The Polonium Halides. Part I. Polonium Chlorides.

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Polonium dichloride and tetrachloride have been prepared on the milligram scale and some of their chemical properties have been investigated. A chloride ammine and ammonium and cæsium hexachloropolonite have also been prepared. The dichloride is orthorhombic and ammonium hexachloropolonite is face-centred cubic. The deposition of milligram amounts of ^{210}Po on to gold foil and wire is described.

The probable existence of a quadrivalent chloride of polonium was suggested by Guillot (*J. Chim. phys.*, 1931, **28**, 107) as a result of tracer experiments in which polonium was co-precipitated from hydrochloric acid solution on ammonium salts of the type $(NH_4)_2MCl_6$ (M= Pb, Sn, Te, Pt) under conditions indicating isomorphism. However, it was also found that polonium was co-precipitated on the corresponding tervalent iridium salt under similar conditions so that the quadrivalency of polonium in hydrochloric acid solution could not be unambiguously established.

More recently Staritzky (American report LA-1286, 1951) has prepared compounds of the type M_2PoCl_6 [M = Cs, Rb, K, NH_4, and $(CH_3)_4N$] on the milligram scale, which were identified by optical crystallographic studies. *X*-Ray diffraction measurements of the cæsium salt were also made.

Burbage (American report MLM 885, 1953, 18) has reported preparation of polonium tetrachloride by treatment of the dioxide with carbon tetrachloride vapour at 200°, by heating the metal in excess of chlorine at the same temperature and by evaporation of a solution of polonium in hydrochloric acid to dryness in an atmosphere of carbon tetrachloride vapour. In the last case some dichloride was also formed by thermal decomposition of the tetrachloride, and it is said that carrying out the decomposition in a vacuum gave the dichloride. Burbage (*loc. cit.*) also describes the reduction of the tetrachloride in hydrogen, first to a dichloride and finally to what was assumed to be the metal. These compounds were analysed by estimating the polonium calorimetrically and the halogen by potentiometric titration.

Since elementary polonium is the most convenient starting material for preparations, the deposition of polonium on to gold foil and wire was investigated as a preliminary to the present work. The cathodic and anodic deposition of tracer quantities of polonium on to gold has been described by many authors (Joliot, *J. Chim. phys.*, 1930, **27**, 119; Haïssinsky, *ibid.*, 1932, **29**, 453; 1933, **30**, 27 *et seq.*). The factors influencing deposition were studied quantitatively by Joliot (*loc. cit.*), and more recently Broda and Wright (British report B.R. 641, 1945) investigated the deposition of millicurie quantities of ^{210}Po on to platinum electrodes from trichloroacetic acid solutions.

Experimental

Experimental work was carried out in dry-boxes in order to minimise the hazards associated with the high level of α-activity.

Electrodeposition on Gold.—Choice of cathode material. Wertenstein (*Compt. rend. Soc. Sci. Varsovie*, 1917, **6**, 771) and later Joliot (*loc. cit.*) noted that the deposition of polonium on to platinum does not proceed as smoothly as on to gold. Joliot attributes this to surface oxidation of the platinum under the intense α-bombardment, and Haïssinsky (*J. Chim. phys.*, 1935, **32**, 116) suggests that compound formation may take place. The observations of these authors have been confirmed and, since sublimation of polonium takes place more readily from gold than from platinum, the former was used for routine depositions.

Choice of solvent. Since polonium is very soluble in hydrochloric acid and is probably largely involved in complex-formation (*e.g.*, as $PoCl_6^{2-}$), the acid should be a suitable solvent, but the deposits obtained were patchy and tended to flake from the cathode. This may be due to the action on the electrodes of chlorine produced by the α-bombardment of the solvent, as shown by the dissolution of gold in a solution of polonium in hydrochloric acid. In the presence of hydrazine, which acts as a depolariser and also reduces the polonium to the bivalent state, better deposits were obtained, but the method was not used owing to the difficulty of controlling the marked potential drift during the deposition. The low solubility of polonium in dilute nitric acid, and the rapid dissolution of the metal from the electrodes in concentrated nitric acid, limit the use of nitric acid as a solvent for deposition. However, a solution containing 65 mc/ml. in N-nitric acid was found satisfactory.

Electrode potential Po/Po^{4+}. The electrode potential E_0 Po/Po^{4+} has been determined on the tracer scale in nitric acid solution (10^{-13} to 10^{-8}M) by Hevesy and Paneth (*Sitzungsber. Akad. Wiss. Wien*, **1914**, **123**, 1619), Wertenstein (*loc. cit.*), Joliot (*loc. cit.*), Haïssinsky (*loc. cit.*), and Heal (Canadian Report N.R.C. 1567, 1943). The mean value of their results was $E_0 + 0{\cdot}77$ v. In the approximately 10^{-5}M-solutions employed for deposition E was found to be $+0{\cdot}68$ v, giving a value of $E_0 + 0{\cdot}76$ v. Work on the accurate determination of the electrode potential is still in progress.

Deposition apparatus. The apparatus was designed to minimise the radioactive contamination which is associated with the transfer of liquids of high specific activity. Fig. 1 shows the electrolysis cell B, which is connected by poly(vinyl chloride) tubing of 2-mm. internal diameter to flask A, which contains the stock polonium solution in nitric acid, and to flask C, which contains the residues from the electrolysis and is fitted with electrodes to scavenge the residual polonium. E, F are rubber bulbs fitted with one-way valves, and G is a simple rubber bulb.

FIG. 1.

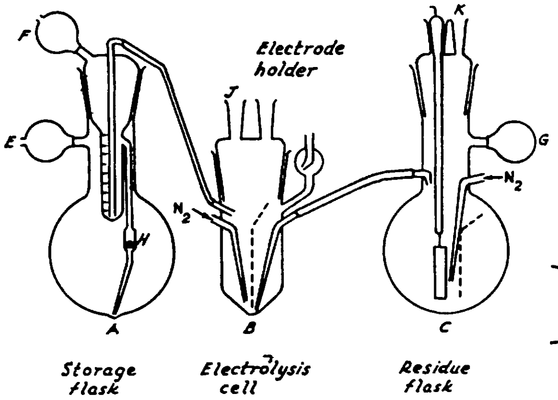


FIG. 2.

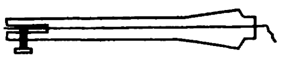
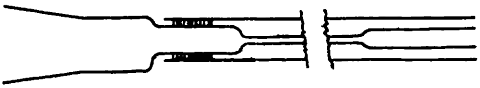


FIG. 3.



H is a one-way ground-glass valve. The required volume of stock solution is transferred into the measuring tube by manipulation of bulb E. On completion of the electrolysis the spent solution is sucked into the flask C by manipulating bulb G.

Joliot (*loc. cit.*) considered that the efficiency of deposition was increased by rapid stirring but, since it was undesirable to leave a stirrer running unattended in a dry-box for long periods, agitation was effected by bubbling nitrogen through the solution. This also removed the gases formed by radiation decomposition of the solvent.

Fig. 2. shows the Perspex electrode holder.

Preparative.—The preparations were carried out in X-ray capillaries of 0·4-mm. internal diameter for convenient examination of the reaction products by X-ray powder photography. For this purpose a simple reaction tube made in Pyrex was devised (Fig. 3). Approx. 0·2 mg. of polonium electrodeposited on a one-inch length of 0·01″-diameter gold wire was placed in the open end which was then sealed. The tube was evacuated and the polonium metal sublimed to the centre of the capillary. Volatile reactants could then be admitted and the products sealed off in the capillary for X-ray and subsequent chemical analysis. The outer glass tube, held on to the main stem by plasticine, protected the capillary from accidental damage.

Preparations for chemical analysis only were made in a larger version of the reaction tube with the centre capillary replaced by tubing of 4 mm. internal diameter and with the end section enlarged to 8 mm. internal diameter to accommodate foils.

The standard centrifugation technique for precipitates was not practicable for preparations of polonium compounds formed by precipitation, owing to gas-evolution and consequent scattering of the centrifuged precipitate. A form of microfilter stick was therefore devised. A fine piece of hair capillary of *ca.* 0·1 mm. internal diameter was lodged inside an open X-ray capillary which was mounted in a rubber bung held in a 15-ml. centrifuge tube. A slurry of finely powdered Pyrex glass in distilled water was then placed in the tube and centrifuged. The larger particles lodged on top of the interior tube, forming a filter pad. The finer particles which had passed through during the centrifugation were then replaced in the *X*-ray capillary and the procedure repeated in order to build up the pad. After thorough washing with distilled water the precipitation was carried out in the capillary and the precipitate centrifuged on to the filter pad. After washing and drying, the capillary was sealed off for photography.

Powder Photographs.—Samples were mounted in a 19-cm. Unicam camera and photographed, filtered Cu-$K\alpha$ radiation being used.

Analysis.—Samples for analysis were dissolved in 0·1N-nitric acid, and the chloride content estimated by potentiometric titration against 0·01N-silver nitrate solution. Titration of chloride in the presence of polonium is complicated by the tendency of the polonium to be deposited spontaneously on silver (*e.g.*, see Marckwald, *Ber.*, 1905, **38**, 591) and, at low acid concentrations, its salts are hydrolysed and are deposited on glass (*e.g.*, see Starik, *Trans. Inst. Radium, Leningrad,* 1933, **2**, 91). The addition of coagulants or indicators is also undesirable since they would complicate the recovery and estimation of the polonium.

FIG. 4.

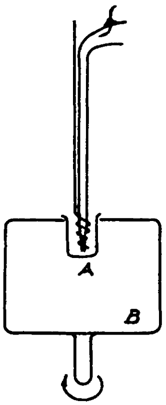
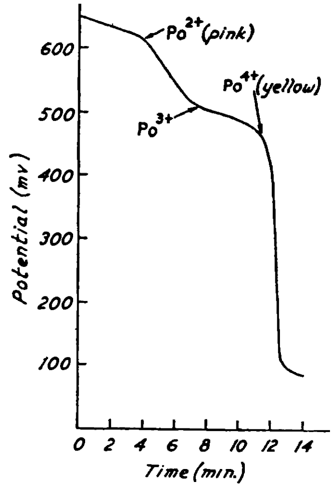


FIG. 5.



The titration unit (Fig. 4) consisted of a silver–silver chloride and a platinum electrode, with an Agla micrometer syringe burette. The burette had a capacity of 0·5 ml. (minimum delivery 0·002 ml.) and was fitted with a glass delivery tip into which the platinum reference electrode was sealed. Immersion of the burette tip, filled with titrant, into the solution to be titrated ensured electrical contact. To obtain a better end-point, the 1-ml. titration cell (*A*, Fig. 4) was cooled by immersion in the ice-filled jacket *B*.

Stirring was effected by rotating the cell and jacket by means of a small electric motor. All potential measurements were made on an Electronic Instruments Ltd. pH-meter. Under these conditions, control experiments with 0·01N-potassium chloride gave well-defined curves, the error in the range 30—100 μg. of chloride ion being ±0·5%.

On completion of the titration the solution was transferred to a 10-ml. graduated flask, and the cell and burette tip were washed with 2N-hydrochloric acid (10 × 0·5 ml.), the washings were combined in the flask, and the volume was made up to 10 ml. with N-nitric acid. Aliquot parts (0·01 ml.) of this solution were evaporated to dryness on glass counting trays, and the polonium content was estimated in an air ionisation chamber reading directly in the range 5 μc to 20 mc (Cuykendall and Finlayson, American report MDDC-341, 1946). In some experiments the polonium was estimated calorimetrically before the chloride estimation.

RESULTS

Electrodeposition.—The optimum applied voltage was found to lie in the range 2·0—2·2 v. Below this value the voltage tends to drift, and at higher voltages there is considerable gas evolution at the electrodes and the rate of deposition is not greatly increased.

More than 95% deposition in 4 hr. was obtained for a foil of surface area 2 cm.^{2}, but gold wire of 0·01″ diameter (surface area 0·15 cm.^{2}) required 16—20 hr. for the same efficiency of deposition.

Analytical.—In all calculations of the weight of polonium determined from α-counting the half-life of ^{210}Po was taken to be 138·4 days (Curtis, *Phys. Rev.*, 1953, **92**, 489). The atomic ratio of chlorine to polonium in the tetrachloride was found to be 4·06 ± 0·10 and in the dichloride 1·99 ± 0·19. The variation in the results for the dichloride is due to partial decomposition to the metal (low results) and to the presence of traces of the tetrachloride. The weight of polonium used for the analytical samples varied from 45 to 260 μg.

Polonium Tetrachloride.—The tetrachloride is a bright yellow solid, melting in chlorine (sealed tube) at about 300°. National Nuclear Energy Series, IV-19B, 1950, 256, gives m. p. 294°, b. p. 390°/1 atm.: it is not possible to determine these values with great accuracy since the temperature of the sample itself will be higher than ambient owing to the heat released in the stoppage of α-particles from the disintegration. A sealed thin-walled Pyrex tube containing 3 mg. of ^{210}Po was found to have an external temperature of 75°, the ambient temperature being 20°. The molten salt is straw-coloured up to 350°, at which temperature it becomes scarlet, and it volatilises at 400° to a purple-brown vapour. At temperatures above 500° the vapour becomes blue-green.

The tetrachloride has been prepared by dissolving metallic polonium in hydrochloric acid and slowly evaporating the solution to dryness; by heating the metal in dry chlorine; by heating the dioxide in dry hydrochloric acid or thionyl chloride vapour, or with phosphorus pentachloride. *X*-Ray results have shown that the tetrachloride is converted into the dioxide when heated in dry air or oxygen at 300° or on long storage in dry oxygen.

The tetrachloride is extremely hygroscopic and in moist halogen-free air is rapidly hydrolysed to a white solid of variable composition (chlorine : polonium ratio varying from 0·5 to 1·5) which is possibly a mixture of a basic chloride and a hydroxide or hydrated oxide. A similar result is obtained by hydrolysis of a solution of the tetrachloride in boiling water. Bouissières (*Bull. Soc. chim.*, 1952, 536), from tracer experiments, considered that this product was an oxychloride. The tetrachloride is soluble in hydrochloic acid, in water with slow hydrolysis, and in thionyl chloride, and appears to be moderately soluble in ethyl alcohol, acetone, and other ketones. With 0·1N-nitric acid it gives a white insoluble solid, containing no chlorine, which is being investigated.

Solutions in hydrochloric acid are bright yellow in concentrations as low as 5 × 10^{-5}M, and addition of a solution of cæsium chloride in ethyl alcohol yields a greenish-yellow precipitate of Cs_2PoCl_6, as found by Staritzky (*loc. cit.*).

Addition of ammonia or sodium hydroxide solution to solutions in dilute hydrochloric acid precipitates a buff to pale-brown flocculent solid (solubility 75 μg. of ^{210}Po per l. of water or excess of alkali). When the suspension is boiled, the precipitate becomes crystalline and yellow-brown and the solubility in excess of potassium hydroxide increases to 12 mg. of ^{210}Po per l. The precipitate, which is probably a hydrated oxide, appears to be feebly amphoteric and is being further investigated.

Reduction in Solution.—In hydrochloric acid solution the tetrachloride is reduced rapidly to the pink, bivalent state by sulphur dioxide or hydrazine in the cold and by arsenious oxide on warming. Hydroxylamine and oxalic acid have no effect, and Joliot's electrochemical observations (*loc. cit.*) on the latter may therefore be due to the formation of a complex oxalate. The reduced solutions autoxidise back to the quadrivalent state in *ca.* 480 seconds after the excess of reducing agent has been eliminated. The change of potential with time at a platinum electrode (*v.* a reference electrode) was measured in order to determine the valency state of the reduced polonium. A typical curve is shown in Fig. 5. The values of the potential given on the graph are not absolute. The break in the potential–time curve would correspond to the intermediate formation of a trichloride, but there is no other evidence for the existence of this compound.

From the time taken for the reduced state to oxidise back to the quadrivalent state, it should be possible to calculate the valency of the lower oxidation state, by assuming that the oxidation is due to the hydrogen peroxide formed in the solution under the α-bombardment from the polonium. With a *G* value of unity for the formation of hydrogen peroxide (Allen, *J. Phys. Chem.* 1948, **52**, 479), the equation $Po^{2+} + 2H^+ + H_2O_2 \longrightarrow Po^{4+} + 2H_2O$ would require 327 sec. for the complete oxidation of Po^{2+} to Po^{4+}. This time will be independent of the amount of polonium present since the polonium is itself the source of the oxidising agent. The time found (480 sec.) gives a value for the valency of the reduced state between 1 and 2, so that it is probable that the reaction is not as simple as that quoted.

However, since sulphur dioxide rapidly reduces both moist and dry solid polonium tetrachloride to the dichloride and since solutions of the dichloride in dilute hydrochloric acid give a potential–time oxidation curve identical with that obtained by reducing the tetrachloride in solution, it seems certain that the reduced solutions contain bivalent polonium.

Polonium Dichloride.—The dichloride is a dark ruby-red solid which sublimes, with some decomposition, at *ca.* 200°. National Nuclear Energy Series (*loc. cit.*) give 190° for the sublimation temperature and give the m. p. as $>355°$; the compound is described as a red-orange orthorhombic solid. It is prepared by careful thermal degradation of the tetrachloride at 200° in a vacuum, by reaction of sulphur dioxide with slightly moist tetrachloride in the cold, the product being dried in a stream of nitrogen, and by heating the tetrachloride in a stream of carbon monoxide or hydrogen sulphide at 150°. The reduction of tetra- to di-chloride by hydrogen sulphide and by sulphur dioxide was confirmed by *X*-ray powder photography. The dichloride is further reduced to the metal by hydrogen sulphide.

The dichloride dissolves readily in dilute hydrochloric acid to a pink solution which rapidly autoxidises to the quadrivalent state and is immediately oxidised by hydrogen peroxide or chlorine water. Addition of potassium hydroxide solution to this solution gives a dark brown precipitate (solubility 1·4 mg. of ^{210}Po/l.) which may be the hydrated bivalent oxide or hydroxide and which is very rapidly oxidised to the quadrivalent state. With 0·1N-nitric acid it gives a dark red solution and then rapidly a white flocculent precipitate, the composition of which is not known.

Polonium–Chlorine–Ammonia System.—When kept in dry ammonia gas at room temperature the tetrachloride is reduced to the metal and a trace of a compound, possibly a bivalent chloride ammine. Initially a slight orange colour was observed which could be due to the formation of an ammine of higher valency. At 100°, however, yellow $(NH_4)_2PoCl_6$ was formed. It is possible that traces of chlorine adsorbed on the walls of the reaction tube first react with the ammonia to give ammonium chloride which then combines with the polonium tetrachloride. Microgram amounts of chlorine were detected on the walls of the reaction capillary after preparation of the tetrachloride, even after evacuation to 20 μ for 30 min. Specimens of the ammonium compound were also prepared by heating polonium tetrachloride with ammonium chloride at 100° (see *X*-ray results).

At 200° polonium dichloride and tetrachloride were found by *X*-ray analysis to give an identical product, which is possibly a dichloride ammine. This is a brownish-black solid which, by analogy with tellurium (Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1931, Vol. XI, p, 100), might be expected to be $PoCl_2,2NH_3$.

Polonium–Chlorine–Hydrogen Sulphide System.—Solid polonium tetrachloride is reduced first to the dichloride and then to the metal when heated in dry hydrogen sulphide. Solutions of the two chlorides in hydrochloric acid yield black precipitates with hydrogen sulphide, together with much sulphur. Specimens of these precipitates gave poor *X*-ray diffraction patterns. Heating them in a vacuum gave sulphur and metallic polonium. These precipitates may be sulphides, but we have been unable to determine their composition. The system is being further investigated.

X-*Ray Analysis.*—(a) *Polonium dichloride.* The diffraction photographs of polonium dichloride prepared by reduction of the tetrachloride both by hydrogen sulphide and by sulphur dioxide showed no lines attributable to the oxide, metal, or tetrachloride. The observed $\sin^2\theta$ values can be indexed on the basis of an orthorhombic cell with $a = 3·66 \pm 0·01$, $b = 4·34 \pm 0·01$, and $c = 4·49 \pm 0·01$ kX. The agreement between the observed and calculated $\sin^2\theta$ values is seen from Table 1 to be fairly good considering the rather poor quality of the photographs. The calculated cell volume is 71·3 kX^3 which can be compatible only with one molecule of $PoCl_2$ per unit cell, giving a calculated density of 6·50 g./c.c.

TABLE 1.

hkl	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	*I* (obs.)	*hkl*	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	*I* (obs.)
001	0·0294	0·0294	s	012	0·1491	0·1491	m
010	0·0315	0·0315	w	021	0·1555	0·1554	vvw
100	0·0441	0·0441	w+	200	0·1769	0·1764	vw
011	0·0607	0·0609	s	210	0·2078	0·2079	vw
101	0·0726	0·0735	vw	022	0·2427	0·2436	diffuse
110	0·0751	0·0756	w	003	0·2648	0·2646	,,
111	0·1046	0·1050	w	030	0·2834	0·2835	,,
002	0·1180	0·1176	m+	013	0·2964	0·2961	,,

The observed indices of the reflections show that there are no apparent systematic absences. It appears to be rather unusual that polonium dichloride should be orthorhombic with only one molecule per unit cell. It would be more likely that this small cell was a pseudo-cell and the true cell had, for example, four times the volume. However, no extra lines attributable to a larger cell could be found.

If the small cell is really the true cell, then it should be possible to find positions for the atoms such that the observed and the calculated intensities are compatible. The space group P222 (also Pmm2 and Pmmm) requires no systematic absences and has 1- and 2-fold positions. Accordingly, with the space group D_2^1-P222, polonium was placed on the 1(*a*) position (000) and the chlorine atoms on special positions 1(*e*) and 1(*f*) ($\frac{1}{2}\frac{1}{2}0$ and $\frac{1}{2}0\frac{1}{2}$). This arrangement would give reasonable Po–Cl distances. For this space group the structure amplitude B ($= -4 \sin 2\pi hx \sin 2\pi ky \sin 2\pi lz$) is zero, as each set of atomic co-ordinates contains a zero value. It is found for the 111, 002, and 020 planes that, with a structure factor $A = 4 \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz$, the chlorine atoms scatter completely in phase with the polonium atoms. Further, these planes are all in the same θ range (19—21°), and therefore the Lorentz polarisation correction factor and the atomic scattering factors for the atoms will be both approximately constant. Thus the calculated intensities will be proportional to the multiplicity constant p. The values of the multiplicity constant are 8, 2, and 2 for the 111, 002, and 020 planes respectively. The strongest plane should therefore be the 111 plane, and the other two planes should be of equal intensity. This is, in fact, not the case. The 111, 002, and 020 planes have the respective intensities weak, medium+, and zero. The same result is arrived at irrespective of which possible space group is used. It would appear therefore that the small orthorhombic cell is a pseudo-cell.

We are grateful to a Referee for suggesting another possibility. The dichloride might have a space group of lower symmetry, belonging to the monoclinic or even the triclinic system, but with the cell angle or angles near 90°. The single molecule might then occupy a general position.

TABLE 2.

I (obs.)	vw	w	w	w	vw	vw
$\sin^2 \theta$ (obs.)	0·0098	0·0176	0·0280	0·0303	0·0381	0·0480
I (obs.)	vvw	w	vw	vvw	vvw	vvw
$\sin^2 \theta$ (obs.)	0·0513	0·0625	0·0819	0·1530	0·1627	0·1716

(b) *Polonium tetrachloride.* The photographs of this compound were very poor. No lines attributable to the metal or oxide were observed. The $\sin^2 \theta$ values together with the observed intensities are given in Table 2. So far it has not been possible to index the pattern owing to the rather poor values and the apparent low symmetry of the structure.

(c) *Ammonium hexachloropolonite.* The *X*-ray diffraction data showed that the product formed by treating solid polonium tetrachloride with dry ammonia and then evacuating the reaction tube was free from metallic polonium, chlorides, and dioxide. It contains, however, two phases, the major phase being face-centred cubic. From volume considerations the cell could contain four molecular units of $(NH_4)_2PoCl_6$. Polonium tetrachloride was then heated with ammonium chloride, and the product gave diffraction data identical with those of the above major phase. The existence of this compound was tentatively suggested by Guillot (*loc. cit.*) and it was prepared by Staritzky (*loc. cit.*) for optical crystallographic analysis by evaporating solutions of polonium tetrachloride and ammonium chloride in hydrochloric acid. In order to confirm the existence of this compound a complete structure analysis was carried out (Table 3).

TABLE 3.

hkl	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	I (obs.)	I (calc.)	*hkl*	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	I (obs.)	I (calc.)
111	0·0166	0·0166	s	100·0	422	0·1336	0·1332	w—	7·0
200	0·0220	0·0222	s—	83·4	511 333	0·1500	0·1499	w	21·6 2·0
220	0·0440	0·0444	w	17·7					
311	0·0608	0·0610	m	45·0	440	0·1776	0·1776	w—	16·6
222	—	0·0666	—	0	531	0·1941	0·1942	w—	22·6
400	0·0884	0·0888	m—	29·5	600 442	0·1997	0·1998	w—	4·2 13·4
331	0·1056	0·1055	w	14·9					
420	0·1109	0·1110	m—	36·2	620	0·2218	0·2220	vw	4·5

The agreement between the observed and the calculated values of $\sin^2 \theta$ shows that the symmetry is unambiguously face-centred cubic, with the cell constant $a = 10{\cdot}33 \pm 0{\cdot}01$ kX. There are four molecules per unit cell, giving a calculated density of 2·76 g./c.c.

The compound is most probably isostructural with $(NH_4)_2PtCl_6$ (Wyckoff and Posnjak, *J. Amer. Chem. Soc.*, 1921, **43**, 2292) which has the space group O_h^5-Fm3m with the platinum, nitrogen, and chlorine atoms on the 4(*a*), 8(*c*), and 24(*e*) special positions respectively.

Accordingly, in the present case, the same special positions were used for the polonium, nitrogen, and chlorine atoms. The variable parameter for the chlorine positions was taken as $x = 0{\cdot}23$. The contribution of the nitrogen and hydrogen atoms to the calculated intensities has been neglected as it will necessarily be swamped by the contribution from the 4 polonium and 24 chlorine atoms. It is seen from Table 3 that the agreement between the observed intensities and the calculated intensities, where $I(\text{calc.}) \propto F^2p(1 + \cos^2 2\theta)/\sin^2\theta\cos\theta$ (where F is the structure factor, p the multiplicity constant, and the function of θ is the Lorentz correction factor) is reasonably good. It appears therefore that $(NH_4)_2PoCl_6$ is isostructural with $(NH_4)_2PtCl_6$.

In this structure each polonium atom is surrounded by 8 nitrogen atoms with a Po–N distance of 4·47 kX, and by six chlorine atoms, in octahedral array, with the Po–Cl distance 2·38 kX. If this bonding is assumed to be ionic and the ionic radius of chlorine is assumed to be 1·81 kX (Pauling, " Internationale Tabellen," Vol. II, p. 611) the radius of the Po^{4+} ion is calculated to be 0·57 kX. However, it is known that the ionic Po^{4+} radius is 1·04 (Bagnall and D'Eye, *J.*, 1954, 4295), thus the Po–Cl bonding must, as would be expected, be largely covalent in character in $(NH_4)_2PoCl_6$.

This structure can be considered to be a large fluorite cell with the $PoCl_6$ ions replacing the Ca^{2+} ions and the $(NH_4)^+$ ions replacing F^- ions.

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