The Polonium Halides. Part II. Bromides.*

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Polonium dibromide and tetrabromide and ammonium and cæsium hexabromopolonite have been prepared. A dichlorodibromide and a tetrabromide ammine have also been obtained. Some properties of these compounds have been investigated. The crystal structures of the tetrabromide, ammonium and cæsium hexabromopolonite, and cæsium hexabromotellurite have been determined.

JOY (*Chem. Eng. News*, 1954, **32**, 3848) has reported the existence of polonium tetrabromide as a dark red solid (m. p. 324°, b. p. 360°/200 mm.) which was prepared (Burbage, American report MLM 885, 1953, 18) by heating the metal in bromine vapour at 200 mm. for one hour at 250°. The polonium content was determined calorimetrically, and the bromide content by potentiometric titration against silver nitrate. Burbage (*loc. cit.*) reports that attempts to prepare polonium dibromide were unsuccessful.

EXPERIMENTAL

The preparative and analytical techniques described in Part I * were used in this work.

Handling of High-level Sources.—Some of the difficulties experienced in handling high-level sources of high specific activity have been mentioned in previous papers (Bagnall and D'Eye, *J.*, 1954, 4295; Part I, *loc. cit.*) and it is desirable to repeat that the specific activity of ^{210}Po is 4·5 c/mg. and that 1 curie represents 5×10^7 tolerances of ingested ^{210}Po. It is therefore essential to keep curie quantities of the element under control in sealed systems. This is complicated, in the *X*-ray work, by the disruptive effect of the α-bombardment on the glass capillary, which after a few days begins to show a crazed appearance around the polonium, possibly owing to recrystallisation of the glass. The area in contact with the polonium therefore becomes very fragile, and after a week the capillaries tend to break around the contact area and, in some cases, to explode under the gas pressure within the tube. For an *X*-ray capillary 1 cm. long and of 0·2 mm. internal diameter (volume = 0·3 mm.^{3}) the helium generated per day per curie would occupy 0·12 mm.^{3} at S.T.P. and would therefore exert a pressure of approximately 0·4 atm. The halogen liberated in the change from quadrivalent polonium to bivalent lead would also generate an equivalent increase in pressure. It will therefore be seen that the total pressure inside the capillary could build up to about 6 atm. in a week for a 1-curie sample. With a 19-cm. Unicam Debye-Scherrer powder camera, exposure times in the range 24—36 hr. were used and increasing the amount used for each *X*-ray photograph increased both the rate of attack on the glass and the rate of increase of gas pressure within the capillary. The vigorous radiation decomposition of solvents under the intense α-bombardment has been described before (Bagnall and D'Eye, *loc. cit.*; Part I, *loc. cit.*) and this is also accompanied by erosion of the glass container.

Owing to the readiness with which the element and its compounds react with oxygen, and to the high vapour pressures of the halides, it has not been found practicable to handle this element or its compounds in open tubes.

On the last occasion when an *X*-ray capillary was broken on transfer to the camera, the laboratory could only be entered by persons wearing gas-masks or air-hoods and the floor covering had to be removed in its entirety owing to the widespread contamination.

In this work one curie (0·2 mg.) has been used for each experiment and all reported results

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* Part I, *J.*, 1955, 2320.

are the product of duplicate (in the case of analyses quadruplicate) experiments. It should also be noted that lead grows into each preparation at the rate of 0·5% per day, so that each preparation must be recovered and purified by electrodeposition (Part I, *loc. cit.*) before it can be used again.

RESULTS

Analytical.—The atomic ratio of bromine to polonium in the tetrabromide was found to be 4·1 ± 0·1, and in the dibromide 1·85 ± 0·05. The low results are believed to be due to adsorption of bromide ions on the precipitate formed by the decomposition of the dibromide by 0·1N-nitric acid for analysis. The bromine content of the cæsium hexabromopolonite preparations was always 5—10% high (Br/Po = 6·3—6·6), owing to occluded cæsium bromide in the precipitates, identified by *X*-ray powder photography. The dichlorodibromide analyses gave a total halogen content consistent with the formula $PoCl_2Br_2$, although the chloride end-point was not well defined. In view of the method of preparation the composition must be $PoCl_2Br_2$.

Polonium Tetrabromide.—The tetrabromide is a bright red solid, melting in bromine vapour (sealed tube) at about 330° (cf. Joy, *loc. cit.*, 324°) to a dark liquid. At 250° in air or oxygen it is converted into the dioxide.

It was prepared by dissolving polonium metal or dioxide in hydrobromic acid and slowly evaporating the resulting solution to dryness, by heating the metal in a stream of dry bromine vapour, diluted with nitrogen, at 200—250° for 5 min., and by heating the dioxide in dry hydrogen bromide. Polonium metal does not react readily with bromine (liquid or vapour) in the cold.

The tetrabromide dissolves in dilute hydrobromic acid to give an orange red (10^{-3}M) or carmine-red (0·025M) solution. Addition of aqueous cæsium bromide solution to a 10^{-3}M-solution of the tetrabromide in 2N-hydrobromic acid yields an immediate precipitate of dark red cæsium hexabromopolonite. This compound decomposes at 300° into cæsium bromide and polonium bromides and is immediately hydrolysed by cold water. Preparations for *X*-ray powder photography were washed with absolute alcohol. The corresponding potassium and rubidium salts are soluble in 2N-hydrobromic acid.

The tetrabromide is soluble in hydrobromic acid solution, in ethyl alcohol, acetone, and some other ketones. It is sparingly soluble in liquid bromine and is insoluble in benzene and carbon tetrachloride. It is hygroscopic and on hydrolysis yields a white solid of indefinite composition, presumably a basic bromide.

A blackish-brown precipitate was obtained by cooling a hydrobromic acid solution of the tetrabromide to −30°. This is possibly a complex acid of the form $PoBr_4,xHBr,yH_2O$ (cf. tellurium) and is unstable at room temperature, forming a solution of the tetrabromide in hydrobromic acid.

The tetrabromide is rapidly reduced in solution to the purple, bivalent state by sulphur dioxide or hydrazine in the cold. The reduced solutions are re-oxidised to the quadrivalent state in *ca.* 480 sec. as found for the tetrachloride (Part I, *loc. cit.*). Unlike the tetrachloride, the oxidation potential–time curve shows no evidence for the existence of an intermediate tervalent bromide.

Polonium Dibromide.—The dibromide is a purple-brown solid which sublimes with slight decomposition at 110°/30 microns). It melts in nitrogen, apparently with disproportionation, at 270—280° (sealed tube) and the products appear to recombine on cooling. It is prepared by thermal degradation of the tetrabromide at 200° under vacuum and by reduction of the tetrabromide by hydrogen sulphide gas in the cold. The identity of these compounds was confirmed by *X*-ray powder photography. Sulphur dioxide gas partially reduces the dry tetrabromide to dibromide.

It is soluble in a number of ketones and in dilute hydrobromic acid, giving purple solutions which are rapidly oxidised to the quadrivalent state. 0·1N-Nitric acid decomposes the dibromide with the formation of a white precipitate of unknown composition.

Interhalogen Compounds.—Polonium dichloride reacts readily with bromine vapour at room temperature to give a salmon-pink product which is probably $PoBr_2Cl_2$. *X*-Ray powder photography indicated the absence of dichloride, tetrachloride, and tetrabromide, but the photographs were too poor to give definite proof of a new compound. Even if the product is an equimolar mixture of tetrachloride and tetrabromide, it could only be formed by disproportionation of a dichlorodibromide, since, under the conditions of the experiment, the dichloride does not disproportionate to tetrachloride and metal, and the metal does not react with bromine.

Solid polonium dibromide does not react with iodine vapour.

Polonium–Bromine–Ammonia System.—The reactions of the tetrabromide with dry ammonia are rather complex. At room temperature one series of preparations gave an unstable yellow addition compound which, when prepared in an *X*-ray capillary tube, blackened after 2 hr. and after 24 hr. was resolved into discrete bands of polonium metal, polonium tetrabromide, and ammonium bromide, indicative of the high internal temperature of the sample. However, when prepared for analysis in a tube of 6 mm. internal diameter, the decomposition products, after 24 hr., appeared to be polonium dibromide and ammonium bromide only. This difference is possibly due to the lower thermal capacity of the capillary and its consequent higher temperature. A second series of preparations for analytical purposes, however, resulted in the disappearance of the polonium tetrabromide in the ammonia stream, presumably in the form of a volatile, colourless ammine. No analytical data on the composition of these compounds could be obtained and the reason for this different behaviour could not be ascertained.

When polonium tetrabromide is heated in dry ammonia gas at atmospheric pressure and at 100°, the product is mainly brick-red ammonium hexabromopolonite, identified by *X*-ray powder photography, which sublimes, apparently unchanged, at 200°/1 atm. When this compound was heated in a sealed tube at 200° it blackened and detonated, shattering the container, suggesting the possible formation of polonium nitride, analogous to the explosive tellurium nitride, Te_3N_4 (Strecker and Ebert, *Ber.*, 1925, **58**, 2527).

No dibromide ammines were obtained, and polonium dibromide is immediately reduced to the metal when heated in ammonia gas.

Organic Compounds.—Polonium tetrachloride and tetrabromide appear to condense with mono- and di-ketones to form compounds which may be analogous to the corresponding tellurium derivatives (*e.g.*, see Morgan and Drew, *J.*, 1925, **127**, 531). Two series of crystalline compounds have been prepared, one containing halogen [chloride (yellow) or bromide (orange)] and one containing no halogen (purple-violet) obtained from the first series by heating or by shaking with potassium hydroxide solution, and by reaction of polonium dihalides with ketones. Work on the analysis of these compounds is continuing.

X-*Ray Crystallography.*—The crystallography of the polonium compounds has been complicated by the poor diffraction photographs (Bagnall and D'Eye, *loc. cit.*; Part I, *loc. cit.*). The lines were rather diffuse and faded away at a Bragg angle $\theta = 40°$. In our earlier work the poor photographs were attributed mainly to the small amount of sample used (0·2 mg.), a micro-focus tube not being available. More recently, the quantity of sample used has been increased but with no substantial improvement in the diffraction photographs. The background on the photograph is necessarily high owing to the γ-radiation from the sample.

Line broadening on powder photographs is mainly caused by: (i) small crystallite size, (ii) thermal motion of the atoms, (iii) structural irregularities, and (iv) composition irregularities. We have endeavoured to diminish the effect of small crystallite size by annealing the specimens where possible for prolonged periods. The second cause is applicable in the present case, as the heat evolved in the stoppage of the α-particles within the sample (27·4 cals. per hr. per c of ^{210}Po) is sufficient to give a temperature of *ca.* 80° at the surface and an internal temperature probably much greater than this. Apart from line broadening the elevated temperature also causes the intensity I_T to be reduced according to the relation $I_0 = I_T \exp. -B(\sin\theta/\lambda)^2$, where I_0 is the observed intensity and $\exp. -B(\sin\theta/\lambda)^2$ is the temperature or Debye factor (Internationale Tabellen, Vol. II, p. 570). For the remaining two causes of line broadening we have insufficient evidence to say whether or not they affect the photographs. However, it seems unlikely that irregularities occur in the composition of compounds such as Cs_2PoBr_6. It would be of interest to repeat the crystallographic studies at low temperatures.

Polonium tetrabromide. Photographs of the tetrabromide were obtained free from the metal, oxide, or dibromide. The diffraction pattern was not similar to that of the tetrachloride (Part I, *loc. cit.*). The pattern was indexed on the basis of a face-centred cubic cell with $a = 5{\cdot}60 \pm 0{\cdot}01$ *kX*, giving a calculated volume of 176 $(kX)^3$. On spatial considerations the cell can only contain one molecule of $PoBr_4$, and hence one atom of polonium. The face-centred cubic space-groups, which contain no one- or two-fold symmetry positions, require a minimum of four Po atoms per unit cell, which is impracticable on spatial considerations. The chemical evidence, which strongly supports a formula $PoBr_4$, is apparently at variance with the crystallographic data.

In order to correlate the *X*-ray crystallographic data with the chemical data two postulates can be made. The first is that the face-centred cubic cell is a pseudo-cell, the true cell being of lower symmetry, and that the lines due to this true cell are extremely weak and therefore not observed on the photographs. The second is that the one polonium atom is randomly distributed over a 4-fold position. With this statistical distribution of the polonium atoms and the bromine atoms on a 4-fold position the face-centred cubic symmetry would be preserved. This can readily be tested by intensity calculations.

Accordingly, with the polonium atom on the 4(*a*) and the bromine atom on the 4(*b*) special positions of space group O_h^5–*Fm*3*m*, the intensities I_c, where $I_c \propto F^2m(1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$ (*F*, *m*, and the function of θ are respectively the structure factor, multiplicity constant, and the Lorentz polarisation correction factor), were calculated. The following Table shows that the agreement of the observed with the calculated intensities is fair.

hkl	111	200	220	113	222	400	351	420
I_c	9·9	100·0	68·6	2·8	23·7	10·8	1·3	20·0
I_o	vw	s	m	vvw	vw	vvw	—	vvw

The polonium is in octahedral co-ordination with bromine with a Po–Br distance of 2·8 *kX*. The intensities and interatomic distances are not incompatible with the postulate of random distribution of the polonium atoms in the tetrabromide.

Polonium dibromide. Photographs have been obtained of samples free from the tetrabromide, oxide, or metal, but so far attempts to index the diffraction pattern unambiguously have been unsuccessful. The $\sin^2\theta$ values for the stronger lines are recorded in the following Table for identification purposes.

$\sin^2\theta$	0·0176	0·0412	0·0494	0·0682	0·0749	0·1401	0·1602	0·1657
I_o	w+	w+	w+	vw	w+	vw	vw	w−

Ammonium hexabromopolonite. The *X*-ray diffraction photographs were indexed on the basis of a face-centred cubic cell with $a = 10·82 \pm 0·02$ *kX*. With four molecules per unit cell the calculated density is 3·78 g./c.c. The nitrogen, polonium, and bromine atoms were placed on the special positions 8(*c*), 4(*a*), and 24(*e*), respectively, of space-group O_h^5–*Fm*3*m*. The variable parameter for the bromine atoms was found from the intensity calculations to be $x = 0·24$. The agreement between the observed (I_o) and calculated (I_c) intensities is seen from the following table to be very fair.

hkl	I_o	I_c	*hkl*	I_o	I_c	*hkl*	I_o	I_c	*hk*	I_o	I_c
111	w+	73·8	222	vw	19·3	422	—	0·8	531	—	20·8
200	m	100·0	400	w	59·7	511 333	vvw	19·3	600 442	vvw	24·4
220	—	2·84	331	vw	10·3						
113	vw	32·6	420	w−	49·4	440	w	39·5			

The Po–Br distance is 2·60 *kX*, giving a Po^{4+} radius of 0·65, if the ionic radius of bromine is taken as 1·95 showing that the bonding is largely covalent in character. $(NH_4)_2PoBr_6$ is isostructural with $(NH_4)_2PoCl_6$ (Part I, *loc. cit.*).

Cæsium hexabromopolonite. Cs_2PoBr_6 is face-centred cubic with $a = 10·99 \pm 0·02$ *kX*, and with four molecules per unit cell the density is 4·75 g./c.c. It is isostructural with $(NH_4)_2PoCl_6$ (Part I, *loc. cit.*). The variable parameter for the bromine atoms is $x = 0·24$. The agreement between the observed (I_o) and calculated (I_c) intensities is good :

hkl	I_o	I_c	*hkl*	I_o	I_c	*hkl*	I_o	I_c	*hkl*	I_o	I_c
111	m	73	400	m+	100	440	m+	68	620	vvw	12
200	—	10	331	vvw	14	531	vw	30	533	—	5
220	m−	52	420	—	4	600 442	—	1	622	vw	24
311	w−	29	422	w	24				444	vw	23
222	m	77	511 333	vw	16						

The Po–Br distance is 2·6 *kX*, giving a Po^{4+} radius of 0·69 *kX*. The bonding, as in $(NH_4)_2PoBr_6$, is largely covalent in character.

Cæsium hexabromotellurite. This compound was prepared in order to determine whether the tellurium compound was isostructural with its polonium analogue.

Photographs were obtained by using a Guinier-type focusing camera with a bent quartz crystal monochromator and Cu-*K*α radiation (D'Eye, A.E.R.E. C/R 1524, S.O.70-674-1-78). In this way $\sin^2\theta$ values were obtained free from absorption and eccentricity errors. By photographing a 0·1-mm. scale on to the film, before processing, shrinkage errors were also eliminated. The expression for the intensity of a line with this camera is $I_c \propto A_1A_2pF^2 (1 + \cos^2 2\theta_m \cos^2 2\theta)/(\sin^2\theta \cos\theta) \cos (2\theta - \alpha)$, where I_c is the calculated intensity, θ the Bragg angle, θ_m the angle the *X*-ray beam from the anticathode makes with the monochromator (for Cu, $\theta_m = 13°21'$), A_1 the absorption factor for the specimen, A_2 the absorption factor for film emulsion, *p* the multiplicity constant, α the angle the beam from the monochromator makes with the specimen (in our case = 30°), and F the structure factor (Hagg, personal communication); but for cases where the absorption in the specimen is low (in this case because of the extreme thinness of the specimen) and where extreme accuracy is not required the expression simplifies to $I_c \propto pF^2 (1 + \cos^2 2\theta m \cos^2 2\theta)/(\sin^2\theta \cos\theta)$ and this expression has been used throughout in calculating the intensities.

Cs_2TeBr_6 was found to be face-centred cubic with $a = 10{\cdot}888 \pm 0{\cdot}005$ *kX* and has a density of 4·47 g./c.c. The agreement between the observed and calculated $\sin^2\theta$ values is good. The variable parameter for the bromine atom was found to be $x = 0{\cdot}24$.

hkl	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$	I_o	I_c	*hkl*	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$	I_o	I_c
111	0·0149	0·0150	w	29·9	511	1347	1348	w⁻	9·1
200	0199	0200	vvw	0·1	333				
220	0399	0399	m	34·6	440	1598	1598	s⁻	71·9
311	0547	0549	w	11·4	531	1746	1747	vw	7·2
222	0597	0599	s	100·0	600	—	1797	—	0·0
400	0799	0799	s⁻	99·8	442				
331	0947	0949	vw	2·3	620	1999	1997	vw	8·1
420	—	0999	—	0·1	533	—	2147	—	1·6
422	1197	1198	w+	15·4	622	2197	2197	m⁻	42·3
					444	2397	2397	w+	25·2

Cs_2TeBr_6 is thus isostructural with Cs_2PoBr_6.

The Te–Br distance is calculated as 2·61 *kX*, giving a Te^{4+} radius of 0·66 *kX*. Pauling gives the ionic radius of Te^{4+} as 0·81 *kX* (Internationale Tabellen, Vol. II) which indicates that the Te–Br bonding in Cs_2TeBr_6 is largely covalent in character.

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