

## Ammoniates of Plutonium(III) and (IV) Halides

J.M. Cleveland, G.H. Bryan, and R.J. Sironen

Received June 17, 1971

*Plutonium triiodide and trichloride react with gaseous and liquid ammonia to form ammine complexes, the initial products containing approximately nine ammonia molecules in the case of the iodide and eight NH<sub>3</sub> ligands with the chloride. These products are not stable and lose ammonia over a period of weeks to quasi-stable species such as PuI<sub>3</sub>·(5.5-6.0)NH<sub>3</sub> and PuCl<sub>3</sub>·(4.1-4.5)NH<sub>3</sub>. The plutonium(IV) compound Cs<sub>2</sub>PuCl<sub>6</sub> also reacts with ammonia at low temperature to form a product with seven to eight NH<sub>3</sub> groups. The product of reaction with liquid ammonia, which appears to be a complex of plutonium tetrachloride, PuCl<sub>4</sub>·~7NH<sub>3</sub>, decomposes over a period of weeks to the relatively stable composition PuCl<sub>4</sub>·~5NH<sub>3</sub>. Both PuF<sub>3</sub> and PuF<sub>4</sub> fail to react with ammonia, probably because the strong plutonium-fluoride bond energy inhibits bonding to ammonia. Infrared spectra indicate that the ammonia is bonded to the plutonium ion, so that the compounds are actually ammine complexes. Although there are regions of quasi stability, none of the compounds studied (with the exception of PuCl<sub>4</sub>·~5NH<sub>3</sub>) appears to be stable at room temperature.*

### Introduction

Plutonium ions, being «hard» acids, would be expected to react with ammonia, a «hard» base, to form ammine complexes, but no such reactions have been reported. The strong tendency of plutonium ions to hydrolyze [ $K_{sp}$  values: Pu(OH)<sub>3</sub> ≅ 2 × 10<sup>-20</sup>; Pu(OH)<sub>4</sub> ≅ 7 × 10<sup>-56</sup>]<sup>1</sup> precludes formation of ammine complexes in aqueous media, and high-temperature reaction of a plutonium compound (specifically the hydride) with NH<sub>3</sub> produces PuN<sup>2</sup>. Thus the only feasible route to complex formation involves reaction of a plutonium compound with anhydrous ammonia at lower temperatures, and this paper reports the results stream of argon; the product sublimed and was deposited as blue-green, crystalline needles in the cold zone

### Experimental Section

**Reagents.** Plutonium trichloride was prepared by the reaction of PuO<sub>2</sub> at 760° with CCl<sub>4</sub> vapor in a stream of argon; the product sublimed and was deposited as blue-green, crystalline needles in the cold zone

of the reaction tube. Preparation of apple-green PuI<sub>3</sub> was hindered by the low thermal stability of this compound, but was finally accomplished by reaction of an excess of iodine with plutonium hydride in a pressure bomb at 240° followed by heating the product *in vacuo* at 90-100° to drive off excess iodine.

Since solid PuCl<sub>4</sub> does not exist,<sup>3</sup> Cs<sub>2</sub>PuCl<sub>6</sub> was used as a plutonium(IV) chloride because of its ease of preparation in an anhydrous condition. It was prepared by the reaction of CsCl with a solution of plutonium(IV) in HCl,<sup>4</sup> and was dried by heating at 110° under vacuum. Plutonium trifluoride was made by the hydrogen reduction at 600° of PuF<sub>4</sub>, which in turn was prepared by the thermal decomposition of PuF<sub>6</sub>. (The latter compound was available in this laboratory as the product of the high-temperature fluorination of PuO<sub>2</sub>.) Ultrahigh-purity ammonia (Air Products and Chemicals Company) was used in all experiments.

**Experimental Procedure.** All reactions with anhydrous ammonia were conducted in inert atmosphere gloveboxes containing less than 0.5 part per million moisture and 25-30 parts per million oxygen. Liquid ammonia was piped directly into the boxes to avoid contact with room air.

Since none of the compounds under study were appreciably soluble in liquid ammonia, all preparative procedures involved heterogeneous liquid-solid or gas-solid reactions.

Liquid reactions were conducted by treating the starting compound with a large excess of liquid ammonia and allowing the liquid to evaporate. Gas-phase reactions were conducted at room temperature (~27°) and at the boiling point of liquid ammonia (-38° at 6,000 feet, the elevation of this laboratory). Open glass vials containing samples of the starting compounds were placed in a closed (but not gas-tight) vessel containing a beaker of liquid ammonia, so that the samples were exposed to ammonia gas at a pressure of essentially one atmosphere (610 torr at this elevation). For the reactions at room temperature, the vials were suspended well above the beaker, while for the low-temperature reactions, the vials were partially immersed in the ammonia in a manner that allowed the ammonia to cool the samples without coming into direct contact with them. The progress of the gas-phase reactions was monitored by weighing, and with the exception of the room-temperature reac-

(1) Katz J.J. and Seaborg G.T., *The Chemistry of the Actinide Elements*, pp. 299-300, John Wiley and Sons, New York, 1957.

(2) Carroll D.F., USAEC Report HW-SA-2755, August 17, 1962.

(3) Cleveland J.M., *The Chemistry of Plutonium*, p. 358, Gordon and Breach Science Publishers, Inc., New York, 1970.

(4) Miner F.J., De Grazio R.P., and Byrne J.T., *Anal. Chem.*, **35**, 1218 (1963).

tions with  $\text{PuCl}_3$  and  $\text{Cs}_2\text{PuCl}_6$ , all experiments were allowed to continue until there was no further weight gain.

Unless otherwise stated, all experiments were repeated several times, using different preparations of each starting compound in most cases. All product samples were stored at room temperature and in an inert atmosphere at atmospheric pressure unless noted otherwise. Reproducibility was generally very good; the concentration limits of the products, given in the Results section, represent the extremes found in each family of experiments.

**Analytical Procedures.** Ammonia analyses were performed by the standard Kjeldahl method. A controlled-potential coulometric method<sup>5</sup> in 0.5 M  $\text{H}_2\text{SO}_4$ , employing an MT Electronics Company coulometer, was used for plutonium analyses. Chloride and iodide analyses involved dissolution of the sample in dilute  $\text{HNO}_3$  and potentiometric titration with  $\text{AgNO}_3$  using a silver indicator electrode and a calomel reference electrode.

To determine the stabilities of the products it was necessary to monitor the compositions as a function of time, but such frequent analyses by the above methods would require excessive quantities of sample. Since the infrared spectra indicated the absence of appreciable quantities of other possible nitrogen-containing groups, such as ammonium and amido ions, and since the method of preparation did not permit escape of any of the ions present in the starting compounds, it was concluded that the weight gains in the samples were due entirely to ammonia. This conclusion was confirmed by the close agreement in ammonia analyses in duplicate cuts of samples analyzed both by the Kjeldahl method and by weighing. Consequently, the ammonia contents of the products were routinely determined by weighing to four decimal places. The calculated compositions were rounded off to one decimal place and should be accurate to within 0.1 molecule of  $\text{NH}_3$ .

Visible absorption spectra were determined using a Cary Model 14 recording spectrophotometer. Liquid ammonia solutions were run in 16-mm-diameter cylindrical culture tubes with screw caps, and argon was passed through the cell compartment to prevent moisture condensation on the cell walls. Although this procedure was satisfactory, it cannot be recommended because of the explosion hazard; at the temperature within the cell compartment, the vapor pressure of ammonia is greater than 10 atm., and culture tubes are not designed to contain such pressures.

Infrared spectra were determined on a Beckman IR-12 infrared spectrophotometer. Solid samples were mullied in mineral oil and mounted between KBr plates within the inert-atmosphere box.

## Results

**Plutonium Triiodide.** Treatment of  $\text{PuI}_3$  with liquid ammonia caused an immediate change in color of the solid from apple green to pale blue. Although  $\text{PuI}_3$  has a low solubility in ammonia, it is soluble

enough to permit an absorption spectrum to be obtained, and this spectrum is shown in Figure 1 along with that of plutonium(III) in a noncomplexing aqueous medium. The spectra are very similar except for small shifts in absorption maxima; for example, the characteristic peak at 601 nm is shifted to 611 nm in ammonia solution, and there are comparable shifts in other peaks.

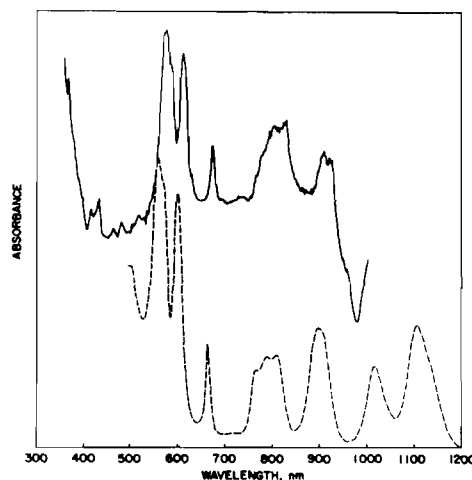


Figure 1. Visible absorption spectra of  $\text{PuI}_3$ .  
 —  $\text{PuI}_3$  in liquid  $\text{NH}_3$ ; - -  $\text{PuI}_3$  in 1 M  $\text{HClO}_4$ .  
 (Arbitrary absorbance scale).

The product remaining after evaporation of excess ammonia had the composition  $\text{PuI}_3 \cdot (7.8-8.8)\text{NH}_3$ , but there is some uncertainty because of the difficulty of determining when evaporation is complete. Thus the values found after overnight storage are considered more reliable; they corresponded to the composition  $\text{PuI}_3 \cdot (7.6-8.0)\text{NH}_3$ . The product continued to lose ammonia at a slow but steady rate; after eight weeks' storage the composition was  $\text{PuI}_3 \cdot (6.5-6.7)\text{NH}_3$ , and after 13 weeks it was  $\text{PuI}_3 \cdot (5.6-6.0)\text{NH}_3$ .

Treatment of  $\text{PuI}_3$  with gaseous  $\text{NH}_3$  at room temperature continued until there was no further weight gain (3-4 hours). The product was pale blue and fluffy, having a bulk volume at least three times greater than the starting compound. Immediately after removal from the ammonia atmosphere, it had the composition  $\text{PuI}_3 \cdot (8.9-9.1)\text{NH}_3$ , but this compound lost ammonia relatively rapidly, and after overnight storage it was  $\text{PuI}_3 \cdot (7.5-7.7)\text{NH}_3$ . Further weight loss was slow; eight weeks after preparation the composition was  $\text{PuI}_3 \cdot (6.8-6.9)\text{NH}_3$ , decreasing to  $\text{PuI}_3 \cdot 5.7\text{NH}_3$  after 13 weeks.

The composition of the pale blue, fluffy product formed by exposure of  $\text{PuI}_3$  to ammonia gas at low temperature could not be determined immediately after termination of the exposure (4-4½ hours) because of uncertainties in composition caused by possible condensation and adsorption of ammonia. Instead, the samples were allowed to stand for 50-70 minutes until the initial rapid weight loss leveled out; at this time the composition was  $\text{PuI}_3 \cdot (8.6-9.0)\text{NH}_3$ . This species continued losing weight and after storage overnight, the composition was  $\text{PuI}_3 \cdot (7.5-7.7)\text{NH}_3$ . Con-

(5) Schults W.D., *Talanta*, 10, 833 (1963).

tinued slow decomposition of a single sample resulted in the compound  $\text{PuI}_3 \cdot 6.8\text{NH}_3$  after eight weeks' storage and  $\text{PuI}_3 \cdot 5.7\text{NH}_3$  after 13 weeks. Another sample stored under low vacuum ( $\sim 1$  torr) lost ammonia more rapidly initially; the compositions after storage periods of 16 hours and one week were  $\text{PuI}_3 \cdot 5.7\text{NH}_3$  and  $\text{PuI}_3 \cdot 5.5\text{NH}_3$ , respectively.

An infrared spectrum of a product with the composition  $\text{PuI}_3 \cdot 8\text{NH}_3$  is shown in Figure 2. Other preparations, with different ammonia contents, had essentially the same spectrum.

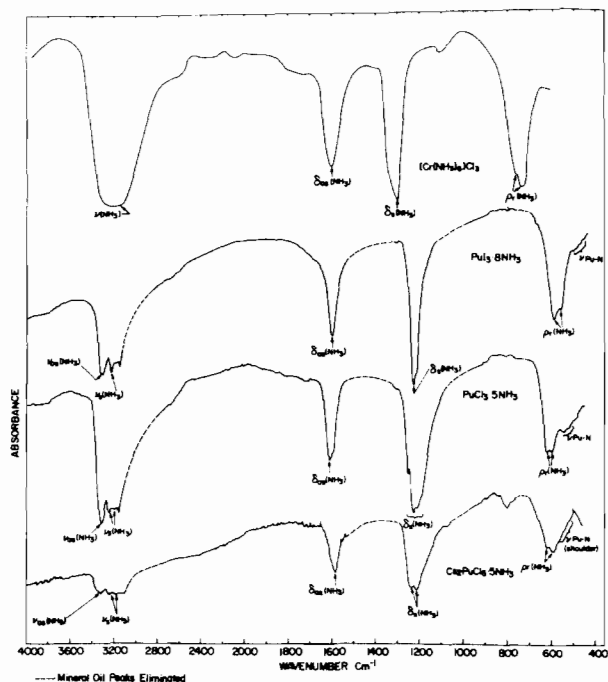


Figure 2. Infrared spectra of metal-ammine complexes. (Arbitrary absorbance scale).

$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  spectrum and peak assignments from K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edition, p. 150, Wiley-Interscience, New York, 1970. Spectra and assignments of plutonium complexes by R.S. Cichorz of this laboratory.

**Plutonium Trichloride.** Treatment of  $\text{PuCl}_3$  with liquid ammonia caused an immediate color change of the solid from blue-green to pale blue. The initial product after evaporation of the excess ammonia had the composition  $\text{PuCl}_3 \cdot (7.5-7.8)\text{NH}_3$ , and after overnight storage, this product had decomposed to  $\text{PuCl}_3 \cdot (5.4-6.5)\text{NH}_3$ . The larger range of ammonia contents in the latter samples apparently was merely due to differences in the initial rate of decomposition, since after seven weeks' storage all samples fell within the narrow composition range  $\text{PuCl}_3 \cdot (4.4-4.7)\text{NH}_3$ , and after 12 to 13 weeks, they were  $\text{PuCl}_3 \cdot (4.1-4.3)\text{NH}_3$ .

A single sample of the product of the liquid-phase reaction, having the initial composition  $\text{PuCl}_3 \cdot 7.5\text{NH}_3$ , was stored under vacuum ( $\sim 1$  torr). The compositions, after overnight and three weeks' storage, respectively, were  $\text{PuCl}_3 \cdot 3.0\text{NH}_3$  and  $\text{PuCl}_3 \cdot 1.7\text{NH}_3$ .

Reaction of ammonia gas with  $\text{PuCl}_3$  at low temper-

ature was complete in 3-4 hours and produced a fluffy, pale blue product with a bulk volume greater by a factor of at least three compared to that of the starting compound. The initial product, of composition  $\text{PuCl}_3 \cdot (8.0-8.1)\text{NH}_3$ , lost ammonia slowly to give the product  $\text{PuCl}_3 \cdot 7.5\text{NH}_3$  after overnight storage. Seven weeks after preparation the composition was  $\text{PuCl}_3 \cdot (4.8-4.9)\text{NH}_3$ , and after 13 weeks it was  $\text{PuCl}_3 \cdot (4.5-4.7)\text{NH}_3$ .

To ascertain the influence of surface area of the  $\text{PuCl}_3$  on the rate and product of the low temperature gaseous reaction, two runs were made using needle-like crystals of  $\text{PuCl}_3$  and two using the same batch of  $\text{PuCl}_3$ , but with the crystals ground to a fine powder. Except for the difference in surface area, all other conditions were identical. Both types of material reacted at comparable rates to produce products identical in appearance and composition.

To determine the effect of storage conditions on product decomposition, two product samples of the low-temperature gaseous ammonia reaction, each with initial composition  $\text{PuCl}_3 \cdot 8.0\text{NH}_3$ , were stored under vacuum, one at room temperature and one at  $-32^\circ$  in a Cole-Parmer Cryo-Bath. The room temperature sample decomposed to  $\text{PuCl}_3 \cdot 3.1\text{NH}_3$  overnight and to  $\text{PuCl}_3 \cdot 1.9\text{NH}_3$  after seven days, while the low-temperature sample was  $\text{PuCl}_3 \cdot 7.8\text{NH}_3$  after overnight storage and  $\text{PuCl}_3 \cdot 7.6\text{NH}_3$  after storage for seven days.

Reaction of  $\text{PuCl}_3$  with gaseous ammonia at room temperature was very slow. After exposure for seven hours the reaction was terminated; the product had the composition  $\text{PuCl}_3 \cdot (1.5-1.6)\text{NH}_3$ , and was still slowly taking up ammonia. After storage for four days the product was  $\text{PuCl}_3 \cdot (1.0-1.1)\text{NH}_3$ , and this species was relatively stable, since 25 days later it had only decomposed to  $\text{PuCl}_3 \cdot 0.9\text{NH}_3$ .

An infrared spectrum of a product of composition  $\text{PuCl}_3 \cdot 5\text{NH}_3$  is shown in Figure 2.

**Cesium Hexachloroplutonate(IV).** Addition of liquid ammonia to  $\text{Cs}_2\text{PuCl}_6$  caused an immediate color change of the solid from yellow to pale brick-red, which soon changed to green as more liquid was added. After evaporation of excess ammonia, the product initially had the empirical composition  $\text{Cs}_2\text{PuCl}_6 \cdot (6.6-7.2)\text{NH}_3$ , but this species was unstable, and lost ammonia overnight to become  $\text{Cs}_2\text{PuCl}_6 \cdot (4.8-4.9)\text{NH}_3$ . This compound was remarkably stable; after storage for three weeks it was  $\text{Cs}_2\text{PuCl}_6 \cdot (4.6-4.7)\text{NH}_3$  and after six to eight weeks it still had the composition  $\text{Cs}_2\text{PuCl}_6 \cdot (4.6-4.9)\text{NH}_3$ .

Treatment with gaseous ammonia at low temperature produced a pale brick red compound of composition  $\text{Cs}_2\text{PuCl}_6 \cdot (7.6-8.0)\text{NH}_3$ . Separate samples decomposed at varying rates; after overnight storage the composition range was  $\text{Cs}_2\text{PuCl}_6 \cdot (6.5-7.7)\text{NH}_3$ . After storage for three weeks, all samples had decomposed to similar degrees, and had the composition  $\text{Cs}_2\text{PuCl}_6 \cdot (3.9-4.1)\text{NH}_3$ . After 10 weeks the composition was  $\text{Cs}_2\text{PuCl}_6 \cdot (3.4-3.5)\text{NH}_3$ . Reaction with ammonia gas at room temperature was inconsequential; after exposure periods greater than five hours the ammonia uptake was less than 0.1 molecule per  $\text{Cs}_2\text{PuCl}_6$  unit, and this small amount was probably due to adsorption.

An infrared spectrum of the compound  $\text{Cs}_2\text{PuCl}_6 \cdot 5\text{NH}_3$  is shown in Figure 2.

*Plutonium Trifluoride and Tetrafluoride.* Both  $\text{PuF}_3$  and  $\text{PuF}_4$  failed to react appreciably with ammonia under any experimental condition; weight gains corresponded to less than 0.1 molecule for each  $\text{PuF}_3$  or  $\text{PuF}_4$  unit, and as in the case of  $\text{Cs}_2\text{PuCl}_6$ , this small gain was probably caused by adsorption.

## Discussion

The results indicate that ammonia reacts with  $\text{PuI}_3$ ,  $\text{PuCl}_3$ , and  $\text{Cs}_2\text{PuCl}_6$  to form ammoniates. That the products contain chemically bound, rather than adsorbed, ammonia is demonstrated by the independence of the reaction rate and final product on surface area of the starting compound, by the large and reproducible amount of ammonia taken up, and by the infrared spectra of the products. The latter are compared to the spectrum of  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  in Figure 2, and the similarity strongly suggests that the plutonium compounds contain the ammonia molecules bound to the metal ion, and are in fact ammine complexes.

The product of reaction with  $\text{Cs}_2\text{PuCl}_6$  is probably  $\text{PuCl}_4 \cdot n\text{NH}_3$ . Although, as stated previously,  $\text{PuCl}_4$  does not exist as a solid, adducts of it with acetamide and *N,N*-dimethylacetamide have been prepared<sup>6</sup> from  $\text{Cs}_2\text{PuCl}_6$ , and it is reasonable to expect analogous adducts with ammonia. A separate experiment indicated that  $\text{CsCl}$  does not react with ammonia under these conditions, so this salt apparently is present in the products as an inactive diluent.

Except for  $\text{PuCl}_4 \cdot \sim 5\text{NH}_3$  and to a lesser extent  $\text{PuI}_3 \cdot \sim 5.5\text{NH}_3$ , none of the products appear to be stable at room temperature, and thus the composition vs. time results in the previous section may be considered as approximately isothermal decomposition data at 27°, or 65° above the boiling point of ammonia. Because of their instability even at room temperature, it was concluded that high-temperature thermogravimetric studies of these compounds would not be fruitful.

In the case of  $\text{PuI}_3$  the initial product contains nine molecules of ammonia. This compound loses one molecule of ammonia overnight to form the octammine species. The latter is somewhat more stable, requiring about 13 weeks to lose two additional molecules of ammonia. The similarity in compositions of the final products,  $\text{PuI}_3 \cdot (5.5-6.0)\text{NH}_3$ , resulting from prolonged storage at atmospheric pressure or shorter storage under vacuum, suggests the presence of a relatively stable species in this composition range.

The product of the  $\text{PuCl}_3$  reactions initially contains only eight  $\text{NH}_3$  molecules and lower complexes appear to be less well defined than in the case of  $\text{PuI}_3$  adducts. The greatly reduced rate of weight loss as the composition approaches  $\text{PuCl}_3 \cdot 4\text{NH}_3$  suggests the likelihood that this is a relatively stable species.

Although the  $\text{PuCl}_3$  adducts are obviously less stable than those of  $\text{PuI}_3$ , they are apparently quite stable at temperatures near that of liquid ammonia, the oct-

amine decomposing only slightly, even under vacuum, after eight days at -32°. At room temperature similar storage causes decomposition to yield the diammine. The most stable product is that formed by the reaction of liquid ammonia with  $\text{Cs}_2\text{PuCl}_6$ . The initial product, containing about seven  $\text{NH}_3$  molecules, rapidly decomposes to the pentammine, which remains essentially unchanged for periods as long as seven weeks.

The greater stability of the plutonium(IV) complex is also demonstrated by the infrared spectra in Figure 2, in which the Pu-N stretching band of  $\text{PuCl}_4 \cdot 5\text{NH}_3$  is shifted to a higher frequency than the ammine complexes of  $\text{PuI}_3$  and  $\text{PuCl}_3$ , indicating greater strength for the  $\text{Pu}^{\text{IV}}-\text{N}$  bond.

The product of the low-temperature gaseous reaction is somewhat less stable, decomposing in the same period to a species containing less than four  $\text{NH}_3$  groups. The lack of appreciable reaction at room temperature suggests that under these conditions, the free energy of the reaction is insufficient to overcome the stability of the  $\text{PuCl}_6^{2-}$  ion.

The results are qualitatively explainable on the basis of the known chemistry of plutonium. Among the plutonium(III) compounds, the stability of the ammonia adducts varies inversely with the energy of the respective metal-halogen bond. Thus the high energy of plutonium-fluoride bonds, which inhibits the entry of  $\text{NH}_3$  ligands into the coordination sphere, partially explains the failure of  $\text{PuF}_3$  and  $\text{PuF}_4$  to react with  $\text{NH}_3$ . This order of stability also prevails with ammine complexes of other metal halides.<sup>7</sup> Plutonium(IV), having a higher ionic potential than the trivalent ion<sup>8</sup>, forms stronger complexes; hence the greater stability of amines of the former.

It is interesting to speculate on the possible coordination number of plutonium in these compounds. In the product containing the most ammonia,  $\text{PuI}_3 \cdot 9\text{NH}_3$ , it is possible that the  $\text{NH}_3$  groups occupy the inner coordination sphere exclusively (although the presence of one or more iodide groups cannot be ruled out), in which case the coordination number is nine:  $[\text{Pu}(\text{NH}_3)_9]\text{I}_3$ . The most stable iodide species,  $\text{PuI}_3 \cdot \sim 6\text{NH}_3$ , would exhibit the same coordination number if all the  $\text{NH}_3$  and iodide groups were present in the inner coordination sphere:  $[\text{Pu}(\text{NH}_3)_6\text{I}_3]$ . Similarly, in the case of the most stable plutonium(IV) complex—assumed to be  $\text{PuCl}_4 \cdot 5\text{NH}_3$ —a coordination number of nine is possible:  $[\text{Pu}(\text{NH}_3)_5\text{Cl}_4]$ . The two extra ammonia molecules present in the initial product,  $\text{PuCl}_4 \cdot 7\text{NH}_3$ , being unable to displace chloride ligands, are presumably in the outer coordination sphere and hence are rapidly lost. It thus appears plausible that the maximum coordination number of both plutonium(II) and plutonium(IV) in these compounds is nine.

A comparison of these results with those from the reaction of  $\text{UCl}_3$  and  $\text{UCl}_4$  is perhaps instructive. Berthold and Knecht<sup>9</sup> found that the product of the reaction of  $\text{UCl}_3$  with gaseous or liquid  $\text{NH}_3$  was  $\text{UCl}_3 \cdot$

(7) Wendlandt W.W. and Smith J.P., *The Thermal Properties of Transition Metal-Ammine Complexes*, p. 3, Elsevier Publishing Company, Amsterdam, 1967.

(8) Cleveland J.M., *The Chemistry of Plutonium*, p. 92, Gordon and Breach Science Publishers, Inc., New York, 1970.

(9) Berthold H.J. and Knecht H., *Z. anorg. allg. Chem.*, 356, 151 (1968).

(6) Bagnall K.W., Deane A.M., Markin T.L., Robinson P.S., and Stewart M.A.A., *J. Chem. Soc.*, 1611 (1961).

$\sim 7\text{NH}_3$ . This product, when held in a stream of nitrogen at  $30^\circ$ , decomposed over a period of about 10 hours to  $\text{UCl}_3 \cdot 3\text{NH}_3$ , which was thermally stable at this temperature. The rapid decomposition of the initial product at a temperature only slightly greater than that employed in the present work indicates that the  $\text{UCl}_3$  ammoniates are less stable than those of  $\text{PuCl}_3$ .

The product of reaction of  $\text{UCl}_4$  with liquid or gaseous ammonia was  $\text{UCl}_4 \cdot (7.3-7.5)\text{NH}_3$ <sup>10</sup>. This product was found to decompose after six hours in nitrogen at  $45^\circ$  to  $\text{UCl}_4 \cdot 4\text{NH}_3$ , which was thermally stable at room temperature. (No decomposition data at  $30^\circ$  were reported, so direct comparison to the

<sup>(10)</sup> Berthold H.J. and Knecht H., *Z. anorg. allg. Chem.*, 366, 249 (1969).

present work is not possible.) In both  $\text{UCl}_3$  and  $\text{UCl}_4$  reactions, there was a large volume increase just as observed in the plutonium reactions, and it was established that all the ammonia was coordinated to the central metal ion. Both compounds were found to undergo a slight ammonolysis in liquid ammonia; in the case of the plutonium compounds there was no evidence in the infrared spectra for such products, but the possibility of a slight amount of ammonolysis cannot be ruled out.

*Acknowledgments.* The authors wish to thank R. S. Cichorz for determining the infrared spectra reported in this paper. This work was supported by the U. S. Atomic Energy Commission under Contract AT(29-1)-1106.