	—	15·4
222	0·512	0·0512	w	86·5
400	0·683	0·0683	w+	100·0
331	—	0·0811	—	3·3
420	—	0·0854	—	7·4
422	—	0·1025	—	7·3
511 333	—	0·1153	—	12·7
440	0·1366	0·1366	w	69·5
531	—	0·1495	—	11·4
600 442	—	0·1537	—	4·3
620	—	0·1708	—	4·1
533	—	0·1836	—	2·4
622	0·1874	0·1879	vw	36·6
444	0·2047	0·2050	vw	26·1

* $I_c \propto F^2 p(1 + \cos^2 2\theta)/\sin^2\theta\cos\theta$.

From the earlier studies it was found that the complex compounds M_2PoX_6 (M = Cs or NH_4, X = Cl or Br) were isostructural with their tellurium analogues. The compound Cs_2TeI_6 should therefore be isostructural with Cs_2PoI_6. As the tellurium compound presents no handling difficulties, the diffraction photographs were obtained by using the Guinier-type camera.[3] The weak lines due to the true unit cell of Cs_2TeI_6 were thus readily observed. The structure is face-centred cubic, with $a = 11{\cdot}698 \pm 0{\cdot}005$ kX, and the compound is isostructural with its polonium analogue. With 4 molecules per unit cell the calculated density is 4·76 g./c.c. The cæsium, tellurium, and iodine atoms were placed on the 8(c), 4(a), and 24(e) special positions respectively of the space group O^5_h–Fm3m. The weakness of the diffraction lines due to the true cell made it difficult to determine the variable parameter for the iodine atom in both the polonium and the tellurium compound; the value found from the intensity calculations was 0·248 which gave a Te–I distance of 2·90 kX. Agreement between the observed and the calculated values of $\sin^2\theta$ and the observed (I_0) and calculated (I_c) intensities is seen to be good (Table 2).

TABLE 2.

hkl	$\sin^2\theta_0$	$\sin^2\theta_c$	I_0	I_c *
111	0·0130	0·0130	vw	6·9
200	0·0173	0·0173	vvw	3·5
220	0·0347	0·0346	vw⁻	5·6
311	0·0475	0·0476	vw	5·8
222	0·0518	0·0519	s	100
400	0·0692	0·0692	m+	83·4
331	0·0821	0·0822	vvw	2·4
420	0·0865	0·0865	vvw	2·6
422	0·1039	0·1038	vvw	2·5
511 333	0·1171	0·1168	vvw	2·7
440	0·1385	0·1384	m	59·4
531	0·1514	0·1514	vvw	2·8
600 442	0·1562	0·1557	vvw	1·4
620	—	0·1730	—	1·2
533	—	0·1860	—	0·9
622	0·1903	0·1903	m–	45·7
444	0·2076	0·2076	w+	21·3

* See Table 1.

The Octahedral Covalent Radius of Polonium.—Pauling has derived the octahedral covalent radius of tin (46 silver core $5s^25p^2$) and lead (78 gold core $6s^26p^2$) from the experimentally determined interatomic distances in the complex ions $[SnCl_6]^{2-}$ and $[PbBr_6]^{2-}$ respectively. These radii, which are about 3% greater than their corresponding tetrahedral (sp^3) radii, correspond to sp^3d^2 bonds and not to d^2sp^3 bonds. However, the octahedral radius of selenium (28 copper core $4s^24p^4$) was found to be 23% greater than its tetrahedral radius. There is in Se^{IV}, in the ion $[SeBr_6]^{2-}$, an unshared pair of electrons which occupy the 4*s* orbital, and this orbital is therefore not available for use in forming sp^3d^2-type bonds. Pauling[4] suggests that it is the 5*s* orbital which is used for bond formation, the bonds being $4p^34d^25s$ bonds, and that the use of the 5*s* orbital explains why the octahedral radius is greater than the tetrahedral.

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[3] D'Eye, British report A.E.R.E. C/R 1524, 1954, SO-70-674-1-78.

[4] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 2nd Edn., 1944.

A recent *X*-ray structural investigation [5] of the compound $(NH_4)_2SbCl_5$ shows that in the $[SbCl_5]^{2-}$ ion, the antimony is at the centre of an octahedron of which five corners are occupied by chlorine with the unshared electron pair of the antimony directed towards the sixth corner. From the stereochemical aspect an unshared pair in an ion of this type is not an " inert " pair. In the $[SeBr_6]^{2-}$ ion, the 4*s* pair must be truly inert since the 5*s* orbital has replaced the 4*s* orbital with respect to bond formation and the configuration, but not the size, of the complex is the same as it would be if the inert pair were not present.

Tellurium (46 silver core $5s^25p^4$) and polonium (78 gold core $6s^26p^4$) have the same outer-electron configuration as selenium and it might therefore be expected that their octahedral radii would be greater than their tetrahedral radii and that the orbitals used in bond formation would be $5p^35d^26s$ and $6p^36d^27s$ respectively. The octahedral radius of tellurium is, in fact, 17% greater than the tetrahedral radius. Our value for the octahedral radius of Te^{IV}, in the $[TeBr_6]^{2-}$ ion, agrees with the value of 1·52 kX quoted by Pauling,[4] but the value obtained from the $[TeI_6]^{2-}$ ion is 1·62 kX. It is probable that this high value results from the difficulty in determining the variable parameter for the iodine atom, since the diffraction lines attributed to the true cell have small structure factors.

The values of the octahedral covalent radius of Po^{IV}, obtained from the different complex compounds, are given in Table 3. These values can only be approximate since the unit-cell dimensions for these compounds were determined from low-angle diffraction lines : high-angle diffraction lines were not available owing to the rather poor diffraction photographs.[2] The tetrahedral radius of polonium has not been determined experimentally, but a value of 1·46 kX has been obtained by extrapolation from the tetrahedral radii of silver, mercury, thallium, lead, and bismuth. The octahedral radius of Po^{IV}, if taken to be about 1·52 kX, is about 4% greater than the tetrahedral radius : this small difference would be expected from the progressive decrease observed from selenium to tellurium.

TABLE 3.

Compound	Po–halogen distance (kX)	Po^{IV} radius (kX)	Ref.
$(NH_4)_2PoCl_6$	2·38	1·39	2
Cs_2PoCl_6	2·54	1·55	6
$(NH_4)_2PoBr_6$	2·60	1·49	2
Cs_2PoBr_6	2·64	1·53	2
Cs_2PoI_6	2·82	1·54	—

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[5] Edstrand, *Svensk Kem. Tidskr.*, 1955, **67**, 230.
[6] Staritzky, American Report LA-1286, 1951.