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ALKALI METAL CARBONATES OF PLUTONIUM

James D. Navratil

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C O N T E N T S

ABSTRACT	1
INTRODUCTION	1
SUMMARY AND CONCLUSIONS	2
EXPERIMENTAL	2
Reagents	2
Precipitation Procedure	2
Characterization Methods	3
RESULTS AND DISCUSSION	
PLUTONYL(VI) SYSTEM	3
Preparation and Composition of Compounds	3
Electronic Spectra	5
Titration Curves	5
Infrared Spectra	7
X-Ray Diffraction	10
Thermogravimetric Analysis	10
RESULTS AND DISCUSSION	
PLUTONIUM(IV) SYSTEM	11
Preparation and Composition of Compounds	11
Characterization of the Compounds	12
RESULTS AND DISCUSSION	
PLUTONIUM(III) SYSTEM	14
Preparation of Compounds	14
Composition of Compounds	15
Electronic Spectra	15
Infrared Spectra	15
Titration Curves	17
X-Ray Diffraction	17
Thermogravimetric Analysis	17
REFERENCES	18

ALKALI METAL CARBONATES OF PLUTONIUM

James D. Navratil

Abstract. Preliminary identification and characterization of compounds precipitated from plutonyl(VI), plutonium(IV), and plutonium(III) solutions upon alkali metal carbonate addition is reported. Various precipitation conditions and precipitate washing solvents were tried. Plutonyl (VI) carbonate was precipitated at pH 4-7 regardless of the alkali metal carbonate. Further addition of carbonate solution to the PuO_2CO_3 precipitate and supernate gave soluble green solutions and a residue of major composition MPuO_2CO_3 , where $\text{M}=\text{K}, \text{Rb}, \text{and Cs}$. Ethanol salting out of the soluble complex gave precipitates of composition $\text{M}_4[\text{PuO}_2(\text{CO}_3)_3]$, ($\text{M}=\text{Li}, \text{Na}, \text{K}$), and $\text{M}_6[(\text{PuO}_2)_2(\text{CO}_3)_5]$, ($\text{M}=\text{Rb}, \text{Cs}$). The plutonium(IV) and (III) systems appeared to yield impure $\text{Pu}(\text{OH})_4$ (or hydrated PuO_2) and PuOCO_3 , and $\text{Pu}_2(\text{CO}_3)_3$, respectively, regardless of the alkali metal carbonate used. The compounds were characterized by electronic and infrared spectrophotometry, thermogravimetric analysis, and x-ray diffraction techniques.

INTRODUCTION

Alkali metal carbonates of plutonium have been considered as potential reactor fuel materials.^(1,2) They also have possible applications analogous to other actinide processes, e.g., the dissolution and recovery of uranium in alkali carbonate solutions,⁽³⁾ uranyl carbonate as an intermediate for reactor fuel,⁽⁴⁾ and separating americium from curium in aqueous potassium carbonate solutions.⁽⁵⁾ Interest in plutonium carbonates by this laboratory first arose from the persistent occurrence of unknown carbonate complex impurities during the preparation of alkali metal polyplutonates. These unknown compounds could have a possible use in aqueous plutonium recovery operations.

Several plutonyl(VI) carbonates have been reported by precipitation with alkali metal carbonates^(1,2,6) but the composition of the precipitates was not determined. The early literature also notes the existence of complex plutonium(IV) carbonates,⁽⁶⁾ but the data are of a qualitative character. Later reported alkali metal carbonates of hexa-, penta-, and tetravalent plutonium are shown in Table 1. A host of ammonium carbonate species of plutonyl(VI) and (V) and plutonium(IV), including hydroxo complexes and barium derivatives, has also been reported.⁽¹⁴⁾ However, no plutonium(III) carbonates have been characterized.

Table 1. Reported Simple and Alkali Metal Carbonates of Plutonium.

Reported Formula	Method of Preparation	Reference
$\text{K}_4\text{PuO}_2(\text{CO}_3)_3$	Ozone oxidation of Pu(IV) in conc. K_2CO_3 soln.	7
PuO_2CO_3	$(\text{NH}_4)_4[\text{PuO}_2(\text{CO}_3)_3]$ heated to 120-30 °C.	8
KPuO_2CO_3 $\text{NaPuO}_2\text{CO}_3$	Solid M_2CO_3 added to Pu(V) soln. until pH~7 was reached.	9
$\text{K}_4[\text{Pu}(\text{CO}_3)_4] \cdot n\text{H}_2\text{O}$ $\text{K}_6[\text{Pu}(\text{CO}_3)_5] \cdot (3-4)\text{H}_2\text{O}$ $\text{K}_8[\text{Pu}(\text{CO}_3)_6] \cdot n\text{H}_2\text{O}$ $\text{K}_{12}[\text{Pu}(\text{CO}_3)_8] \cdot n\text{H}_2\text{O}$	Pu(IV) oxalate dissolved in various conc. of K_2CO_3 , 15, 25, 30-40, and 50%, which gave increasing Pu: CO_3 ratios respectively upon separation by alcohol.	10
$\text{Na}_4[\text{Pu}(\text{CO}_3)_4] \cdot 3\text{H}_2\text{O}$ $\text{Na}_6[\text{Pu}(\text{CO}_3)_5] \cdot 4\text{H}_2\text{O}$	Precipitated by adding 18% and 20% Na_2CO_3 soln. respectively to Pu(IV) soln. followed by alcohol addition.	11
$\text{Na}_6[\text{Pu}(\text{CO}_3)_5] \cdot 2\text{H}_2\text{O}$	Heating $\text{Na}_6[\text{Pu}(\text{CO}_3)_5] \cdot 4\text{H}_2\text{O}$.	11
$\text{PuOCO}_3 \cdot 2\text{H}_2\text{O}$	Decomposition of $(\text{NH}_4)_4\text{Pu}(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$.	12
$\text{PuO}_2 \cdot \text{PuOCO}_3 \cdot 3\text{H}_2\text{O}$	Decomposition of $(\text{NH}_4)_6\text{Pu}(\text{CO}_3)_5 \cdot n\text{H}_2\text{O}$.	12
$\text{PuO}_2 \cdot \text{PuOCO}_3$	Heating $\text{PuO}_2 \cdot \text{PuOCO}_3 \cdot 3\text{H}_2\text{O}$ to 105-10 °C.	12
$2.5 \text{ PuO}_2 \cdot \text{PuOCO}_3 \cdot n\text{H}_2\text{O}$	Heating solutions of ammonium carbonatoplutonates.	12
$\text{Pu}(\text{CO}_3)_2$	Heating of hydrated Pu(IV) oxalate in N_2 to 200-90 °C.	13

Evidence of plutonium(III) carbonate complexes was observed first when plutonium(III) hydroxide and sulfate were dissolved in potassium carbonate solutions.⁽⁶⁾ For the preparation of anhydrous plutonium(III) sulfate, plutonium(III) "carbonate" was made by adding an excess of ammonium carbonate to a hydrochloric acid solution of plutonium(III),⁽¹⁵⁾ but the precipitate was not analyzed. Plutonium(III) carbonate was also reported prepared by precipitating plutonium(III) sulfate with ammonium hydroxide and reacting the precipitate with carbon dioxide.⁽¹⁾ This compound was not analyzed, but was found to be insoluble in water and carbonic acid and soluble in 45% sodium carbonate.

Since the reported plutonium carbonates were not well characterized or studied in detail, this investigation was undertaken. The primary goal was to systematically study the compounds precipitated by the addition of alkali metal carbonate to hexa-, tetra-, and trivalent plutonium solutions. Preliminary results have already been summarized,⁽¹⁶⁾ and preliminary details are reported.

SUMMARY AND CONCLUSIONS

Compounds were precipitated by the addition of alkali metal carbonate to plutonyl(VI) and plutonium(IV) in nitric acid, and plutonium(III) in hydrochloric acid. The effect of compound composition on a variety of precipitation conditions and washing solvents was studied. The compounds were also characterized using electronic and infrared spectrophotometry, thermogravimetric analysis, and x-ray diffraction techniques.

In the plutonyl(VI) system, tan plutonyl (VI) carbonate was precipitated in >99% yield at pH 4-7 regardless of the alkali carbonate used.

Further addition of carbonate solution to the PuO_2CO_3 precipitate and supernate dissolved the precipitate above pH ~ 8. A small residue of impure MPuO_2CO_3 remained after separation of the soluble green complex, when M=K, Rb, and Cs. The existence of the pentavalent compound was substantiated by infrared spectroscopy and x-ray diffraction techniques.

Ethanol addition to the green complex salted out precipitates of variable composition: $\text{M}_6[(\text{PuO}_2)_2(\text{CO}_3)_5]$, where M=Rb and Cs; and $\text{M}_4[\text{PuO}_2(\text{CO}_3)_3]$, where M=Li, Na and K. Infrared studies indicate that the MPuO_2CO_3 and lithium compounds are unidentate carbonate complexes, while the remaining tend toward bidentate or bridging coordination of the carbonate ion. The heating of $\text{Na}_4[\text{PuO}_2(\text{CO}_3)_3]$

and $\text{K}_4[\text{PuO}_2(\text{CO}_3)_3]$ to 350 and 450°C resulted in the formation of a probable plutonyl(V) compound of questionable composition.

Preliminary investigation of the plutonium(IV) system indicates plutonium hydroxide (or hydrated PuO_2) is precipitated at pH ~ 5, and PuOCO_3 formation occurs upon further addition of carbonate. Ethanol salting out of the soluble green complex yields impure PuOCO_3 .

Addition of all alkali metal carbonates to plutonium(III) in hydrochloric acid solution appears to give impure $\text{Pu}_2(\text{CO}_3)_3$ under a variety of precipitation conditions. The conclusions are preliminary, however.

EXPERIMENTAL

Reagents

A 0.063M solution of plutonium nitrate in 0.69M nitric acid, previously purified by ion exchange, was used for the plutonium(IV) precipitations. The above solution was oxidized with ozone at 80°C for the plutonyl(VI) precipitations. Oxidation completeness was checked by monitoring the plutonium(IV) absorption band at 470 nm. Plutonium(III) solutions were prepared immediately before each precipitation by dissolving 1.0 gram of 99.9% pure plutonium metal in 20 ml of 5.0M hydrochloric acid and diluting with 0.10M HCl to a 100 ml volume.

The alkali metal carbonates and bicarbonates were all reagent grade. They were used as 2.5M solutions except for lithium carbonate which was added as the solid due to its insolubility.

Precipitation Procedure

Plutonyl(VI) or plutonium(IV) precipitations were conducted by adding carbonate solution or solid lithium carbonate, with stirring, to either 200 or 400 ml of the plutonium solution at either 26 to 30°C or 75 to 80°C. The addition of carbonate was stopped at either a pH of approximately 5, 8, or 11, which resulted in alkali metal carbonate to plutonium ratios of 7 to 8:1, 8 to 9:1, and 10 to 11:1, respectively. The precipitates were then digested for 5, 15, 30, or 240 minutes. At high carbonate-to-plutonium ratios (pH>8), the compound was salted out from the soluble complex by the addition of an equal volume (~200 or ~400 ml) of ethanol followed by 3 to 4 minutes of stirring. After digestion, the precipitates were separated by centrifugation and washed with 15-ml volumes of solvent (type and number of washings specified in tables). In some cases,

the precipitate was split before washing to evaluate the effect of different solvents (these are designated with capital letters after the run numbers) Finally, the isolated precipitates were vacuum-dried over night at room temperature, ground in a mortar, and sampled

Precipitation with the freshly prepared plutonium(III) solution was similar to the above procedure except for the following carbonate was added until the desired carbonate-to-plutonium ratio was reached, digestion was for 5, 15, or 30 minutes under a stream of argon, and the precipitate was treated without delay between the digestion and drying steps

Characterization Methods

The oxidation state of all the compounds was verified by spectrophotometry A small amount of the plutonium(VI) and plutonium(IV) compounds and the plutonium(III) compound was dissolved in 3M nitric acid and 1M hydrochloric acid, respectively Their spectra were then determined on a Cary Model 14 recording spectrophotometer Electronic spectra were also run on the compounds (as a mull in fluorocarbon grease) and the supernates

The plutonium content was determined in the solids and supernates by potentiometric titration with ceric ion and radiometric techniques, respectively Lithium and sodium were determined by atomic absorption spectroscopy, and potassium, rubidium, and cesium analyzed by a combined ion exchange-x-ray fluorescence method Carbon was determined by a combustion-absorption technique

Infrared spectra of the compounds were obtained by incorporation into potassium bromide pellets and scanning on a Beckman IR 12 infrared spectrophotometer

The pH titration curves were constructed from data obtained using a Fisher Accumet pH meter with glass and calomel electrodes

X-ray diffraction powder patterns of the samples were run with a solid state Norelco diffractometer using Cu-K radiation

Thermogravimetric curves were obtained on either a Dupont 900 or Mettler Recording Thermoanalyzer No. 27, using 5 and 6° per minute heating rates, respectively, under argon

RESULTS AND DISCUSSION PLUTONYL (VI) SYSTEM

Preparation and Composition of Precipitates

Addition of alkali metal carbonates to plutonyl(VI) solutions precipitated tan PuO_2CO_3 at pH 4 to 7, regardless of the alkali metal carbonate used Details of PuO_2CO_3 preparation and characterization will be reported later ⁽¹⁷⁾

At pH7, the tan solution containing plutonyl(VI) carbonate turned brown, with the addition of M_2CO_3 , and above ~ pH 8 the precipitate dissolved to yield a green soluble complex A small brown residue usually resulted In the case of lithium and sodium, the residue dissolved completely at pH>9 Although there was not enough for elemental analysis, the residue remaining at pH<9 was identified by IR as PuO_2CO_3 and M_2CO_3 , where M=Li and Na Potassium, rubidium, and cesium precipitations usually gave residue yields of 1 to 10% for which the larger yields were analyzed However, the analyses were hampered by the small size which reflects disagreement in the probable formula, especially in runs Rb-2A and Rb 2B (Table 2) No correlation between precipitation conditions and residue yield could be made Also, since the accuracy of the analytical data is questionable, no relation between precipitation conditions and residue composition was attempted The formula $\text{MPuO}_2(\text{CO}_3)(\text{OH})$ was a likely candidate for the brown residue, since an analogous compound was reported where M= NH_4 ^(18,19) However, x-ray and infrared investigations (discussed later) will conclude that the probable formula is reasonable The residue-free soluble green complexes formed at about pH 8 yielded precipitates when salted out with an equal volume of ethanol The precipitation of pink $\text{Li}_4\text{PuO}_2(\text{CO}_3)_3$ was hampered by the poor solubility of Li_2CO_3 Precipitates (not shown in Table 2) containing an excess of Li_2CO_3 contamination usually resulted when precipitated at 30°C and stirred for 30 minutes Green $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$ was precipitated at a pH of 11 and the precipitates were usually contaminated by Na_2CO_3 and NaNO_3 from poor washing The effect of various temperatures and digestion times on $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$ composition was minimal, and at pH 8.5 (run Na-2A) the formula $\text{Na}_3\text{PuO}_2(\text{CO}_3)_2.5$ could be assigned Lime green $\text{K}_4\text{PuO}_2(\text{CO}_3)_3$ was prepared here in a different manner than the method reported ⁽⁷⁾ Table 2 shows that the time, temperature, and solvent parameters tried had little effect on composition of $\text{K}_4\text{PuO}_2(\text{CO}_3)_3$ except for the K_2CO_3 contamination (verified by IR) resulting from poor washing Precipitate composition of $\text{Rb}_3\text{PuO}_2(\text{CO}_3)_2.5$ is in agreement with the probable formula under the various washing conditions and concentrations of carbonate solutions tried Precipitation of the cesium complexes was definitely hampered at

Table 2. Effect of Precipitation Conditions on Compound Composition.

Run Numbers	Precipitation Conditions				Analysis-Molar Ratio M : PuO ₂ : CO ₃	Probable Formula
	pH	Time (min.)	Temp. (°C)	Washing		
Li-1 ^a	11	240	80	3 EtOH	4.4 : 1.0 : 3.3	Li ₄ PuO ₂ (CO ₃) ₃
Li-2 ^a	11	30	80	3 95% EtOH	5.3 : 1.0 : 3.2	Li ₄ PuO ₂ (CO ₃) ₃
Na-1A ^a	11	30	30	2 H ₂ O	4.6 : 1.0 : 3.0	Na ₄ PuO ₂ (CO ₃) ₃
Na-1B ^a	11	30	30	3 80% MeOH	4.3 : 1.0 : 2.9	Na ₄ PuO ₂ (CO ₃) ₃
Na-2A ^a	8.5	240	80	2 MeOH	3.9 : 1.0 : 2.8	Na ₄ PuO ₂ (CO ₃) ₃
Na-2B ^a	11	240	80	3 MeOH	4.7 : 1.0 : 3.1	Na ₄ PuO ₂ (CO ₃) ₃
Na-3 ^a	11	30	80	3 50%MeOH+3MeOH	4.6 : 1.0 : 3.0	Na ₄ PuO ₂ (CO ₃) ₃
Na-4 ^a	11	30	80	2 50%MeOH+1 MeOH	4.4 : 1.0 : 3.1	Na ₄ PuO ₂ (CO ₃) ₃
K-1	7.4	30	30	2 Acetone	1.7 : 1.0 : 1.4	KPuO ₂ CO ₃
K-2	7.4	30	30	2 H ₂ O	1.2 : 1.0 : 1.2	KPuO ₂ CO ₃
K-3	8	30	80	2 H ₂ O	0.77 : 1.0 : 1.2	KPuO ₂ CO ₃
K-4	11	30	80	3 50%MeOH	1.2 : 1.0 : 0.93	KPuO ₂ CO ₃
K-5 ^a	11	5	30	1 H ₂ O	4.2 : 1.0 : 3.2	K ₄ PuO ₂ (CO ₃) ₃
K-6A ^a	11	30	80	4 50%MeOH	4.2 : 1.0 : 3.0	K ₄ PuO ₂ (CO ₃) ₃
K-6B ^a	11	30	80	4 MeOH	3.9 : 1.0 : 3.0	K ₄ PuO ₂ (CO ₃) ₃
K-7 ^a	11	30	80	3 MeOH	4.4 : 1.0 : 3.1	K ₄ PuO ₂ (CO ₃) ₃
Rb-1	7	5	30	1 H ₂ O	0.73 : 1.0 : 1.2	RbPuO ₂ CO ₃
Rb-2A	8	30	30	2 H ₂ O	2.4 : 1.0 : 1.1	RbPuO ₂ CO ₃
Rb-2B	8	30	30	3 Acetone	2.5 : 1.0 : 1.3	RbPuO ₂ CO ₃
Rb-3	11	30	80	4 50%MeOH	0.78 : 1.0 : 1.8	RbPuO ₂ CO ₃
Rb-4B ^a	8.5	5	30	2 H ₂ O	3.0 : 1.0 : 2.7	Rb ₃ PuO ₂ (CO ₃) _{2.5}
Rb-5 ^a	11	30	80	2 EtOH+2MeOH+2 Ac	3.0 : 1.0 : 2.4	Rb ₃ PuO ₂ (CO ₃) _{2.5}
Rb-6A ^{ac}	11	30	80	4 50% MeOH	3.0 : 1.0 : 2.6	Rb ₃ PuO ₂ (CO ₃) _{2.5}
Rb-6B ^{ac}	11	30	80	3 50% MeOH+1 H ₂ O	3.0 : 1.0 : 2.5	Rb ₃ PuO ₂ (CO ₃) _{2.5}
Rb-7A ^{ad}	11	30	80	4 50% MeOH	3.0 : 1.0 : 2.4	Rb ₃ PuO ₂ (CO ₃) _{2.5}
Rb-7B ^{ad}	11	30	80	3 50% MeOH+1 H ₂ O	2.8 : 1.0 : 2.4	Rb ₃ PuO ₂ (CO ₃) _{2.5}
Rb-8A ^a	11	30	80	4 50% MeOH	3.0 : 1.0 : 2.5	Rb ₃ PuO ₂ (CO ₃) _{2.5}
Rb-8B ^a	11	30	80	2 H ₂ O	3.0 : 1.0 : 2.6	Rb ₃ PuO ₂ (CO ₃) _{2.5}
Cs-1 ^b	7	5	30	2 H ₂ O	— : 1.0 : 1.2	CsPuO ₂ CO ₃
Cs-2A	8	30	30	3 H ₂ O	1.6 : 1.0 : 1.0	CsPuO ₂ CO ₃
Cs-2B	8	30	30	3 Acetone	1.8 : 1.0 : 1.5	CsPuO ₂ CO ₃
Cs-3	8	30	80	3 H ₂ O	1.1 : 1.0 : 1.2	CsPuO ₂ CO ₃
Cs-4 ^{ab}	8.5	5	30	None	3.1 : 1.0 : 2.9	Cs ₃ PuO ₂ (CO ₃) _{2.5}
Cs-5 ^a	11	30	30	3 MeOH	5.1 : 1.0 : 2.9	Cs ₃ PuO ₂ (CO ₃) _{2.5}
Cs-6 ^a	11	30	30	3 Acetone	6.7 : 1.0 : 2.5	Cs ₃ PuO ₂ (CO ₃) _{2.5}
Cs-7 ^a	11	30	80	3 50%MeOH	2.7 : 1.0 : 2.2	Cs ₃ PuO ₂ (CO ₃) _{2.5}
Cs-8 ^a	11	30	80	3 MeOH	3.5 : 1.0 : 2.6	Cs ₃ PuO ₂ (CO ₃) _{2.5}

^aEqual volume of ethanol added and digested 3-4 minutes.^bPrecipitated with 2.5M MHCO₃.^cPrecipitated with 1.25M M₂CO₃.^dPrecipitated with 5.0M M₂CO₃.

30°C by ethanol salting out of CsNO_3 (identified by IR) as indicated by the high $\text{M}:\text{PuO}_2$ ratio in runs Cs-5 and Cs-6. Run Cs-4 was contaminated with Cs_2CO_3 (identified by IR) from poor washing. As expected, high $\text{M}:\text{PuO}_2$ ratios were encountered when little or no washing was performed.

The contamination of the compounds by alkali metal carbonates and nitrates was also caused by the salting-out procedure, using equal volumes of ethanol (runs Na-1A, Na-1B, Cs-5, and Cs-6). Precipitating in the absence of plutonyl, i.e., salting out a comparable amount of nitric acid and alkali metal carbonate solution with ethanol, gave small amounts of white precipitates at room temperature using all the alkali metal carbonates except potassium carbonate. The precipitates were identified by IR as carbonates of lithium and sodium, and nitrates of rubidium and cesium. At 80°C, reagent precipitation was observed only after digestion with ethanol for longer than 5 minutes.

The use of MHCO_3 in runs Cs-1 and Cs-4 apparently did not have any significant effect on precipitate composition. Also, the use of 1.25 and 5.0M Rb_2CO_3 gave identical results as when 2.5M Rb_2CO_3 was used.

The above compounds varied in yield between 80 and 95%, with $\text{Li}_4\text{PuO}_2(\text{CO}_3)_3$ being generally the lowest. It is notable that the $\text{M}_3\text{PuO}_2(\text{CO}_3)_{2.5}$, ($\text{M}=\text{Rb}, \text{Cs}$), precipitates are analogous to the reported compound $\text{NH}_6[(\text{PuO}_2)_2(\text{CO}_3)_5]$,⁽¹⁹⁾ and the $\text{M}_4[\text{PuO}_2(\text{CO}_3)_3]$, ($\text{M}=\text{Li}, \text{Na}$), precipitates are identical to the reported compound $\text{K}_4[\text{PuO}_2(\text{CO}_3)_3]$.⁽⁷⁾ The former composition, based also on the analogous carbonato-uranylates,⁽²⁰⁾ is probably better represented as $\text{M}_6[(\text{PuO}_2)_2(\text{CO}_3)_5]$.

Representative samples of the above compounds were randomly stored in closed vials for two months, and re-analyzed. None of the analyses varied significantly between these periods, and the compounds were assumed to be stable.

Electronic Spectra

The hexavalent state of the compounds was verified by dissolving a small amount of the precipitate in 3M HNO_3 and measuring its absorption spectra between 400 and 1100 nm. All the compounds had negligible plutonium(IV) present except for the MPuO_2CO_3 compounds which contained from 5 to 20% plutonium(IV).

When plutonyl(V) was suspect in the MPuO_2CO_3 compounds and several intermediate thermogravimetric analysis products, the compounds were dissolved in

0.2M HClO_4 at 10°C and scanned. These spectra were then compared to the plutonyl(V) spectrum reported by Cohen⁽²¹⁾ under these conditions. The MPuO_2CO_3 spectra contained the major plutonyl(V) bands and the plutonyl(VI) band at 830 nm corresponding to <10% plutonium(VI). The appearance of plutonyl(V) was thought to be caused mainly by the self-reduction of the plutonium by its alpha radiation, and the plutonyl(V) inherent in the starting plutonyl(VI) nitrate solution. The spectra of decomposed $\text{Na}_4[\text{PuO}_2(\text{CO}_3)_3]$ and $\text{K}_4[\text{PuO}_2(\text{CO}_3)_3]$, heated to 350°C and 450°C, respectively, and run as above, were the same as the MPuO_2CO_3 spectra.

Table 3 summarizes representative electronic spectra of the supernates of the precipitates and fluorocarbon grease mulls of the compounds scanned between 400 and 1100 nm. Calculation of the molar absorptivity index for the supernates was not attempted since the concentrations were not known. A wavelength difference of 5 nm is considered insignificant in the following discussion. The supernate spectra of the $\text{MPuO}_2(\text{CO}_3)$ and $\text{M}_4\text{PuO}_2(\text{CO}_3)_3$ precipitates are similar as are the $\text{M}_3\text{PuO}_2(\text{CO}_3)_{2.5}$ spectra except for a notable shift in maximum absorption from between 570 and 575 to 585 nm. There was strong absorption below 500 nm with these supernates, and the spectra are similar to the maximum absorption bands reported by Moore⁽⁶⁾ of plutonyl(VI) in 45% K_2CO_3 : <500 high absorption, 588, 800, 950, and 1080 nm; and by Gel'man, et al.,⁽¹⁸⁾ of plutonyl(VI) in $(\text{NH}_4)_2\text{CO}_3$: <500 high absorption, 570, 720, 800, 940, and 1070 nm. The mull spectra of the compounds have a high absorbance below 500 nm. The MPuO_2CO_3 mull spectra contain some of the PuO_2CO_3 and supernate peaks,⁽¹⁷⁾ probably as contamination, and a new peak around 850 nm of probable plutonyl(V) character. The mull spectra of the $\text{M}_4\text{PuO}_2(\text{CO}_3)_3$ compounds are markedly different amongst themselves, especially $\text{Li}_4\text{PuO}_2(\text{CO}_3)_3$, and the supernate spectra. However, the $\text{M}_3\text{PuO}_2(\text{CO}_3)_{2.5}$ mull spectra are in better agreement with the supernate spectra. The above spectra have indicated that the compounds contain varying anionic complex species.

Titration Curves

Fifty milliliter solutions of 0.063M plutonyl(VI) were titrated with ammonium, sodium, and cesium carbonate solutions (2.5M) as the pH was monitored. The former was used as a comparison. Figure 1 contains plots of the volume of carbonate consumed versus pH. Both plots, using alkali carbonates, are very similar and contain two plateaus at pH of 4.5 and 9 corresponding to PuO_2CO_3 precipitation and PuO_2CO_3 dissolution, respectively. Calculation of the consumption of carbonate solution between a

Table 3. Electronic Spectra of Plutonyl(VI) Supernates and Compounds.

Description	Absorption Wavelengths (nm)															
KPuO ₂ CO ₃																
supernate	<500 ^a	530	575 ^b	620	645	655	690	730	750	815 ^b	860	—	940	—	—	—
mull	<500 ^a	—	—	620	—	650	—	725	795	815 ^b	850	920	—	1015	—	1060
RbPuO ₂ CO ₃																
supernate	<500 ^a	520	575 ^b	615	640	650	685	720	745	810 ^b	—	—	935	—	—	—
mull	<500 ^a	—	—	620	—	655	685	735	—	815 ^b	855	900	—	1020	—	1050
CsPuO ₂ CO ₃																
supernate	<500 ^a	520	575 ^b	615	635	650	685	725	745	810 ^b	850	—	935	—	—	—
mull	<500 ^a	—	—	620	—	650	690	725	750	815 ^b	850	900	925	1015	—	1070
Li ₄ PuO ₂ (CO ₃) ₃																
supernate	<500 ^a	520	570 ^b	615	640	650	685	725	745	810 ^b	855	—	940	—	—	1065
mull	<500 ^a	525	—	610	—	645	—	730	—	805 ^b	845 ^b	920	935	985	1015	—
Na ₄ PuO ₂ (CO ₃) ₃																
supernate	<500 ^a	520	570 ^b	615	635	650	685	720	745	810 ^b	—	—	940	—	—	1070
mull	<500 ^a	520	590 ^b	—	—	650	—	705	745	805 ^b	—	920	940	—	—	1105
K ₄ PuO ₂ (CO ₃) ₃																
supernate	<500 ^a	520	575 ^b	615	640	650	685	720	745	810 ^b	—	—	935	—	—	—
mull	<500 ^a	530	—	620 ^b	—	655	—	710	750	805 ^b	—	925	960	975	1085	1100
Rb ₃ PuO ₂ (CO ₃) _{2.5}																
supernate	<500 ^a	520	585 ^b	615	640	655	690	720	745	810 ^b	—	910	925	940	—	—
mull	<500 ^a	520	585 ^b	—	—	655	690	720	745	810 ^b	—	—	925	945	—	1085
Cs ₃ PuO ₂ (CO ₃) _{2.5}																
supernate	<500 ^a	520	585 ^b	615	640	655	690	720	745	810 ^b	—	—	—	940	—	—
mull	<500 ^a	—	(575) 590	620	645	—	690	710	755	810 ^b	—	—	925	—	—	1085

^aStrong absorption below 500 nm.^bMaximum absorbance peaks.

Figure 1 Titration Curves (pH) of 50 ml Plutonyl(VI) Solutions (0.063M)

pH of 4 and 5.5 gave a CO_3/PuO_2 molar ratio of 1:1. This is in agreement with PuO_2CO_3 formation. Between pH 4 and 9.5, the consumption of Na_2CO_3 and Cs_2CO_3 gave CO_3/PuO_2 molar ratios of 3:3 and 2:8, respectively. These molar ratios also are similar to the composition of precipitates formed with these reagents. The $(\text{NH}_4)_2\text{CO}_3$ is different than the two discussed above. In the absence of plutonyl, the plot resembled a normal acid-base titration curve.

Infrared Spectra

Representative infrared spectra of all the plutonyl compounds in Table 2 are shown in Figure 2. The compounds are probably carbonate complexes since they contain more than just a few bands typical of the high D_{3h} symmetry of the CO_3^{2-} ion⁽²²⁾. Classification of the compounds as unidentate or bidentate carbonate complexes will be made based on known and accepted spectral differences of the C_{2v} symmetry^(22,23). However, bidentate and bridging coordination of carbonate cannot be differentiated by IR. Assigned frequencies of unidentate species are ν_5 at ~ 1449 to 1495 , ν_1 at ~ 1360 to 1370 , and ν_2 at ~ 1063 to 1070 , and the bidentate species are ν_1 at ~ 1590 to 1643 , ν_5 at ~ 1260 to 1292 , and ν_2 at ~ 1026 .

to 1033 ⁽²²⁾. Other assignments will also be made in the ensuing discussion of infrared spectra agreement.

The infrared spectrum of KPuO_2CO_3 is representative of all the MPuO_2CO_3 spectra except for minor variations in the peak intensities, especially in the broad plutonium dioxide band between 400 and 500 cm^{-1} . The major bands are different than either the PuO_2CO_3 ⁽¹⁷⁾ and $\text{M}_4\text{PuO}_2(\text{CO}_3)_3$ spectra. The spectra represent impure compounds, but unidentate assignments could be rationalized as well as the following: plutonyl asymmetric stretch at 910 cm^{-1} as minor constituent, and the plutonyl(V) asymmetric stretch at $\sim 810\text{ cm}^{-1}$. The latter is based on an analogous shifting of bands in the americium and neptunium(VI) and (V) spectra⁽²⁴⁾.

The lithium spectrum definitely contains Li_2CO_3 , noted by the following bands: 1090 , 860 , 740 , and 520 cm^{-1} . The asymmetric plutonyl stretch can probably be assigned at 930 cm^{-1} , and this spectrum is definitely unlike the heavier alkali metal carbonates of similar composition. Mixtures of PuO_2CO_3 and Li_2CO_3 are unlikely because of the lack of PuO_2CO_3 bands⁽¹⁷⁾. Other mixtures of Li_2CO_3 and, for example, $\text{Li}_2\text{PuO}_2(\text{CO}_3)_2$ cannot be ruled out.

The spectrum of $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$ is representative of the sodium compounds precipitated with ethanol except for the precipitations performed at 30°C . Spectra of runs Na 1A and 1B had additional bands resembling Na_2CO_3 , and more notable is the shifting of the plutonyl band down to 890 cm^{-1} . The $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$ spectra tend toward a bidentate carbonate complex since there is spreading of the ν_1 and ν_5 bands and a shifting of the ν_2 species to a lower wave number as compared to the KPuO_2CO_3 spectrum.

The spectrum of $\text{K}_4\text{PuO}_2(\text{CO}_3)_3$ is very similar to the above, except for the following major differences: shifting of the plutonyl band to 890 cm^{-1} as in the spectrum of $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$, a slight shift in all bands including ν_2 to 1050 cm^{-1} , and more spreading of ν_1 and ν_5 with the splitting of ν_5 .

The spectrum in Figure 2 of $\text{Rb}_3\text{PuO}_2(\text{CO}_3)_2$ is representative of all the rubidium runs, except run Rb 5 (see Table 2) which was identical to the potassium spectra except for the shifting of the plutonyl peak to 880 cm^{-1} . These compounds probably contain carbonate of bidentate or bridging coordination.

The infrared spectra of all the cesium precipitates were very similar to the spectrum in Figure 2. Therefore

Figure 2. Representative Infrared Spectra of the Plutonyl(VI) and (V) Compounds.

Figure 2. Representative Infrared Spectra of the Plutonyl(VI) and (V) Compounds. (Continued)

it was concluded that these runs produced $\text{Cs}_2\text{PuO}_2(\text{CO}_3)_{2.5}$ with varying contamination of cesium nitrate and carbonate.

In summary, MPuO_2CO_3 compositions probably contain complex anions of the unidentate type, whereas the remaining anions of the compounds tend toward bidentate or bridging coordination. To speculate, the structures of the complex anions in $\text{M}_4[\text{PuO}_2(\text{CO}_3)_3]$ and $\text{M}_6[(\text{PuO}_2)_2(\text{CO}_3)_5]$ are probably analogous to the suggested structures of the carbonatouranylates.⁽²⁰⁾ Therefore, the plutonium atom would probably have a coordination number of eight in these complexes.

Spectra of intermediate thermogravimetric products from $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$ and $\text{K}_4\text{PuO}_2(\text{CO}_3)_3$ heated to 350 and 450°C, respectively, are also shown in Figure 2. The strong band about 800 to 810 cm^{-1} could be assigned to the plutonyl(V) asymmetric stretching frequency as mentioned above.⁽²⁴⁾ These products appear to have unidentate character, no plutonium dioxide contamination, and are unlike any of the above spectra; therefore indicating a different plutonyl(V) compound as observed above.

X-Ray Diffraction

The majority of the compounds precipitated were crystalline and gave good x-ray diffraction patterns. This work is incomplete;⁽¹⁷⁾ however, some of the results are as follows: $\text{K}_4[\text{PuO}_2(\text{CO}_3)_3]$ was reported isomorphous with $\text{K}_4[\text{UO}_2(\text{CO}_3)_3]$,⁽⁷⁾ and this work is in fair agreement (Table 4). Moreover, because of the complexity of the crystal structure in relation to our computer program, and the lack of data in the reported structure of $\text{K}_4[\text{UO}_2(\text{CO}_3)_3]$,⁽²⁵⁾ we were unable to evaluate the powder pattern. The reported powder patterns of KPuO_2CO_3 and $\text{RbAmO}_2\text{CO}_3$ ⁽²⁶⁾ are in agreement with the representative MPuO_2CO_3 residues characterized in this study. However, the suspected plutonyl(V) compounds isolated as intermediate thermogravimetric products were not isomorphous with any of the reported plutonyl(V) carbonates.

Thermogravimetric Analysis

Thermogravimetric curves of some representative plutonyl compounds are shown in Figure 3.

Curves 4 and 5 in Figure 3 are impure KPuO_2CO_3 and $\text{RbPuO}_2\text{CO}_3$, respectively, heated to 950°C. No accurate correlations could be made with MPuO_2CO_3 thermogravimetric data because of the impurity and incomplete decomposition of the compounds.

Table 4. X-Ray Powder Pattern of $\text{K}_4\text{PuO}_2(\text{CO}_3)_3$.

d Spacing (Å)	Intensity (I/I ₁)	d Spacing (Å)	Intensity (I/I ₁)
6.80	10	2.52	15
6.10	65	2.40	20
5.85	60	2.34	50
4.30	25	2.26	60
3.73	45	2.14	40
3.56	15	2.08	15
3.38	90	2.05	45
3.23	75	2.01	35
3.13	70	1.920	<10
3.03	20	1.688	25
3.00	20	1.665	20
2.93	15	1.603	<15
2.72	65	1.557	15
2.66	100	1.355	20
2.61	15		

Figure 3. Thermogravimetric Curves of Plutonyl(VI) Compounds.

$\text{Li}_4\text{PuO}_2(\text{CO}_3)_3$ heated to approximately 1600°C (Curve 6 in Figure 3) was not completely decomposed, and calculated plutonium dioxide residue (12.7 mg) verified this. Therefore, the last plateau is probably PuO_2 and $2\text{Li}_2\text{O}$ (bp $\text{Li}_2\text{O} = \sim 1700^\circ\text{C}$).⁽²⁷⁾ Infrared spectra were run on the intermediate products at 200 and 450°C. At 200°C there was no significant change in the compound, and at 450°C the product was mostly a mixture of PuO_2 and Li_2CO_3 . By correcting for Li_2CO_3 impurity present in the starting compound, approximately two moles of water were lost upon heating to 200°C.

The curve of $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$ (Curve 3 in Figure 3) is similar in shape to the last curve. The final plateau probably contains some Na_2O (sublimes at about 1275°C)⁽²⁷⁾ with the PuO_2 residue. Infrared spectra of the first three plateau products indicated no change at 200°C, the diminishing PuO_2^{2+} band and strong appearance of the PuO_2^{+} band at 350°C (Figure 2), and a mixture of PuO_2 and Na_2CO_3 at 600°C. Since NaCO_3 starts losing CO_2 at 400°C,⁽²⁷⁾ it is difficult to accurately determine the composition at 600°C. After back calculating from the amount of PuO_2 present (14.4 mg), the starting material has about 1.5 moles of H_2O . Run Na-4 is in agreement. The intermediate product at 350°C was analyzed for plutonium and carbon and the resultant $\text{CO}_3:\text{PuO}_2$ ratio was 2.8. By assuming the 350°C intermediate product is all PuO_2^{+} , a composition of $\text{Na}_4\text{PuO}_2(\text{CO}_3)_{2.5}$ can be calculated with the loss of $\frac{1}{2}\text{CO}_2 + \frac{1}{2}\text{O}_2$. However, other possibilities exist, including a mixture of $\text{Na}_3\text{PuO}_2(\text{CO}_3)_2$ and $\frac{1}{2}\text{Na}_2\text{O}_2$.

The final residue from heating $\text{K}_4\text{PuO}_2(\text{CO}_3)_3$ (Curve 1 in Figure 3) is in agreement with the calculated 8.00 mg of PuO_2 . Identification by IR of the products at 200°, 450°, and 600°C was found identical to $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$. Curves of runs K-6A and K-7 were calculated for water loss and are $\frac{1}{2}$ and $\frac{1}{3}$ mole of H_2O , respectively. Moreover, the curves were similar. The intermediate product at 450°C was analyzed for plutonium and carbon, yielding a plutonyl to carbonate ratio of 1:2.5. Again a likely composition would be $\text{K}_4\text{PuO}_2(\text{CO}_3)_{2.5}$, and the thermogravimetric curve is in agreement. Both curves of runs K-6A and K-7 correlate with the following possible decomposition sequence:

$\text{Rb}_3\text{PuO}_2(\text{CO}_3)_{2.5}$ (Curve 7 in Figure 3) from runs Rb-6, Rb-7A, and Rb-8B were similar and calculate to contain about 3 moles H_2O . There is a slight plateau between 350 and 450°C, similar to the above compounds, but no identification was made of the product. Infrared identification of the 200° and 600°C intermediate products was identical to the above.

The TGA curve of the cesium compound (Curve 2 in Figure 3) has the same disadvantage as the rubidium curve, i.e., incomplete decomposition. The sharp weight loss is attributed to the high CsNO_3 impurity. Notable is the plateau at 450°C which is typical of all these compounds.

The water of hydration in the $\text{M}_4\text{PuO}_2(\text{CO}_3)_3$ compounds was not verified because of the lack of data. However, the approximate hydration numbers determined were 2, 1.5, 0.35-0.5, and 3, corresponding to $\text{M}=\text{Li}$, Na , K and Rb , respectively. The cesium compound and plutonium(V) compounds remain undetermined.

RESULTS AND DISCUSSION PLUTONIUM(IV) SYSTEM

Preparation and Composition of Compounds

A limited number of plutonium(IV) runs was conducted because more is known about this system. With the addition of alkali metal carbonate solutions to plutonium(IV) solutions, a green gelatinous precipitate formed at about pH 4 to 5 and partially re-dissolved at about pH 9 to 11. The precipitates did not completely re-dissolve at high pH and at longer stirring times and temperatures which were tried.

The analytical results of the few plutonium(IV) precipitations made are shown in Table 5.

The sodium precipitates washed with acetone apparently gave high M:Pu ratios as indicated in comparing Na-1A and 1B. Both carbonate and nitrate impurity were identified by IR in run Na-1B, and the impurity in run Na-2 was mostly Na_2CO_3 . The ethanol salting-out procedure was used, and its disadvantages have already been discussed.

The rubidium and cesium precipitations, both washed or not washed with organic solvents, had high M:Pu ratios. This was confirmed by IR, as well as carbonate contamination in run Cs-3. Scrutiny of the analytical data in Table 5 generally indicates the following: (1) impure plutonium hydroxide or hydrated PuO_2 is the primary compound

Table 5. Effect of Precipitation Conditions on Plutonium(IV) Compound Composition.

Run Numbers	Precipitation Conditions				Analysis-Molar Ratio		
	pH	Time (min.)	Temp (°C)	Washing	M	Pu	CO ₃
Na-1A	11	30	30	3 H ₂ O	1.2	1.0	1.6
Na-1B	11	30	30	3 Acetone	3.0	1.0	1.7
Na-2 ^a	11	30	30	3 Acetone	0.78	1.0	3.6
K-1 ^a	11	30	30	3 EtOH+	1.5	1.0	1.3
				3 Acetone			
Rb-1	8.5	5	30	None	0.89	1.0	0.38
Rb-2	8.5	5	30	3 H ₂ O	—	1.0	0.30
Rb-3	11	30	80	3 EtOH+	1.7	1.0	1.3
				3 Acetone			
Rb-4 ^a	11	5	30	None	1.3	1.0	1.2
Rb-5 ^a	11	30	30	3 EtOH+	1.2	1.0	1.2
				3 Acetone			
Rb-6 ^a	11	30	80	3 EtOH+	0.99	1.0	0.97
				3 Acetone			
Cs-1A	5	30	30	3 H ₂ O	0.23	1.0	0.32
Cs-1B	5	30	30	3 Acetone	1.1	1.0	0.35
Cs-2	5	30	80	3 EtOH+	0.64	1.0	0.16
				3 Acetone			
Cs-3	8.5	5	30	None	5.1	1.0	0.92
Cs-4	8.5	5	30	3 H ₂ O	0.50	1.0	0.54
Cs-5 ^a	11	30	30	3 EtOH+	0.77	1.0	0.90
				3 Acetone			
Cs-6 ^a	11	30	80	3 EtOH+	0.83	1.0	0.89
				3 Acetone			

^aEqual volume of ethanol added and digested 3 to 4 minutes.

precipitated between pH 5 and 8.5, (2) probable PuOCO₃ is formed with mixtures of Pu(OH)₄ (or hydrated PuO₂) and PuOCO₃ becoming apparent at higher pH, and (3) ethanol salting-out of impure PuOCO₃ from the soluble complex occurs at high pH.

Characterization of the Compounds

Titration curves were constructed in a manner analogous to the plutonyl(VI) study, but all curves were without inflections and resembled a normal acid-base titration curve.

Electronic spectra of the pH 11 supernates were scanned between 400 and 1000 nm. The following absorptions were observed: high absorption <500, 545, 575, 635-40, 690, 735, 760, and 810-15 nm.

Representative infrared spectra of all the compounds in Table 5 are shown in Figure 4. The first group of spectra (Cs-2 and 1) is probably Pu(OH)₄ (or hydrated PuO₂). Cs-2 apparently contains less carbonate impurity (~1500 cm⁻¹) and the bands at about 1100 cm⁻¹ are due probably to the hydroxide. The bands at 1380 and 820 cm⁻¹ are nitrate impurity. The spectrum of run Cs-4 is representative of runs Na-1, Rb-1, 2, 3, and Cs-3. The last spectrum is representative of all the compounds salted out with ethanol (runs Na-2, K-1, Rb-4, 5, 6, and Cs-5, 6). The two spectra (Cs-4, Cs-5) are indicative of unidentate carbonate complexes. They are also very similar except for Cs-5 which shows spreading of ν_3 and ν_1 and increased intensity of the band at 500 cm⁻¹. The infrared spectra support the hypothesis that Pu(OH)₄ (or hydrated PuO₂) is formed at low pH and results in PuOCO₃ at high pH.

Figure 5 contains thermogravimetric curves of runs Cs-1B, Rb-5, and Cs-5. The Cs-1B curve is probably impure plutonium hydroxide, and it is somewhat different than the

Figure 4. Infrared Spectra of the Plutonium(IV) Compounds.

Figure 5. Thermogravimetric Curves of Plutonium(IV) Compounds.

remaining two, representative of impure PuOCO_3 . The rubidium curve is not decomposed completely to PuO_2 at 1000°C , as is Cs-5. The calculated PuO_2 is in agreement with residue weight in the last curve and calculates as $0.8 \text{ CsNO}_3 \cdot \text{PuOCO}_3$.

RESULTS AND DISCUSSION PLUTONIUM(III) SYSTEM

Preparation of Compounds

The solids were checked for plutonium(IV) content and discarded if over approximately 5%. The compounds reported herein averaged about 2% plutonium(IV). Generally, the increased plutonium(IV) content (>5%) was found in compounds prepared at 80°C , at greater than 30-minute digestion, and by fast addition of carbonate solution. Recommended preparation conditions

yielding low plutonium(IV) content (<1%) are: precipitation at between 26 and 30°C , about 3-ml-per-minute carbonate solution addition to a $\text{Pu}:\text{M}_2\text{CO}_3$ ratio of 1.0:30, digestion for less than 30 minutes, and 50% methanol washing.

After washing and centrifuging the precipitates, a thin, green layer of PuO_2 was present on top of the blue precipitates. This was scraped off prior to vacuum drying.

At $\text{Pu}:\text{M}_2\text{CO}_3$ ratios of 1.0:30 to 36, the cesium and rubidium precipitates re-dissolved. The potassium and sodium precipitates did not re-dissolve at maximum $\text{Pu}:\text{M}_2\text{CO}_3$ ratios of 1.0:42 and 1.0:75, respectively. The percent plutonium found in the supernates agrees with the above observations. At $\text{Pu}:\text{M}_2\text{CO}_3$ ratios of 12, 24, and 30, the cesium and rubidium supernates contained approximately <1, 30, and 70% plutonium, respectively. In the potassium and sodium precipitations, the percent plutonium in the supernates was <1% at a $\text{Pu}:\text{M}_2\text{CO}_3$ ratio of 1.0:12. The plutonium

content did not significantly change over the values of 15% for potassium supernates and 4% for sodium supernates between the Pu:M₂CO₃ ratios of 1.0:24 1.0:30 and 1.0:24 to 1.0:60, respectively. Higher concentrations of potassium and sodium carbonate solutions have been reported to dissolve plutonium(III) compounds^(1, 6) and should be tried in future work.

The re-dissolved precipitates of cesium and rubidium were re-precipitated by ethanol addition, but analysis was not performed on the products which were heavily contaminated with plutonium(IV).

Composition of Compounds

Table 6 contains the analytical results using various preparation conditions. Molar ratios were again used to avoid the effect of water of hydration. The digestion time appeared to have no significant effect on precipitate composition. Three rubidium precipitations were treated similarly, except for carbonate concentrations of 1.25, 2.5, and 5M. These were found to be identical in composition.

The compounds precipitated were all blue with varying, but minor, amounts of white impurity present. The mixture of blue and white was more evident using potassium and sodium carbonates; however, the runs K-5, K-7, Rb-2, and Cs-5 appeared to be pure, dark blue compounds.

The lithium precipitations were performed by the addition of solid Li₂CO₃ which gave precipitates that were highly contaminated with plutonium(IV) and Li₂CO₃. The results of two plutonium(IV)-free precipitations are shown in Table 6 and include mostly Li₂CO₃ with a minor constituent of speculative composition.

In the sodium precipitations, runs Na-10 and 11A have significant Na₂CO₃ contamination (identified by IR). When absolute alcohol or no washing were used, high M:Pu:CO₃ ratios were evident. From studying the results of the sodium runs, no obvious correlation between compound composition and Pu:M₂CO₃ ratio or stirring time can be made. The averaging of the M:Pu:CO₃ ratios of all the runs except Na-1, 10, and 11A, gives 1.5:1.0:1.6. The average molar ratio indicates several possibilities in compound composition: Pu(OH)₃·1.5NaHCO₃, Pu₂(CO₃)₃·3NaCl, and others.

Run K-1 could be a mixture of Pu(OH)₃ and K₂CO₃, and the high M:Pu:CO₃ ratios of runs K-3A and 7 are the result of washing with poor solvents. Examining the

composition of the remaining runs indicates a reasonably steady Pu:CO₃ ratio of about 1.5 and a fluctuating M:Pu ratio. One explanation again could be a mixture of Pu₂(CO₃)₃ and nKCl.

As before, no significant effect between added Pu:M₂CO₃ ratio and compound composition in the remaining precipitations in Table 6 is evident. Not considering the poorly washed rubidium and cesium precipitates, the evidence for a composition of MPu(CO₃)₂ is substantial. However, runs Rb-5, Cs-1, and Cs-3 could be analogous in composition to the sodium and potassium precipitations.

By examining the split runs (Na-6, Na-11, K-3, Rb-6, and Cs-4) for hydrolysis effects, it appears that there is less change in the heavier alkali metal compound composition. The increased solubility of the heavier alkali metal impurities is probably the reason for the above, although plutonium(IV) contamination was more predominant in water-washed sodium and potassium precipitates.

Several compounds were randomly stored for two months in closed vials and re-analyzed to determine their stability. No significant difference in compound composition was found.

Electronic Spectra

Scans of the solid form of the compounds discussed showed the following absorption bands: 565, 605, 665, 780-785, 895-900, 1015, and 1090 to 1100 nm. The spectra of the supernates and re-dissolved precipitates also contained these bands along with the plutonium(IV) peak at 480 nm which increased with time. The above spectrum resembles a typical spectrum of a hydrochloric acid solution of plutonium(III). However, compounds in carbonate solutions yield a similar spectrum, and complex formation is reported not to produce appreciable changes in the absorption spectrum of plutonium(III).^(6, 28)

Infrared Spectra

The spectra of the lithium precipitations were typical of Li₂CO₃, although the bands of Figure 6 were vaguely present in Li-2. The infrared spectra of all the remaining precipitates in Table 6 were identical to Figure 6 except for the following differences: (1) notable M₂CO₃ bands present in poorly washed precipitates and all rubidium runs except Rb-5, (2) run K-1 was mostly PuO₂, and (3) the bands of possible PuO₂ at about 500 to 400 cm⁻¹ varied in intensity.

Table 6. Effect of Precipitation Conditions on Plutonium(III) Carbonate Composition.

Run Numbers	Precipitation Conditions			Washing	Analysis-Molar Ratio		
	Added-Molar Ratio		Time (min)				
	Pu	M ₂ CO ₃			M	Pu	CO ₃
Li-1	1 0	10	15	4 50% MeOH	7 7	1 0	4 6
Li-2	1 0	18	30	3 50% MeOH	19	1 0	10
Na-1	1 0	12	5	None	3 4	1 0	2 7
Na-2	1 0	12	5	1 H ₂ O	1 9	1 0	1 8
Na-3	1 0	12	5	1 H ₂ O	1 8	1 0	1 7
Na-4	1 0	12	5	2 H ₂ O	2 0	1 0	1 6
Na-5	1 0	12	5	2 H ₂ O	1 9	1 0	1 6
Na-6A	1 0	15	15	3 MeOH	1 4	1 0	1 8
Na-6B	1 0	15	15	3 50% MeOH	1 3	1 0	1 3
Na-7A	1 0	15	15	2 50% EtOH	1 2	1 0	1 3
Na-7B	1 0	15	15	2 50% MeOH	1 2	1 0	1 3
Na-8	1 0	24	15	3 50% MeOH	1 3	1 0	1 6
Na-9	1 0	30	30	4 50% MeOH	1 2	1 0	2 0
Na-10	1 0	50	15	None	3 4	1 0	2 4
Na-11A	1 0	60	15	3 MeOH	4 4	1 0	3 2
Na-11B	1 0	60	15	3 50% MeOH	1 4	1 0	1 5
Na-12	1 0	75	30	3 50% MeOH	1 4	1 0	1 3
K-1	1 0	12	15	4 50% MeOH	1 1	1 0	0 50
K-2	1 0	24	15	3 50% MeOH	1 0	1 0	1 6
K-3A	1 0	30	15	3 MeOH	3 1	1 0	2 8
K-3B	1 0	30	15	3 50% MeOH	1 9	1 0	1 5
K-4	1 0	30	15	1 50% MeOH + 1 50% EtOH	1 1	1 0	1 3
K-5	1 0	30	15	3 50% MeOH	1 1	1 0	1 7
K-6	1 0	36	15	1 50% MeOH + 1 50% EtOH	3 0	1 0	1 2
K-7	1 0	36	15	3 EtOH	2 8	1 0	2 7
K-8	1 0	42	15	3 50% MeOH	2 2	1 0	1 2
Rb-1	1 0	18	15	3 50% MeOH	1 3	1 0	2 0
Rb-2 ^a	1 0	22	15	2 50% EtOH	1 0	1 0	2 1
Rb-3	1 0	22	15	3 50% MeOH	1 2	1 0	2 0
Rb-4 ^b	1 0	24	15	2 50% EtOH	1 0	1 0	1 9
Rb-5	1 0	24	15	3 50% MeOH	1 1	1 0	1 8
Rb-6A	1 0	30	15	3 MeOH	1 4	1 0	2 3
Rb-6B	1 0	30	15	3 50% MeOH	1 0	1 0	2 0
Rb-7	1 0	30	15	3 MeOH	1 4	1 0	2 3
Cs-1	1 0	12	5	None	3 5	1 0	1 8
Cs-2	1 0	12	5	1 H ₂ O	3 2	1 0	2 1
Cs-3	1 0	24	15	3 50% MeOH	0 81	1 0	1 6
Cs-4A	1 0	30	15	3 MeOH	1 5	1 0	2 1
Cs-4B	1 0	30	15	3 50% MeOH	1 1	1 0	1 9
Cs-5	1 0	30	15	3 50% MeOH	1 3	1 0	2 2
Cs-6	1 0	30	15	3 MeOH	1 8	1 0	2 2

^aPrecipitated with 1 25M Rb₂CO₃^bPrecipitated with 5 0M Rb₂CO₃

Figure 6. Infrared Spectrum of Plutonium(III) Carbonate.

Cesium carbonate, as well as MCl contamination, could have been obscured in the infrared spectra, and no MHCO_3 bands were observed. Therefore, impure plutonium(III) carbonate could be the dominant product of the above precipitations. Also, the presence of PuO_2 bands at about $500\text{--}400\text{ cm}^{-1}$ causes some concern. However, the compounds were $>95\%$ plutonium(III) after preparation, and the stored samples did not appreciably change color after two months. Therefore, plutonium(IV) contamination was considered minor.

Comparison of reported frequencies of unidentate cobalt(III) carbonate complexes⁽²²⁾ with Figure 6 show excellent agreement. The species in agreement are noted in Figure 6, and the plutonium(III) carbonate is considered to contain unidentate coordination.

Titration Curves

Titration curves for the addition of sodium, cesium, and ammonium carbonates to plutonium(III) solutions were constructed and are shown in Figure 7. There was a single plateau in all curves except when no plutonium(III) was present, then the curve resembled a normal acid-base titration curve. The plateaus were between a pH of 5.2 and 5.7 and the consumption of carbonate solution at the plateaus corresponds to a $\text{Pu}:\text{CO}_3$ molar ratio of 2.1:3.3. This ratio rules out a compound of the type $\text{MPu}(\text{CO}_3)_2$ because the plutonium-to-carbonate ratio was not sufficient. This information supports the formula $\text{Pu}_2(\text{CO}_3)_3$ for all alkali metal carbonate solutions used.

X-Ray Diffraction

Most of the plutonium(III) carbonates were crystalline and gave good powder patterns. Cs-6 was one exception, as it was amorphous with a trace of CsNO_3 . Cs-1 had CsCl present, and major Li_2CO_3 was identified in Li-1 and 2. Runs Rb-2, 3, and 4 had identical patterns. This work remains unfinished, however.

Thermogravimetric Analysis

Figure 8 contains the TGA curves of the plutonium(III) compounds precipitated with each alkali metal carbonate, except lithium. Curves of runs K-3B, Rb-1 and 6B, and Cs-5 and 6 were identical to the respective alkali metal curves in Figure 8, even though the composition varied. The intermediate products at 200°C and 600°C were scanned by IR. At 200°C there was slight shifting of most of the bands and increased intensity of the $400\text{--}500\text{ cm}^{-1}$ band. The product at 600°C was a mixture of M_2CO_3 and PuO_2 .

None of the curves in Figure 8 show complete decomposition of the compounds to PuO_2 at about 950°C , and since the impurity content was erratic, no rigorous correlation of weight losses was found. However, the curves are similar, and coupled with the above discussion, these data conform to the preparation of impure $\text{Pu}_2(\text{CO}_3)_3$.

Figure 7. Titration Curves (pH) of 50 ml Plutonium(III) Solutions (0.042M).

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Figure 8. Thermogravimetric Curves of Plutonium(III) Compounds.

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