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AQUEOUS COORDINATION COMPLEXES OF PLUTONIUM

J. M. CLEVELAND

The Dow Chemical Company Rocky, Flats Division, Golden, Colorado (U.S.A.)

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CONTENTS

A. INTRODUCTION

Five different oxidation states are known for plutonium in solution, and four of these (3^+, 4^+, 5^+, 6^+) form strong complexes with a number of ligands. (The recently discovered[1] unstable heptavalent state has not as yet been investigated sufficiently to define the extent of its complex-forming tendencies). Because of differences in the charge and size of the ions, they differ greatly in their complexing abilities:

$$Pu^{4+} > Pu^{3+} \cong PuO_2{}^{2+} > PuO_2{}^{+}$$

(As will be seen in this review, the relative complexing ability of Pu^{3+} and $PuO_2{}^{2+}$ varies with the ligand). The fact that plutonium(V) and (VI) always exist in aqueous solution as linear dioxygenated plutonyl ions attests to the very strong complexing tendencies of the 5^+ and 6^+ ions; as the 1^+ and 2^+ plutonyl ions however, plutonium(V) and (VI) have lower charge and larger size, resulting in their weaker complexing abilities compared to plutonium(IV) and to a lesser extent, plutonium(III).

The halide complex compounds of plutonium and the other actinides have recently been reviewed by Bagnall[2], and a comprehensive review of the entire field of plutonium chemistry has been published by Cleveland[3]. This review will be concerned solely with plutonium complexes in aqueous solution, with compounds being discussed only when used to establish the identity of species in solution. Moreover, the organic-soluble complexes formed between plutonium and organo-phosphorus compounds and organic amines, which are employed in solvent extraction, are outside the scope of this review.

The nomenclature used in this discussion is that employed in Sillen and Martell[4]. Thus, for the reaction of a ligand with a central metal ion,

$$ML_{n-1} + L \rightleftarrows ML_n$$

the stepwise stability constant is expressed as

$$K_n = \frac{[ML_n]}{[ML_{n-1}]\,[L]}$$

while the overall stability constant for the reaction

$$M + nL \rightleftarrows ML_n$$

is described by the expression

$$\beta_n = \frac{[ML_n]}{[M]\,[L]^n}$$

If the reaction involves a protonated species with the resultant liberation of a proton, the symbols $*K_n$ and $*\beta_n$ are used:

$$ML_{n-1}+HL \leftrightarrows ML_n+H^+ \qquad {}^*K_n = \frac{[ML_n][H^+]}{[ML_{n-1}][HL]}$$

$$M+nHL \rightleftarrows ML_n+nH^+ \qquad {}^*\beta_n = \frac{[ML_n][H^+]^n}{[M][HL]^n}.$$

B. FLUORIDE COMPLEXES

Although fluoride would be expected to form strong complexes with plutonium, the system has received very little investigation. Results have been reported only for Pu^{IV}, and these are of limited reliability. The spectrum of Pu^{IV} in the 450–750 nm range is sensitive to increasing HF concentration, the primary effect being a steady decrease in the absorption peaks[5] at 470, 545, and 665 nm. From these data the stability constant of the monofluoro complex PuF^{3+} was calculated to be 5.91×10^6 at $I = 1M$. This value has subsequently been corrected[6] to 8.7×10^7 at $I = 0$. There was evidence that PuF_2^{2+} is formed when the number of equivalents of HF exceeds six times the equivalents of Pu^{IV}, but the data did not permit a calculation of its stability[5]. On the basis of electromigration experiments, the existence of the higher, anionic complexes PuF_5^- and PuF_6^{2-} to any appreciable extent is unlikely, even at high fluoride ion concentrations.

C. CHLORIDE COMPLEXES

(i) *Plutonium(III)*

Plutonium(III) forms only two complexes in aqueous solution, $PuCl^{2+}$ and $PuCl_2^+$, the former predominating at chloride concentrations of about 2M and the latter becoming important only at ligand concentrations of 8M or higher[7]. The failure of the visible absorption spectrum to be influenced by HCl concentrations below 4.4M or LiCl concentrations below 7M suggests that in these concentration ranges the predominant species, $PuCl^{2+}$, exists as a solvent-separated ion-pair in which the ligand is too far removed from the central atom for ligand-field splitting to occur[8]. At higher chloride concentrations some degree of covalent bonding takes place in $PuCl^{2+}$, since changes in the spectrum are observed. Although these changes are not great in the visible region, there are major alterations in the ultraviolet spectrum (Fig. 1).

These new bands for the chloro complexes of plutonium(III) were attributed to allowed $5f^n \rightarrow 5f^{n-1}6d$ transitions[9], in contrast to the forbidden $5f^n \rightarrow 5f^n$ transitions of uncomplexed plutonium(III) at these wavelengths that result in much lower molar absorptivities. The $5f^n \rightarrow 5f^{n-1}6d$ transition in the dichloro complex is probably caused by degeneracy removal because of the lower symmetry

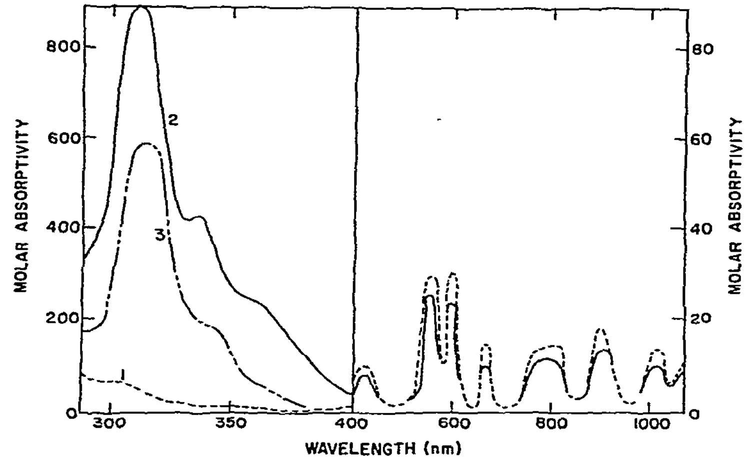


Fig. 1. Absorption spectra of plutonium(III) in (1) dilute HCl - - - - -, (2) 10.2 M LiCl—— and (3) 10.2 M LiBr — — — —; from Ref. 9, p. 2728.

resulting from the replacement of water molecules with partially covalently-bound chloride ligands. The possibility that the spectral changes are due to solvation differences is eliminated by the observation that 10 M perchloric acid, which should be comparable to concentrated LiCl as a dehydrating agent, causes very little change in the spectrum of trivalent neptunium[10], whose changes in LiCl parallel those[9] of plutonium(III). Based on these spectrophotometric data, an estimate of the effective stability constant, β_2^*, of the dichloro complex was made, assuming that at high chloride concentrations $PuCl_2^+$ and uncomplexed (aquo) Pu^{3+} were the only species present[9]. Log β_2^* was determined to be -5.00 ± 0.06 at 25°, and the relative constancy of the value at various LiCl concentrations indicated the validity of the underlying assumptions. The stepwise stability constants, K_1^* ($= \beta_1^*$) and K_2^* ($= \beta_2^*/\beta_1^*$), are nearly equal, so that only a rough estimate of K_1^*, the effective stability constant of $PuCl^{2+}$, can be made. Log K_1^* was estimated to be -2.4 ± 0.1 at 25°.

These values are in sharp disagreement with those of Ward and Welch[11] who found by an ion-exchange technique a value of 0.9 for the stability constant of $PuCl^{2+}$ in 1M HCl and 14.7 corrected to $I = 0$. Part of this discrepancy may be explained on the basis of differences in experimental methods[9], but the latter results have also been cast in doubt by the high ion-exchange distribution coefficients reported for Pu^{III}, suggesting the possible presence of Pu^{IV} in the solution[12].

Other ion-exchange studies have indicated that the actinide elements have a greater tendency toward chloride complex formation than the lanthanides, and this behavior has been explained on the basis of bonds involving hybridized *5f* orbitals[13]. The *5f*, *6d*, and *7s* levels of the early members of the actinide series have comparable binding energies, and this fact, along with the greater spatial percent acetonitrile by reaction of $PuCl_3$ or PuOCl with a moderate excess of HCl (a large excess of HCl reduces the chloride ion activity through formation of such species as HCl_2^-)[14]. Solutions of $PuCl_6^{3-}$ may also be made by dissolution of the triphenylphosphonium salt, itself precipitated by mixing of almost-anhydrous ethanol solutions of $PuCl_3$ and $(C_6H_5)_3PHCl$ that are essentially saturated with HCl. An inert atmosphere is necessary to prevent oxidation of the species to $PuCl_6^{2-}$.

Absorption spectra of $PuCl_6^{3-}$ and, for comparison, aquo Pu^{III} are shown in Fig. 2. In the visible and near-infrared region the $PuCl_6^{3-}$ spectrum differs greatly from that of the aquo ion in the energy, shape, and number of peaks and their molar absorptivities. The approximately 18-fold decrease in molar absorptivities (which in this region are considered to be due to $f \rightarrow f$ transitions) of $PuCl_6^{3-}$ compared to Pu^{3+} and to other Pu^{III} complexes indicates that the hexachloro complex possesses octahedral or near-octahedral symmetry with a center of inversion; other Pu^{III} complexes and the aquo ion lack such symmetry, indicating that they are not octahedral. It is therefore concluded that a coordination number of six is relatively uncommon among the trivalent actinides.

(ii) Plutonium(IV)

Chloride ion forms a series of complexes with Pu^{IV} up to $PuCl_6^{2-}$, but stability constants have been determined only for the lower complexes. By means

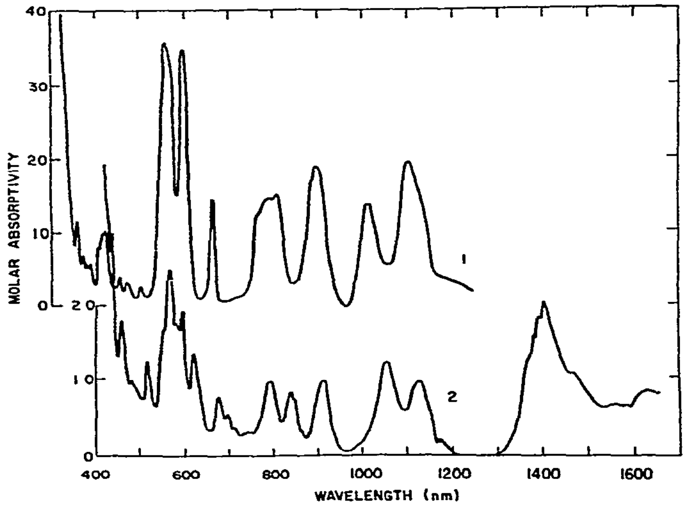


Fig. 2. Absorption spectra of plutonium(III). (1) Pu^{III} in 1M $HClO_4$; (2) the $PuCl_6^{3-}$ ion in 85% succinonitrile–15% acetonitrile. This solution was prepared by dissolving $PuCl_3$ in the solvent saturated with $(C_2H_5)_4NCl$ and containing a small amount of anhydrous HCl. The $PuCl_6^{3-}$ spectrum was corrected for 2.0% Pu^{IV} (as $PuCl_6^{2-}$) which appears to constitute a slight overcorrection, and because of this the fine structure in the 670–870-nm region may not be exactly correct for $PuCl_6^{3-}$; from Ref. 14, p. 333.

extension of the 5*f* orbitals compared to the 4*f*, favors the formation of hybridized 5*f* orbitals. The results of Ward and Welch[11] were also interpreted to indicate the presence of hybridized *f*-orbitals.

Although $PuCl_2^+$ is apparently the highest complex formed in aqueous media, the hexachloro complex, $PuCl_6^{3-}$, can be prepared in the high dielectric nonaqueous solvents acetonitrile or, preferably, 85 percent succinonitrile–15 of cation exchange, the stepwise stability constants of the mono-, di-, and trichloro complexes were found to be 1.4 ± 0.2, 1.2 ± 0.2, and 0.1 ± 0.1, respectively[15], at 20° in 4M $HClO_4$. Earlier values for the stability constants, calculated from the variation of the Pu^{III}/Pu^{IV} potential with chloride concentration[16,17] were incorrect because of the invalid assumption that there is no complexing of Pu^{III} by chloride. Recalculation of some of these results[16] by Rabideau *et al.*[18] to allow for Pu^{III} complexing yielded values of 1.38 for K_1 and 0.67 for β_2. Least-squares analysis of data obtained by a solvent extraction method utilizing thenoyltrifluoroacetone (TTA) indicated K_1 and β_2 to be 2.00 ± 0.06 and 0.16 ± 0.03, respectively[19], at $I = 2M$ and 25.0 ± 0.1°. The agreement among the various values of K_1 is fair, but there is wide discrepancy in values for β_2. This difference was ascribed to differences in experimental methods and in treatment of the data, and reflects the high uncertainties involved in the calculation of successive stability constants, regardless of the method employed.

Although complexing of Pu^{IV} becomes significant at low chloride concentrations, complete coordination to form octahedral $PuCl_6^{2-}$ is not possible in an aqueous medium, even[20] in concentrated HCl. Rough estimates based on spectral data suggest that the abundance of the hexachloro complex decreases from about 75 percent in 12M HCl to perhaps 8 percent in 9M HCl.

The hexachloro complex can be obtained quantitatively in nonaqueous solvents, however, by dissolution of a salt[21] such as $[(C_2H_5)_4N]_2PuCl_6$. Analysis of the spectra of $PuCl_6^{2-}$ in acetonitrile solution (Figs. 3 and 4) indicate the presence of three separate types of transitions (listed in order of increasing band half-width):

(1) Internal 5*f* transitions, in the visible and near infrared, which are weak because the transitions are forbidden. As will be described in the discussion of bromide complexes, these transitions have a large nephelauxetic effect.

(2) $5f^n \rightarrow 5f^{n-1}6d$ transitions, at the lower end of the ultraviolet spectrum, which are sharp and intense ($\varepsilon = 5000$–15000). For $PuCl_6^{2-}$, these transitions occur at a lower wavenumber than for aquo Pu^{IV}.

(3) $\pi^{24}5f^n \rightarrow \pi^{23}5f^{n+1}$ electron transfer bands, which appear at wavelengths above 300 nm as low ($\varepsilon \simeq 2000$) broad peaks. From these bands, which are caused by the transfer of an electron from a chloride ligand to the central metal ion, the optical electronegativity of Pu^{IV} was calculated to be 2.05.

From an evaluation of their own data as well as that cited above[21], Polish workers[22] have concluded that $5f^n \rightarrow 5f^{n-1}6d$ transitions are influenced by the

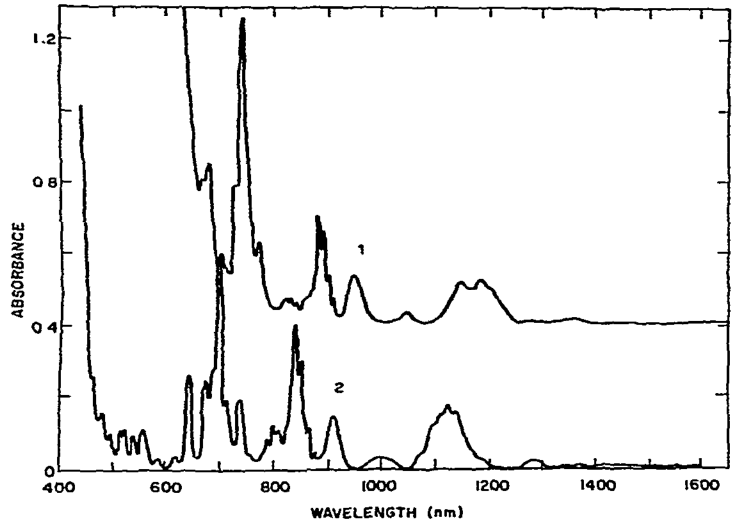


Fig. 3. Visible and near-infrared absorption spectra of acetonitrile solutions of $PuCl_6^{2-}$ and $PuBr_6^{2-}$. (1) 1.27×10^{-2} M $[(C_2H_5)_4N]_2PuBr_6$ (absorbance scale displaced by 0.4). (2) 2.74×10^{-2} M $[(C_2H_5)_4N]_2PuCl_6$. Cell thicknesses 1.00 cm; from Ref. 21, p. 18.

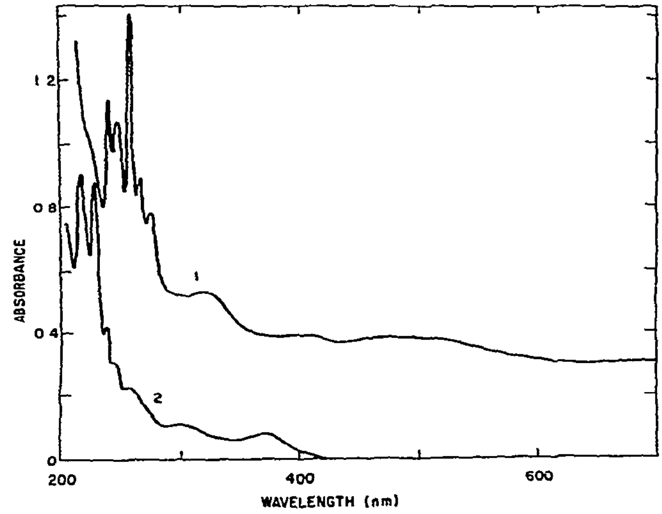


Fig. 4. Ultraviolet absorption spectra of acetonitrile solutions of $PuCl_6^{2-}$ and $PuBr_6^{2-}$. (1) 5.0×10^{-5}M $[(C_2H_5)_4N]_2PuBr_6$ (absorbance scale displaced 0.3). (2) 4.4×10^{-5}M $[(C_2H_5)_4N]_2$-$PuCl_6$. Cell thicknesses 1.00 cm; from Ref. 21, p. 21.

nature of the ligand and the number coordinated to the Pu^{IV} ion, the energy of the transitions decreasing as the number of ligands increases. In the case of charge transfer bands, the energy is primarily a function of the nature of the ligand, with the coordination number having only a negligible effect. The lowest energy for both types of transitions increases with ligand electronegativity.

(iii) Plutonyl(V)

The spectrum of plutonyl(V) in 1–8M NH_4Cl remains constant, from which it was concluded that no complex formation takes place[23]. Later studies, however, have shown this conclusion to be in error; plutonyl(V) is complexed — albeit weakly — by chloride ion. The stability constant of the neutral monochloro complex, PuO_2Cl, has been calculated — apparently from potentiometric data — to be 0.67 (temperature and ionic strength not specified)[24].

(iv) Plutonyl(VI)

Complexing of plutonyl(VI) begins at relatively low chloride ion concentrations. Changes in the visible spectrum indicate the presence of a complex[25] in 0.5M HCl, while electromigration studies indicate the preponderance of anionic complexes at HCl concentrations of 6M and above[26]. From a consideration of both spectrophotometric and paper electrophoresis data, Pozharskii[27] concluded that in 0.21M HCl PuO_2Cl^+ is present and PuO_2Cl_2 begins to form; $PuO_2Cl_3^-$ appears in 0.92M HCl, and $PuO_2Cl_4^{2-}$ commences to form in 2.7M HCl. These conclusions contradict electromigration data, which indicated exclusive presence of cationic plutonium in 2M HCl[26], and are not in accord with the low stability constants of these species. Ergo they should be viewed suspiciously.

Stability constant determinations have been made by several investigators. A spectrophotometric value of 0.73 ± 0.07 has been cited for the stability constant of the monochloro complex[24] at 23° and $I = 1M$. Spectrophotometric data in 0–1.8M HCl (I constant at 2M) resulted in calculated values for K_1 that varied depending on the absorption peak used in the calculation, indicating either that the molar absorptivities change with chloride concentration or else that a second complex is present, or both[28].

On the assumption that the results were due to a second complex — and this was not verified — the values of K_1 and β_2 at 25° were calculated to be approximately 1.25 and 0.35, respectively. An investigation based on the plutonyl(VI) peak at 830 nm gave a value for K_1 of 0.56 at 20.2° and $I = 1M$, and from the variation of K_1 with temperature ΔH for formation of the monochloro complex was calculated[29] to be 3.3 kcal/mole. These results are based on the assumption that only one chloro complex is formed in this concentration range, and must be accepted with caution in light of the findings cited above regarding the existence of more than one complex and/or a variation in molar absorptivities with chloride concentration.

By means of a solvent extraction technique using a solution of thenoyltrifluoroacetone (TTA) in benzene, approximate values of K_1 and β_2 of 1.05 and 0.17, respectively, at $I = 4.1M$ (unspecified temperature) were found[30]. These values are in reasonable agreement with others, but are somewhat clouded due to reported difficulties with photochemical reduction of plutonyl(VI). Even though the studies were conducted in shrouded vessels to lessen this effect, there is still an element of doubt regarding the exact cause of the reduction.

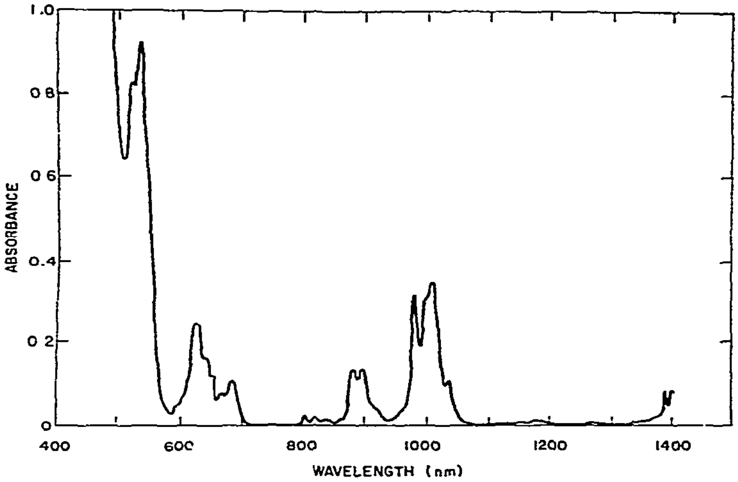


Fig. 5. Absorption spectrum of 0.030 M $[(C_2H_5)_4N]_2PuO_2Cl_4$ in nitromethane; from Ref.31, p.357.

The tetrachloro species has been investigated by Ryan[31], who precipitated its tetraethylammonium and tetrapropylammonium salts from 12M HCl. The spectrum of $PuO_2Cl_4^{2-}$ was determined with solutions of these salts in nitromethane, and is reproduced in Fig. 5. Spectral studies indicated that it is a hydrogen-bonded form of the tetrachloro complex that is adsorbed by anion exchange resins and extracted by tertiary amines.

D. BROMIDE COMPLEXES

(i) Plutonium(III)

Although they are considerably less stable, bromide complexes of Pu^{III} are otherwise comparable to the chloride complexes. The spectral changes illustrated in Fig. 1 are similar to those observed in the chloride system and can similarly be explained as being due to $5f^n \rightarrow 5f^{n-1}6d$ transitions, which are also consistent with the shift in peaks toward lower energies in the bromide compared to the chloride complexes[9]. Greater concentrations of bromide than of chloride are necessary to cause the same change in absorbance, but, as in the chloride system, two complexes are present, $PuBr^{2+}$ and $PuBr_2^+$. Estimates of the effective stability constants of these complexes were made from the spectral data: $PuBr^{2+}$, log K_1^* ($= \beta_1^*$) $= -3.5 \pm 0.1$; $PuBr_2^+$, log $\beta_2^* = -6.48 \pm 0.05$, both at 25°. As in the chloride system, the value of K_1^* is less certain because it is almost equal to $K_2^*(\beta_2^*/\beta_1^*)$.

The hexabromo species $PuBr_6^{3-}$ can be prepared in acetonitrile or 85 percent succinonitrile–15 percent acetonitrile by methods analogous to those used to make $PuCl_6^{3-}$, but it is desirable to use a larger excess of HBr than was required in the analogous chloride system[14]. (There is no significant tendency to form species such as HBr_2^-). Oxidation to $PuBr_6^{2-}$ is avoided by working in an inert atmosphere. Evidence indicates that $PuBr_6^{3-}$, like $PuCl_6^{3-}$, is octahedral or very nearly so.

(ii) Plutonium(IV)

Studies of the TTA extraction of Pu^{IV} from mixed HCl–HBr solutions of varying bromide ion concentration but constant ionic strength (4M) have been used to calculate the stability constants of the mono- and di-bromo complexes[19] of Pu^{IV}. At 25.0 ± 0.1° and $I = 4M$ the values of K_1 and β_2 were found to be 10.0 ± 0.5 and 4.4 ± 0.5, respectively. Contrary to expectations, these values are higher (by a factor of >5 in the case of K_1) than those for the corresponding chloro complexes, and are therefore open to question. The calculations were based on the assumption that no mixed chlorobromo complexes were formed.

In aqueous solution the highest complex, $PuBr_6^{2-}$, cannot be prepared quantitatively, even in concentrated HBr, so investigations of this species have been made in nonaqueous solvents[21]. Dissolution of $[(C_2H_5)_4N]_2PuBr_6$ in acetonitrile produces the undissociated hexabromo complex, and the spectrum of the solution is shown in Figs. 3 and 4. As was described above for the hexachloro complex, the spectrum arises from three types of transitions, *i.e.*, internal $5f$ transitions, $5f \rightarrow 6d$ transitions, and electron transfer. The visible and near-infrared spectrum, due to internal $5f$ transitions, is quite similar to that of $PuCl_6^{2-}$, with the wavenumbers of the $PuBr_6^{2-}$ bands being some 3–5 percent smaller than those of the hexachloro complex. This shift was attributed primarily to a larger nephelauxetic effect in the hexabromide.

E. NITRATE COMPLEXES

(i) Plutonium(III)

By using hydrazine as a reductant, it is possible to prepare Pu^{III} in nitrate media, and spectral studies have been made in such solutions. In 8M $LiNO_3$ the Pu^{III} peaks at 560 and 600 nm undergo greater change than in LiCl solution, but the characteristic Pu^{III} peak at 312 nm is obscured by absorption due to the nitrate ion[9].

Values for the stability constants of the mono-, di- and tri-nitrato complexes of Pu^{III} have been determined from a study of the variation of the extraction coefficient of Pu^{III} from nitrate solutions (containing hydrazine) of various concentrations into tributylphosphate (TBP)–benzene solution[32] at 20 ± 1°. The values obtained ($K_1 = 5.9 \pm 0.5$; $K_2 = 14.3 \pm 0.8$; $K_3 = 14.4 \pm 0.8$) seem high — comparable in fact to the stability constants of the more stable nitrato complexes of plutonium(IV) (see below) — and should therefore be accepted with reservation.

(ii) Plutonium(IV)

Investigation of the Pu^{IV}–nitrate system has been motivated by the widespread application of nitrate complexes in solvent extraction and ion exchange. As a result, this system has been investigated more thoroughly than any other group of plutonium complexes.

Although nitrate forms a series of complexes ranging from $Pu(NO_3)^{3+}$ to $Pu(NO_3)_6{}^{2-}$, with higher nitrate concentrations favoring the latter, it is not known whether all of the intermediate complexes exist in appreciable concentration, and efforts to identify the species present at various nitrate ion concentrations have produced conflicting results. From calculations based on spectrophotometric data Hindman[33] concluded that $Pu(NO_3)^{3+}$ is the principal species in HNO_3 solutions below 4.6M. Brothers and co-workers[34] investigated the system with an amine extraction method, and a mathematical analysis of their data indicated that $Pu(NO_3)_4$ is the predominant complex in the 1–4M HNO_3 concentration range, and at even higher concentrations in nitrate salt solutions. Still another conclusion was reached by Indian workers[35], who employed solvent extraction with tributylphosphate (TBP), diethylene glycol dibutyl ether (butex), and methyl isobutyl ketone (hexone) at various nitrate concentrations and acidities to study the system. They interpreted the data to indicate that an average of 2.6 nitrate ions is associated with each Pu^{IV} ion in the 2–4M nitrate ion concentration range. From plots of the molar absorptivities of various Pu^{IV} absorption peaks as a function of HNO_3 concentration, Lipis and co-workers[36] concluded that the number of nitrate groups coordinated to Pu^{IV} varied with HNO_3 concentration in the manner shown in Table 1.

These assignments are based on the assumption that maxima and minima in molar absorptivities are due solely to changes in the number of nitrate groups coordinated to the Pu^{IV} ion, and their accuracy hinges on the validity of this assumption. A choice between these contradictory results is difficult; indeed, there is no assurance that any are correct. In particular, the predominance of $Pu(NO_3)_4$ at such low HNO_3 concentrations appears unlikely.

The situation regarding the higher complexes is clearer. Ryan[37] has made a thorough spectrophotometric and ion-exchange study of the system at higher

TABLE 1

INFLUENCE OF HNO_3 CONCENTRATION ON Pu^{IV} COMPLEXING[36]

Number of $NO_3{}^-$ groups in predominant complex	*HNO_3 conc. range of stability (M)*
1	<1.5
2	1.5–2.1
3	2.1–3.8
4	3.8–5.6
5	5.6–7.1
6	>7.1

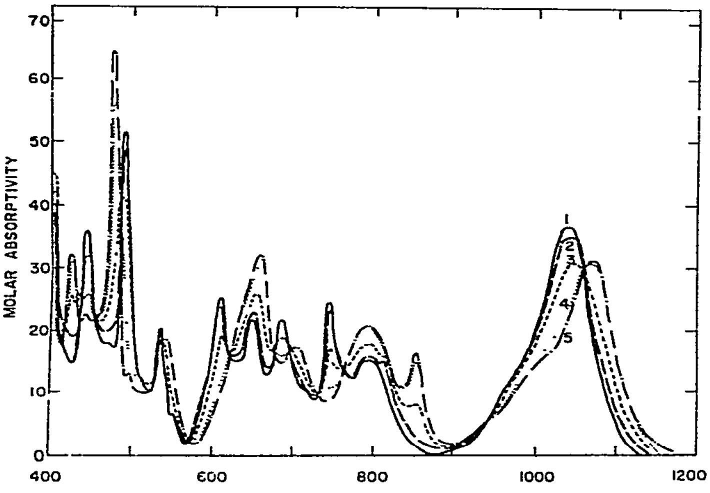


Fig. 6. Absorption spectra of Pu^{IV} in nitric acid: (1) 13.2, 14.0 and 15.5M HNO_3; (2) 10.0M HNO_3; (3) 8.0M HNO_3; (4) 6.0M HNO_3; (5) 5.0M HNO_3; from Ref. 37, p. 1377.

HNO_3 concentrations, and his spectra are shown in Fig. 6. The spectra of Pu^{IV} in $>13M$ HNO_3 were identical to that of Pu^{IV} loaded on Dowex-1 anion-exchange resin from 4 and 8M HNO_3 and to the spectrum of $[(C_2H_5)_4N]_2Pu(NO_3)_6$ in acetonitrile solution [in which $Pu(NO_3)_6^{2-}$ does not dissociate]. It was concluded from these results that the hexanitrato complex is the species adsorbed by anion-exchange resins, and is the predominant species at very high HNO_3 concentrations. A quantitative measure of the abundance of $Pu(NO_3)_6^{2-}$ as a function of HNO_3 concentration was made from absorbance readings at 609 and 744 nm, at which wavelengths the hexanitrato complex has absorption maxima while the lower complexes do not. The results are given in Table 2. The presence of a number of isosbestic points in the spectra indicate that above 5M HNO_3 only two spectrally distinguishable species are present; consequently, either all of the species other than the hexanitrato complex have essentially identical spectra, or else only one species other than $Pu(NO_3)_6^{2-}$ is present in this concentration range.

TABLE 2

ABUNDANCE OF $Pu(NO_3)_6^{2-}$ AT VARIOUS HNO_3 CONCENTRATIONS[37]

$[HNO_3]$ (M)	Abundance of $Pu(NO_3)_6^{2-}$ (%)
5	4
6	10
7	29
8	50
9	75
10	91
11	95
13	100

Formation of the hexanitrato complex is much less complete in $Ca(NO_3)_2$ solutions than in HNO_3. Percentage abundances of $Pu(NO_3)_6{}^{2-}$ at various $Ca(NO_3)_2$ concentrations were as follows: 4.5M $Ca(NO_3)_2$–0.5M $HNO_3(\Sigma[NO_3{}^-] = 9.5M)$, 4 percent; 5.75M $Ca(NO_3)_2$–0.5M $HNO_3(\Sigma[NO_3{}^-] = 12M)$, 26 percent; 9M $Ca(NO_3)_2$–0.25M $HNO_3(\Sigma[NO_3{}^-] = 18.25M)$, 91 percent. The anion-exchange distribution coefficient of Pu^{IV} in $Ca(NO_3)_2$ solutions increases with increasing nitrate concentration, while in HNO_3 solutions the distribution coefficient passes through a maximum at ~ 7.7M HNO_3 and then decreases as the HNO_3 concentration is further increased. This behavior, along with the minimum solubility of $[(C_2H_5)_4N]_2Pu(NO_3)_6$ at 7.7M HNO_3, has been interpreted as due to the formation of $HPu(NO_3)_6{}^-$ and $H_2Pu(NO_3)_6$ at higher HNO_3 concentrations. Ammonium nitrate has also been reported to be less effective in complexing Pu^{IV} than is HNO_3, leading to the suggestion that high acidity, as well as high nitrate ion concentration, is necessary for formation of the higher complexes[36]. It was postulated that hydrogen ions enhance coordination by nitrate by removing H_2O molecules from the coordination sphere to form hydronium ions.

Likewise, the degree of complex formation appears to be temperature-dependent, apparently because of a greater decrease in stability of Pu–H_2O coordinate bonds with increasing temperature compared to Pu–$NO_3{}^-$ bonds[38]. For example, a 2M HNO_3 solution of Pu^{IV} at 60° has the same absorption at 480 nm as a 5M HNO_3 solution at 20°, from which it was concluded that Pu^{IV} is complexed to the same extent in both solutions.

Stability constants for the lower complexes have been determined by a number of investigators. A cation exchange technique gave values of 5.5 ± 0.2, 23.5 ± 1, and 15 ± 10 for K_1, K_2 and K_3, respectively[15], in 4M $HClO_4$ at 20°. As determined by solvent extraction studies[19] with thenoyltrifluoroacetone, $K_1 = 9.0 \pm 0.5$ and $\beta_2 = 28 \pm 2$ at both $I = 4M$ and $I = 6M$ and $25.0 \pm 0.1°$. Zebroski and Neumann[39] also used a thenoyltrifluoroacetone extraction technique to determine K_1 to be 4.7 at $I = 6.0M$; from an estimate of $K_1 = 8.3$ at 45°, the thermodynamic quantities of the reaction were calculated: $\Delta H = 5.3$ kcal/mole; $\Delta S = 21$ e.u. Their estimated values for K_2 (0.96) and K_3 (0.33), both at $I = 6.0M$, are in poor agreement with those of other workers. Hindman's[33] value for K_1 of 2.9 ± 0.6 at $I = 2M$, obtained spectrophotometrically, is in reasonable agreement with other values of K_1 if allowance is made for the apparent increase in stability constant with increasing ionic strength[40]. A determination of K_1 to be 3.48 ± 0.06 at $I = 1M$ and $25.2 \pm 0.1°$ from potentiometric data[41] is of doubtful accuracy because of the assumption that Pu^{III} was not complexed by nitrate ions. Attempts to determine the stability constants by a tributylphosphate extraction technique[35] yielded values that varied greatly depending on the method of calculation and are very dubious because, among other things, of the failure to allow for the activity coefficient of $HNO_3 \cdot TBP$.

In summary, it appears that at room temperature the value of K_1 is in the range 3–10 depending on ionic strength, while K_2 ranges from approximately 20–30. Values for K_3, although of greater uncertainty, appear to be intermediate between K_1 and K_2.

(iii) Plutonyl(VI)

Plutonyl(VI) appears to be less strongly complexed by nitrate ions than by chloride[42]. The plutonyl(VI) spectrum is unchanged up to a HNO_3 concentration of 4M; above this concentration the gradual diminution of the 830 nm peak and the appearance of a new peak at 812 nm have been interpreted to indicate the formation[43] of $PuO_2(NO_3)^+$. Hindman and Ames[42] obtained spectrophotometric evidence for the existence of three species, presumably the mono-, di-, and tri-nitrato complexes. The latter species, $PuO_2(NO_3)_3^-$, exists at high nitrate concentrations; in 14.6M HNO_3 plutonyl(VI) is almost entirely present as an anion, but in 10 M HNO_3 transference measurements indicate it is predominantly cationic[26]. The trinitrato complex is the species extracted by tertiary amines[44]; interestingly enough, however, it is not the principal species adsorbed by anion-exchange resins. From spectral studies Ryan[45] has demonstrated that anion-exchange resins primarily adsorb $PuO_2(NO_3)_4^{2-}$ plus a small amount of $PuO_2(NO_3)_3^-$. This is especially interesting in view of the absence of an appreciable quantity of this complex in aqueous nitrate solutions — even in concentrated HNO_3.

In view of the reluctance of nitrate ions to coordinate plutonyl(VI), the reported stepwise stability constants of the mono- and di-nitrato complexes, 72 and 36, respectively, obtained from hydrolysis studies[46], are too high to merit serious consideration. For instance, the value cited for K_1 is higher by a factor of more than 10 than the stability constant of the corresponding complex of Pu^{IV}, which is known to be more stable. More plausible values have been obtained by a method involving extraction of plutonyl(VI) from aqueous nitrate into a benzene solution of thenoyltrifluoroacetone. Heisig and Hicks[47] found $K_1 = 0.25$ at $25.0 \pm 0.1°$ and $I = 4.6M$, while Indian workers[30] obtained a value for K_1 of 0.93 and a very approximate value of 0.2 for β_2 at $I = 4.1M$ and an unspecified temperature. The former value seems more reliable, since it was calculated on the likely assumption that $PuO_2(NO_3)^+$ is the only complex present up to 4.6M HNO_3, while the latter value was based on the assumption that two complexes were present. Moreover, the latter investigators were plauged by reduction of plutonyl(VI) to Pu^{IV} during extraction; although the reduction was attributed to a photochemical reaction and was largely eliminated by working in shrouded containers, the absence of Pu^{IV} was by no means proven conclusively.

F. SULFATE COMPLEXES

(i) Plutonium(III)

Sulfate ion would be expected to coordinate readily to Pu^{III}, but only recently have quantitative results on this system been reported. Using a cation exchange technique on solutions with $[H^+] = 1M$ and unit ionic strength but varying sulfate concentrations, Nair *et al.*[48] found evidence for two cationic complexes: $Pu(SO_4)^+$ with a stability constant of 18.13 ± 0.44, and $Pu(HSO_4)_2{}^+$ with $K = 9.94 \pm 0.24$, both at 28°. The absence of anionic species was demonstrated by ion exchange and electrical migration studies, and the existence of any other cationic complexes would not be consistent with the data. Higher complexes would be expected in more concentrated sulfate solutions, but so far no quantitative results have been obtained.

(ii) Plutonium(IV)

Plutonium(IV) is strongly complexed by sulfate ion, and complexing commences at low sulfate concentrations; electromigration data suggest that Pu^{IV} exists primarily as an anionic complex[49] in 0.1M H_2SO_4. Using this finding as a starting point, Lipis *et al.*[50] have arrived at the debatable conclusion that as many as eight sulfate groups can be coordinated to a Pu^{IV} ion. In plots of the molar absorptivity of selected Pu^{IV} absorption peaks as a function of H_2SO_4 concentration, it was observed that most of the curves had maxima or minima at the same H_2SO_4 concentrations, and these were assumed to be the points at which there was a change in the degree of complexing. On the basis of the electromigration results cited above, it was assumed that the trisulfato complex is predominant in the 0.1–0.5M H_2SO_4 range, with the formation of successively higher complexes commencing at H_2SO_4 concentrations of 0.5M, 1.1M, 2.4M, 3.7M and 5.8M. Above the latter concentration $Pu(SO_4)_8{}^{12-}$ would predominate. In contrast to the nitrate system, the stability of the complexes was found to decrease with increasing temperature and increasing acidity. These conclusions, however, seem most dubious. Since the maximum number of nitrate or chloride ligands — or indeed, any other ligand except water — coordinated to Pu^{IV} is six, the presence of eight sulfate groups in the coordination sphere is unlikely. Moreover, the existence of a complex with a 12^- charge does not seem consistent with known Pu^{IV} coordination chemistry.

The effect of K_2SO_4 concentration on the degree of complexing has also been investigated[51]. Significant changes in the spectrum of a solution of Pu^{IV} in 1.5M HNO_3 were produced by the addition of even small amounts of K_2SO_4, and it was concluded that at sulfate concentrations up to 0.03M, $Pu(SO_4)^{2+}$ is the principal species. As the K_2SO_4 concentration is further increased, the neutral species $Pu(SO_4)_2$ is formed, reaching a maximum concentration at 0.18–0.20M sulfate, as evidenced by its failure to be adsorbed by either anion- or cation-exchange resins. At still higher sulfate concentrations, the tri- and tetra-sulfato complexes are successively formed, culminating in the precipitation of the salt $K_4Pu(SO_4)_4$ at a K_2SO_4 concentration of 0.65M.

Although the composition of the highest sulfate complex has not been established conclusively, there is no doubt about the existence of the first three complexes, and the stability constants of these have been determined by several workers. From spectrophotometric and electromigration data, $^*K_1$, $^*K_2$, and $^*K_3$ were calculated to be 740, 60, and 5, respectively[52], at $I = 2.3M$, while the respective free energies of formation of the mono-, di-, and tri-sulfato complexes at $I = 2.33M$ were reported[53] as -3.91, -2.93 and -0.95 kcal/mole. The following values were calculated from cation-exchange data[54]: $^*K_1 = 25.2 \pm 3.2$ at $I = 2.33M$; $^*K_1 = 9.45$, $^*\beta_2 = 20.0$ and $^*\beta_3 = 125$ at $I = 0.5M$. The stepwise stability constant, $^*K_2$, of the neutral disulfato complex was determined by a solvent extraction method using trilaurylamine (TLA)[55] to be 3.8 ± 0.7 at $23.0 \pm 0.5°$ and $I = 1M$. Other determinations of the stability constants are flawed by incorrect assumptions or inaccurate data. Thus, values calculated[35] from the tributylphosphate extraction of Pu^{IV} from mixed H_2SO_4–HNO_3 are of dubious value because the stability constants for the nitrate complexes used in the calculation are unreliable. A stability constant for $Pu(SO_4)^{2+}$ of $(4.61 \pm 0.11) \times 10^3$ at $25.0 \pm 0.1°$ and $I = 1M$ was calculated on the invalid assumption that Pu^{III} is not complexed by sulfate[41], and is therefore in error.

G. SULFAMATE COMPLEXES

Sulfamate complexing has been reported only for Pu^{IV}. A spectrophotometric investigation of Pu^{IV} complexing in the sulfamic acid–sulfamate ion system has been described by Cleveland[56]. From changes in the spectrum with varying sulfamate (but approximately constant sulfamic acid) concentration, it was concluded that one or more sulfamate complexes were formed. On the assumption that only the monosulfamate complex was formed, K_1 was calculated to be 1.3 ± 0.4 at $23 \pm 3°$ and $I = 2.1M$. The relatively high uncertainty results from the necessary assumptions made regarding both the ionization constant of sulfamic acid at 2.1M ionic strength, and the molar absorptivity of the monosulfamato complex. Addition of sulfamic acid to solutions containing predominantly the monosulfamate complex caused the spectrum to change to one resembling aquo Pu^{IV}. The possibility that this change resulted from a sulfamate–sulfamic acid interaction to lower the sulfamate ion concentration and thus cause partial dissociation of the monosulfamate complex was investigated by solubility studies, which indicated that the interaction was not sufficient to account for the observed spectral changes. It was therefore concluded that in sulfamate–sulfamic acid solutions mixed complexes are formed containing both sulfamate ions and sulfamic acid molecules as ligands.

H. PHOSPHATE COMPLEXES

(i) Plutonium(IV)

All of the reported studies of Pu^{IV}–phosphate complexes have been based on solubility measurements rather than the more usual techniques, such as spectrophotometry, ion exchange, or solvent extraction. On the basis of the variation in solubility of $Pu(HPO_4)_2 \cdot xH_2O$ in 2M HNO_3 containing various concentrations of H_3PO_4, Denotkina *et al.*[57] concluded that complexes are formed containing up to five HPO_4^{2-} ligands, depending on the H_3PO_4 concentration. At H_3PO_4 concentrations from 0.012 to 0.04M, $Pu(HPO_4)^{2+}$ is the principal species, while in 0.1M H_3PO_4, $Pu(HPO_4)_2$ is predominant. As the H_3PO_4 concentration is further increased, $Pu(HPO_4)_3^{2-}$ forms, and is subsequently converted at even higher H_3PO_4 concentrations to $Pu(HPO_4)_4^{4-}$, which is the principal species in 1.2 and 1.6M H_3PO_4, and finally to $Pu(HPO_4)_5^{6-}$, which predominates[58] in 2.8, 3.9, and 6M H_3PO_4. The stability constants of these complexes were reported as follows[57]: $Pu(HPO_4)^{2+}$, 8.3×10^{12}; $Pu(HPO_4)_2$, 6.7×10^{10}; $Pu(HPO_4)_3^{2-}$, 4.8×10^9; $Pu(HPO_4)_4^{4-}$, 6.3×10^9; $Pu(HPO_4)_5^{6-}$, 6.3×10^8. The close similarity of these instability constants precluded their determination from the data of King[59]. His conclusion that complexes were formed containing up to five phosphate groups is supported by the above results, but he was unable to establish conclusively the number of hydrogen atoms present in the ligands.

(ii) Plutonyl(VI)

Spectrophotometric studies indicated that plutonyl(VI) is complexed even at low H_3PO_4 concentrations, but the observed changes were not sufficient to permit quantitative investigation[60]. Electrophoresis indicated that in 0.02–0.206M H_3PO_4 a cationic complex is formed, which could only be $PuO_2(H_2PO_4)^+$, with a stability constant of $(8.5 \pm 3) \times 10^3$ at 25° (ionic strength not constant). In the 0.206–5.88M H_3PO_4 range the neutral species $PuO_2(H_2PO_4)_2$ was formed, and a solid compound of this composition was isolated by addition to methanol of a 5.88M H_3PO_4 solution containing this species.

J. PEROXIDE COMPLEXES

Peroxide complexes have been reported only in the case of Pu^{IV}. Continued addition of H_2O_2 to a solution of Pu^{IV} in 0.5M HCl results in the formation of first a brown complex, and then a red complex, before insoluble plutonium peroxide is finally precipitated[61]. The spectra of these species, along with that of aquo Pu^{IV}, are shown in Fig. 7. Both complexes have intense absorption peaks; however, their molar absorptivities must be reduced by half in order to be com-

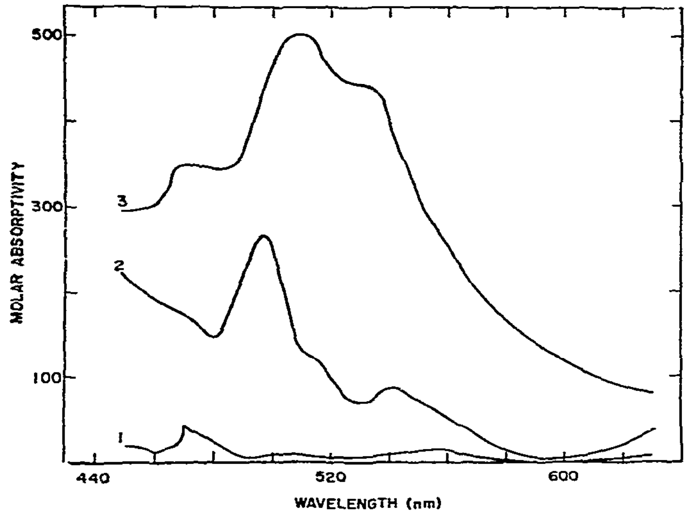
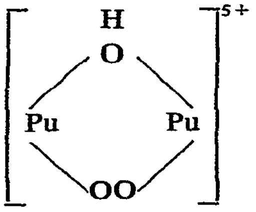


Fig. 7. Absorption spectra of Pu^{IV} peroxy complexes. (1) aquo Pu^{IV}; (2) brown complex; (3) red complex; from Ref. 61, p. 1535.

parable — on the basis of the same number of plutonium atoms — with the aquo Pu^{IV} spectrum since, as will be described below, both peroxy complexes contain two Pu^{IV} ions. From changes in the spectrum caused by varying the H_2O_2 concentration it was concluded that in 0.5M HCl the brown complex contains two Pu^{IV} ions and one peroxide group, and this conclusion was also confirmed by potentiometric studies. The effect of acidity on the spectrum indicated the probable presence of a hydroxide group in the complex. On this basis, the structure was postulated to be either a chain

$$[\mathrm{Pu{-}OO{-}Pu{-}OH}]^{5+}$$

or a ring

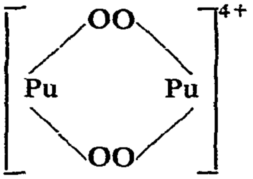


The latter structure would have Pu–OO–Pu bond angles similar to those suggested for HOOH[62]. The equilibrium constant for the formation of the complex in 0.5M HCl,

$$K_1 = \frac{[\mathrm{Pu(OO)\,(OH)Pu^{5+}}]\,[\mathrm{H^+}]^3}{[\mathrm{Pu^{4+}}]^2[\mathrm{H_2O_2}\,]}$$

was determined[61] to be 8.8×10^6 at 25 ± 0.5°. This value is valid only at one acidity, however, because of changes in activity coefficients in other solutions.

Since the red complex occurs at higher H_2O_2 concentrations, it would be expected to contain more peroxide groups, and this was shown to be the case. Analysis of spectrophotometric data at various acidities and concentrations of plutonium and H_2O_2 indicated that the red complex contains two Pu^{IV} ions, two peroxide groups, and probably no hydroxide ions. Again, it was not possible from the data to choose between the two postulated structures,



or $[HO–Pu–OO–Pu–OOH]^{4+}$.

The hydroxide group in the latter would result from the presence of the second peroxide as OOH^-. The equilibrium constant,

$$K_2 = \frac{[Pu(OO)_2Pu^{4+}]\,[H^+]^4}{[Pu^{4+}]^2[H_2O_2]^2}$$

was calculated to be 6.3×10^8 at 25.0 ± 0.5° in 0.5M HCl. Because of changes in activity coefficients the values would be different in other solutions.

K. CARBONATE COMPLEXES

(i) Plutonium(IV)

Plutonium(IV) forms a series of complexes with carbonate reportedly containing as many as eight ligands[63]. Solutions of Pu^{IV} in various concentrations of K_2CO_3 solution were treated with alcohol, causing precipitation of the potassium salt of the respective complex anion, whose composition could then be determined. From these results it was concluded that in 15 percent K_2CO_3 solution the predominant complex is $Pu(CO_3)_4{}^{4-}$, while in 25, 30–40 and 50 percent K_2CO_3 solutions the respective species $Pu(CO_3)_5{}^{6-}$, $Pu(CO_3)_6{}^{8-}$, and $Pu(CO_3)_8{}^{12-}$ predominate. Similar, though less complete, results were obtained in Na_2CO_3 solutions[64].

Conductivity studies indicated that Pu^{IV} has a maximum of eight carbonate ions in the inner sphere[63], and it is likely that carbonate is a bidentate ligand in the higher complexes. The presence of eight carbonate groups in the coordination sphere is doubtful. Lower complexes are also formed, and in these it has been assumed that the carbonate ion can be either monodentate or bidentate[65]. Of the series, the monocarbonato complex is the only one for which the stability constant has been determined; from data on the solubility of $Pu(OH)_4$

as a function of K_2CO_3 concentration, K_1 was calculated to be 9.1×10^{46} at 20° and $I = 10M$. This value appears too high, and should be contemplated with skepticism.

(ii) Plutonyl(VI)

The existence of carbonate complexes of plutonyl(VI) has long been known from spectrophotometric evidence and from the solubility of $PuO_2(OH)_2$ in carbonate solutions[66], but quantitative data on this system are meager. From the variation in solubility of "ammonium diplutonate" [probably $PuO_2(OH)_2$], the formation of three complexes — $PuO_2(CO_3)(OH)_2{}^{2-}$, $PuO_2(CO_3)(OH)^-$, and $PuO_2(CO_3)_2{}^{2-}$ — has been postulated, and their respective overall stability constants were calculated to be 2.3×10^{22}, 4.5×10^{22}, and 6.7×10^{13} at $I = 1M$ and 20 ± 1 °; and 1.0×10^{23}, 7.1×10^{23}, and 1.1×10^{15}, respectively, at $I = 0$ and the same temperature[67]. These stability constants refer to formation of the complex from carbonate, hydroxide, and plutonyl(VI) groups, and not to the simple reaction of partially hydrolyzed plutonyl(VI) with carbonate ligands. Data on the solubility of PuO_2CO_3 in $LiHCO_3$ have been interpreted to indicate the formation of $LiPuO_2(CO_3)(HCO_3)$ with an equilibrium constant[68] of 0.13 at $24 \pm 1°$.

The tricarbonato complex has been precipitated as the ammonium salt[69], $(NH_4)_4PuO_2(CO_3)_3$, but its stability constant has not been determined. This compound is green, suggesting that the tricarbonato complex is responsible for the green color observed in dilute solutions[70] of plutonyl(VI) in 45 percent K_2CO_3. Solutions of plutonyl(VI) in up to 5 percent $(NH_4)_2CO_3$ are red, and analysis of the compound precipitated by the addition of alcohol suggests[71] that the color is due to $PuO_2(CO_3)(OH)^-$.

L. ACETATE COMPLEXES

(i) Plutonium(III)

The Pu^{III}–acetate system has been recently investigated by Magon *et al.*[72] with a potentiometric technique employing Ag–AgCl and glass electrodes. To avoid the errors caused by the presence of even small concentrations of Pu^{IV}, the authors determined by spectrophotometry the conditions under which Pu^{III} is stable toward oxidation. From potentiometric measurements of $[H^+]$ during titrations of Pu^{III} with 0.5M sodium acetate the overall stability constants, K_1 and β_2, of $Pu(C_2H_3O_2)^{2+}$ and $Pu(C_2H_3O_2)_2{}^+$ were calculated to be 105 ± 4 and 2200 ± 250, respectively, at $20.0 \pm 0.1°$ and $I = 2M$.

Considering the care with which they were obtained, and the close agreement with the stability constants of analogous complexes of other actinides and lanthanides, the above values appear more reliable than the results of Moskvin and co-workers[73]. By means of a cation-exchange technique, the latter workers calculated by the method of Fronaeus[74] the following stepwise stability constants: $Pu(HC_2H_3O_2)^{3+}$, $K = 3.2 \times 10^3$; $Pu(C_2H_3O_2)^{2+}$, $K_1 = 3.0 \times 10^4$; $Pu(C_2H_3O_2)_2{}^+$, $K_2 = 4.3 \times 10^3$; $Pu(C_2H_3O_2)_3$, $K_3 = 3.1 \times 10^4$; $Pu(C_2H_3O_2)_4{}^-$, $K_4 = 6.5 \times 10^3$. These values differ greatly (by several orders of magnitude for the higher complexes) from the stability constants of the acetate complexes of other trivalent actinides and lanthanides — all of which are in reasonable agreement with one another — and are highly suspect. Yakovlev and Lebedev[75] have criticized the results, pointing out that proper allowance was not made for the hydrolysis of Pu^{III} or for complexing by sulfite ion formed from the sodium formaldehyde sulfoxylate used as a reducing agent, and also questioned the treatment of the data. Furthermore, the possibility that Pu^{IV} was present in the system has been raised[72]. All of these factors would cause the calculated stability constants to be too high, and lead to the conclusion that the results are of very dubious reliability.

Potentiometric data on the effect of acetate ion on the Pu^{III}–Pu^{IV} couple have been interpreted to indicate the presence of a pentaacetato complex, $Pu(C_2H_3O_2)_5{}^{2-}$, with an estimated overall stability constant[76], β_5, of 5×10^{16} at 25° and $I = 0.1M$. Uncertainties precluded determination of the stability constants of the lower complexes.

(ii) Plutonium(IV)

Acetate forms a series of complexes with Pu^{IV}, containing up to five ligands in solutions[76] of pH below 4.8. The overall stability constants for these species have been calculated from both potentiometric and spectrophotometric data, with the results shown in Table 3.

TABLE 3

OVERALL STABILITY CONSTANTS FOR ACETATE COMPLEXES OF Pu^{IV}

Complex	*Overall stability constant, β*	
	Potentiometric (25.0 ± 0.3°, $I = 0.1M$)[76]	*Spectrophotometric (25.0 ± 0.5°, $I = 0.5M$)*[77]
$Pu(C_2H_3O_2)^{3+}$	$(2.05 \pm 0.23) \times 10^5$	$\sim 7.74 \times 10^4$
$Pu(C_2H_3O_2)_2{}^{2+}$	$\sim 1 \times 10^9$	$\sim 6.91 \times 10^9$
$Pu(C_2H_3O_2)_3{}^+$	$\sim 8 \times 10^{13}$	$\sim 4.39 \times 10^{14}$
$Pu(C_2H_3O_2)_4$	$\sim 2 \times 10^{18}$	$\sim 2.29 \times 10^{19}$
$Pu(C_2H_3O_2)_5{}^-$	$(3.98 \pm 1.03) \times 10^{22}$	$(8.06 \pm 5.69) \times 10^{22}$

Agreement is reasonable, considering the differences in ionic strength. The degree of complexing — and hence the visible spectrum—was found to be very sensitive[77] to pH. An absorption peak at 456 nm was attributed to the pentaacetato complex.

(iii) Plutonyl(VI)

Acetate complexes of Pu^{VI} have been studied by determining the solubility of $NaPuO_2(C_2H_3O_2)_3$ in various concentrations of $NaC_2H_3O_2$ solution[78]. It was concluded that three complexes are formed, with the following overall stability constants at $I = 2M$ (temperature not specified): $PuO_2(C_2H_3O_2)^+$, $K_1 = 1.9\times 10^3$; $PuO_2(C_2H_3O_2)_2$, $\beta_2 = 2.0\times 10^6$; $PuO_2(C_2H_3O_2)_3^-$, $\beta_3 = 2.3\times 10^7$. Ryan and Keder[79] have concluded from a spectrophotometric study that a fourth species, the tetraacetato complex, also exists, and it, along with the triacetato complex, is extracted by tertiary amines. The relative amounts of the two species extracted depends on the dielectric constant of the amine diluent; $PuO_2(C_2H_3O_2)_4^{2-}$ is the principal species extracted into solutions of triisooctylamine (TOA) in CCl_4, which has a relatively low dielectric constant (2.24), while TOA in $CHCl_3$, which has a higher dielectric constant (4.81) extracts primarily the triacetato species. This behavior indicates that the ionizing power (*i.e.*, the dielectric constant) of the solvent has a large influence on the equilibrium constant for formation of the tetraacetato species from the triacetato complex.

M. OXALATE COMPLEXES

(i) Plutonium(III)

A variety of complexes is formed between oxalate ion and Pu^{III}, depending

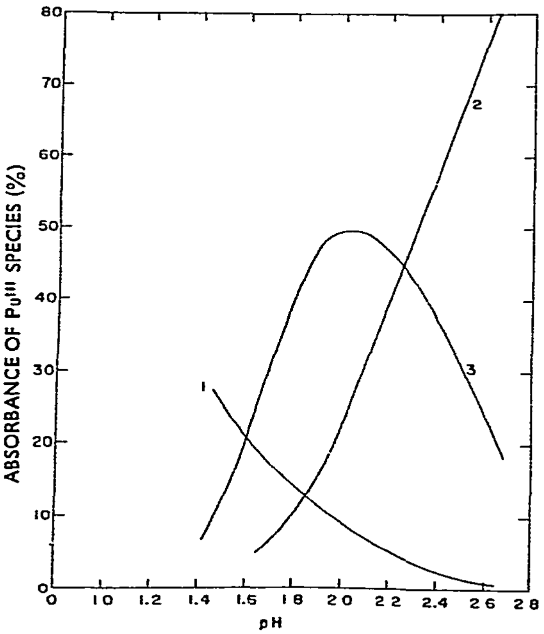


Fig. 8. Effect of solution pH on the concentration of Pu^{III} species. (1) Pu^{3+}; (2) $Pu(C_2O_4)_2^-$; (3) $Pu(HC_2O_4)_4^-$; from Ref. 80, p. 60.

upon pH and ligand concentration. Using a cation-exchange procedure at 20 ± 1° and $I = 1$M, Gel'man *et al.*[80] found that $Pu(HC_2O_4)_4^-$ and $Pu(C_2O_4)_2^-$ were the principal species in 0.005M oxalic acid in the 1.4–3.0-pH range. Their relative concentrations as a function of pH are shown in Fig. 8, and the overall stability constants of $Pu(HC_2O_4)_4^-$ and $Pu(C_2O_4)_2^-$ were calculated to be 9.1×10^{10} and 1.4×10^9, respectively.

The species $Pu(C_2O_4)_4^{5-}$ is present in the 3.5–6.0-pH range at $K_2C_2O_4$ concentrations of 0.1–1.2 M, and its overall stability constant was calculated from solubility studies[81] to be 4.2×10^{11} at 25 ± 0.1° and $I = 3$M. At $K_2C_2O_4$ concentrations below 0.1M in the same pH range the dominant species was found to be $Pu(C_2O_4)_3^{3-}$, with an overall stability constant of 4.5×10^{10}.

In solutions containing 0.01–2.4M $K_2C_2O_4$ at pH 8, solubility studies[82] indicated the presence of $Pu(C_2O_4)_2^-$, $Pu(C_2O_4)_3^{3-}$, and $Pu(C_2O_4)_4^{5-}$ at 20°. At oxalate concentrations below 0.5M, the dioxalato complex was the principal species. At higher $K_2C_2O_4$ concentrations the predominant species was the tetraoxalato complex, while the trioxalato species was a minor constituent at all the concentrations investigated. Solubility studies in $K_2C_2O_4$ solution at 20° and $(NH_4)_2C_2O_4$ solution at 70° yielded the following stability constants, recorded in each case at 20° and 70°, respectively: $Pu(C_2O_4)_2$, 2.0×10^9, 8.6×10^7; $Pu(C_2O_4)_3^{3-}$, 2.44×10^9, 1.8×10^8; $Pu(C_2O_4)_4^{5-}$, 8.40×10^9, 4.0×10^8. The influence of temperature on the stability constants allowed the heats of formation to be calculated as 1300, 1200 and 1300 cal/mole for the di-, tri-, and tetra-oxalato complexes, respectively. These data at 20° are at considerable variance with the results of Fomin and co-workers[81], primarily because the latter investigators used a solubility product for Pu^{III} oxalate (1.1×10^{-26}) lower by a factor of about 15 than that used by Gel'man *et al.*[82]

(ii) Plutonium(IV)

Data on the solubility of the compound $Pu(C_2O_4)_2 \cdot 6H_2O$ in 0.75M HNO_3 containing various concentrations of oxalic acid has been interpreted to indicate the presence of the complexes $Pu(C_2O_4)^{2+}$, $Pu(C_2O_4)_2$, and $Pu(C_2O_4)_3^{2-}$ in the resulting solutions, and a fourth complex, $Pu(C_2O_4)_4^{4-}$, was detected spectrophotometrically[83,84]. It was reported that each of these species had a characteristic absorption peak at a slightly different wavelength, thus making it possible to identify species from the spectrum. The 477 nm peak characteristic of aquo Pu^{IV} is shifted to 488 nm in solutions in which the $[H_2C_2O_4]/[Pu^{4+}]$ ratio is one, and this peak was assigned to the monooxalato complex. Increasing this ratio to two shifts the peak — presumably due to $Pu(C_2O_4)_2$ — to 490 nm, while at an oxalic acid concentration of 0.4M in 0.75M HNO_3 the peak shift to 492 nm was interpreted to indicate the presence of the trioxalato complex. The presence of $Pu(C_2O_4)_4^{4-}$ was inferred from the appearance of a peak at 494 nm when Pu^{IV} oxalate was dissolved in 0.3M ammonium oxalate. The stability constants at 25° were calculated; in 0.5M HCl, $^*K_1 = 8 \times 10^3$, and in 0.75M HNO_3, $^*K_2 = 965$ and $^*K_3 = 25.1$.

Polarographic investigation of Pu^{IV} solutions containing 1M oxalate ($K_2C_2O_4 + H_2C_2O_4$) indicated the presence of the tetraoxalato complex at pH 3.5–6, and of two complexes[81] at pH 6–8. The overall stability constant was calculated to be 3.3×10^{26} at 25.0 ± 0.1°. The stability constants have also been determined from data on the variation in solubility of Pu^{IV} oxalate in 1M HNO_3 at various (0.001–0.35M) ammonium oxalate concentrations[65]. At $I = 1M$ and a temperature of 20.0 ± 0.2°, the stepwise stability constants for the mono-, di-, tri-, and tetra-oxalato complexes were calculated: $K_1 = 5.6 \times 10^8$, $K_2 = 1.5 \times 10^8$, $K_3 = 3.0 \times 10^6$, and $K_4 = 1.3 \times 10^4$, respectively. When compared on the same basis, these values are in satisfactory agreement with those of Reas[83,84]. Moreover, the overall stability constant of $Pu(C_2O_4)_4^{4-}$, 3.1×10^{27}, agrees reasonably well with the polarographic value cited above. Nevertheless, the accuracy of these values is dependent on the validity of the assumptions made in their calculation, namely that the influence of ionic strength on the second dissociation constant of oxalic acid may be ignored, and that there is negligible nitrate complexing in the system.

(iii) Plutonyl(V)

Ion exchange studies in oxalate solutions at pH 3–5 have been interpreted to indicate the presence of two oxalate complexes, with estimated overall stability constants as follows: $PuO_2(C_2O_4)^-$, $K_1 = 3.3 \times 10^4$, and $PuO_2(C_2O_4)_2^{3-}$, $\beta_2 = 2.4 \times 10^7$ at an unspecified temperature and ionic strength[85]. On the assumption that oxalate complexing would weaken the plutonium–oxygen bonds in the plutonyl(V) ion and hence enhance its rate of disproportionation, Eromolaev *et al.*[86] have investigated oxalate complex formation by determining the effect of oxalate concentration and pH on the disproportionation rate. Their data were interpreted to indicate the existence of three complexes, $PuO_2(HC_2O_4)$, $PuO_2(C_2O_4)^-$, and $PuO_2(C_2O_4)_2^{3-}$, with overall stability constants of 210, 7.5×10^3, and 5×10^6, respectively, at 25° and $I = 0.1M$. The values for the latter two complexes were stated to be in reasonable agreement with the ion exchange results after allowance for the difference in conditions.

(iv) Plutonyl(VI)

Plutonyl(VI) is unstable in oxalate solutions[87], and probably for this reason the system has received little study. The only reported results were calculated from the variation in solubility of $PuO_2C_2O_4$ in dilute HNO_3 containing varying concentrations[88] of $(NH_4)_2C_2O_4$. From these data it was concluded that in solutions containing up to 0.4M $(NH_4)_2C_2O_4$, two complexes, $PuO_2(C_2O_4)$ and $PuO_2(C_2O_4)_2^{2-}$, are formed, with overall stability constants of 4.3×10^6 and 2.9×10^{11}, respectively, at 20° and $I = 1M$.

N. LACTATE COMPLEXES

Only Pu^{IV} complexes with lactate ion have been reported. In solutions containing 10^{-2}–10^{-4}M lactate, Pu^{IV} was reported to form the tetralactato complex, $Pu(C_3H_5O_3)_4$, and it was concluded that this is the predominant complex at ligand concentrations[89,90] greater than 5×10^{-5}M. This complex has an absorption maximum at 485 nm in the visible spectrum; and by means of a spectrophotometric method the overall stability constant, β_4, was determined to be $(1.5 \pm 0.3) \times 10^{16}$ at 25° and $I = 0.5$M, a value that was also supported by potentiometric pH titration data. Efforts to investigate the mono-, di-, and trilactato complexes by reducing the lactate ion concentration were hampered by disproportionation and hydrolysis of the Pu^{IV}, and it was concluded that these lower complexes have only a very limited range of stability.

O. GLYCINE COMPLEXES

The only glycine complexes reported are with plutonyl(V). Coordination of plutonyl(V) by glycine occurs through both the nitrogen and the carboxyl oxygen to form a five-membered chelate ring[91]. A cation-exchange procedure indicated $\log K_1$ to be 3.04 ± 0.04 at 25° and $I = 0.1$M. The stability constant of the diglycinate chelate could not be calculated with acceptable precision.

P. CITRATE COMPLEXES

(i) Plutonium(III)

Cation-exchange studies indicated that at pH <1.5 there is only minor complexing of Pu^{III} by 0.01M citrate, while at pH values above 2.5 Pu^{III} is almost entirely complexed[73]. From the variation in adsorption of Pu^{III} as a function of citrate concentration and pH, it was concluded that three complexes are formed, with the following overall stability constants at 20 ± 1° and $I = 1$M: $Pu(C_6H_5O_7)$, $K_1 = 7.3 \times 10^8$; $Pu(H_2C_6H_5O_7)_2{}^+$, $\beta_2 = 4.0 \times 10^6$; $Pu(H_2C_6H_5O_7)_3$, $\beta_3 = 1.0 \times 10^{10}$. These stability constants differ greatly from those of other actinide and lanthanide citrates, and on the basis of criticisms raised by Yakovlev and Lebedev[75] should be regarded with suspicion.

(ii) Plutonium(IV)

Plutonium(IV) is very strongly coordinated by citrate ion; complexing repeatedly occurs even at citrate concentrations[90,92] as low as 10^{-15}M. Spectrophotometric studies have indicated that at citrate ion concentrations up to 10^{-15}M the principal species is $Pu(C_6H_5O_7)^+$, with an absorption peak at 482 nm, while in solutions containing 10^{-15}–10^{-13} M citrate, the dicitrato complex Pu $(C_6H_5O_7)_2{}^{2-}$ with an absorption maximum at 496 nm, appears to predominate. The presence of these complexes of the trivalent citrateanion — as opposed to a partially protonated anion — was inferred from the observation that the spectra were independent of pH at constant citrate ion concentration. The presence of a higher complex at citrate concentrations above 10^{-13}M is suggested by the extinction at 400 nm.

TABLE 4

STABILITY CONSTANTS OF Pu^{IV} CITRATE COMPLEXES

Method	K_1	β_2
Spectrophotometric[a] [25 ± 1 °; $I = 0.5M$[92]]	$(5.3 \pm 2) \times 10^{14}$	$(1.6 \pm 0.8) \times 10^{30}$
Spectrophotometric[b] [25 ± 1 °; $I = 0.5M$[92]]	2.7×10^{15}	6.9×10^{29}
pH Titration [25 ± 0.5 °; $I = 0.5M$[94]]	$(6.9 \pm 1.4) \times 10^{15}$	$(1.0 \pm 0.15) \times 10^{29}$
Potentiometric [25 ± 0.5 °; $I = 0.5M$[94]]	3.5×10^{15}	$(1.0 \pm 0.2) \times 10^{30}$

[a] Data calculated according to method developed in Ref. 92. [b] Data calculated according to method of Yatsimirskii[93].

The stability constants of the mono- and di-citrato complexes have been determined by spectrophotometric, pH titration, and potentiometric methods, and these values are given in Table 4. Agreement appears satisfactory considering the differences in experimental technique. On the other hand, the reported existence of $Pu(C_6H_5O_7)_4{}^{8-}$, with an overall stability constant of 1.7×10^{27} in citrate solutions[95] above pH 5 seems questionable in view of the high charge and the reported stability constants of the lower complexes.

R. TARTRATE COMPLEXES

(i) Plutonium(III)

Although there is little complexing of Pu^{III} by tartrate at pH < 1.8, it is essentially completely complexed[73] at pH > 3. Cation-exchange studies as a function of pH and tartrate concentration indicate the presence of three complexes: $Pu(HC_4H_4O_6)^{2+}$, $Pu(C_4H_4O_6)^{+}$, and $Pu(C_4H_4O_6)_2{}^{-}$, with overall stability constants at 20 ± 1° and $I = 1M$ of 6.3×10^4, 2.1×10^4 and 3×10^7, respectively. These values are of very dubious reliability; Yakovlev and Lebedev[75] have pointed out their disagreement with the stability constants of tartrate complexes of other actinides and lanthanides and raised serious objections to the experimental methods employed.

(ii) Plutonium(IV)

The existence of the hexatartrato complex, $Pu(C_4H_4O_6)_6{}^{8-}$, in tartrate solutions at pH 5–6 has been inferred from polarographic data, and the overall stability constant was calculated[96] to be 2×10^{31}. It is questionable that a complex with such a high negative charge would be so stable, and the results should therefore be regarded with caution.

S. ETHYLENEDIAMINETETRAACETATE COMPLEXES

(i) Plutonium(III)

Three chelate complexes of Pu^{III} with ethylenediaminetetraacetic acid (EDTA; hereafter designated as H_4Y) have been reported: PuY^-, Pu_2Y^{2+}, and PuHY. The first two were identified by Foreman and Smith[97] on the basis of pH titrations of solutions of various P^{III}/H_2Y^{2-} ratios with KOH solution, which indicated that at Pu^{III}/H_2Y^{2-} ratios of two or less, no $Pu(OH)_3$ precipitate was formed, even at pH 11. At higher Pu^{III}/H_2Y^{2-} ratios precipitation did occur, indicating the absence of trinuclear species.

The stability constant of PuY^- was determined to be 1.32×10^{18} at pH 3.30 and 20 ± 0.2° by cation exchange[97] and 3.9×10^{18} at pH 1.5 (temperature not stated, but presumed to be 20°) by a spectrophotometric technique[98], both values at $I = 0.1M$. Gel'man *et al.*[99] obtained a value for this stability constant of 2.3×10^{17} at $I = 1M$ and pH 1.2–3.4. The aproximately ten-fold discrepancy in these values is partially explained by differences in ionic strength. The latter

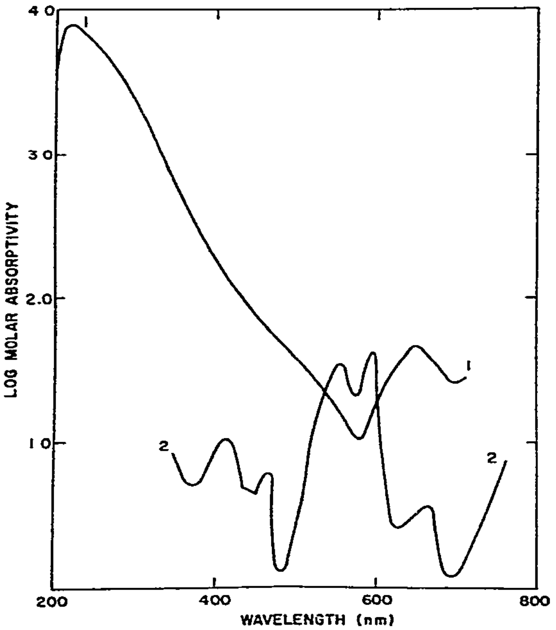


Fig. 9. (1) 1:1 EDTA chelate of plutonium (III) at pH 4.7; (2) unchelated plutonium(III) at pH 1.0; from Ref. 98, p. 1759.

investigators also obtained by ion exchange a value of 1.6×10^9 for the stability constant of Pu(HY) at pH 1.2–3.4 and $I = 1$ M. Investigation of the Pu^{III}–EDTA system by an electromigration method at various pH values from 1.1 to 3.5 also indicated the presence of Pu(HY) (significant only at pH <3) and PuY^- with respective stability constants[100] of 4×10^4 and 1×10^{15} at 25° and $I = 0.1$M.

The spectrum of PuY^- differs greatly from that of the aquo Pu^{III} ion, as can be seen in Fig. 9; in addition to marked changes in intensity and location of peaks, there is a general intensification of the entire spectrum. This effect has been ascribed to the greater electric dipole caused by the strong field associated with the chelating EDTA groups, which results in an enhancement of $5f^n$ electronic transitions[98]. The PuY^- chelate was found to obey Beer's Law.

The great stability of PuY^- is due to the presence of four interlocked chelate rings in the complex. The free energy of formation of chelates, $\Delta G = \Delta H - T\Delta S$, is generally quite negative, primarily due to an increase in the entropy term[101]. This increase may be understood on the basis that each chelating group, being polydentate, will displace two or more water molecules from the coordination sphere of the metal ion. Thus the chelation reaction results in an increase in the number of free molecules, and therefore in an increase in the disorder, or entropy, of the system. That the stability of PuY^- is primarily due to an entropy increase is shown by the results of Fuger and Cunningham[102]. From determinations of the heats of dissolution of anhydrous $PuCl_3$ in solutions of $I = 0.1$ M both in the presence and absence of EDTA, the following thermodynamic quantities for the formation of PuY^- at 25° and $I = 0.1$M were calculated: $\Delta G = -24.65$ kcal/mole; $\Delta H = -4.23 \pm 0.25$ kcal/mole; $\Delta S = 68.6 \pm 2$ e.u. The greater stability constant of PuY^- compared to those of the corresponding complexes of lanthanides of similar ionic radii, however, is primarily due to a more negative value for the enthalpy of formation of the Pu^{III} chelate rather than to the entropy term.

(ii) Plutonium(IV)

Ethylenediaminetetraacetic acid forms exceptionally strong complexes with Pu^{IV}, as evidenced by the fact that highly insoluble $Pu(OH)_4$ is not precipitated from solutions of the complexes[97], even at pH 11. At this pH, precipitation does not occur unless the Pu^{IV}/H_2Y^{2-} ratio exceeds two, from which it was concluded that Pu_2Y^{4+}, as well as the mononuclear species PuY, is formed.

The stability constant of the mononuclear complex was found to be 4.6×10^{17} by cation exchange[97] at 20 ± 0.2°, and 1.3×10^{17} by a spectrophotometric method (presumably at 20°)[98], both values at pH 3.30 and $I = 0.1$M. These values are considerably lower than would be expected. At this pH, however, Pu^{IV} exists primarily as the hydrolyzed species $Pu(OH)^{3+}$, and it was suspected that the reported stability constant actually referred to the formation of a hydrolyzed chelate, $PuY(OH)^-$, rather than PuY. To examine this possibility, a spectrophotometric estimate of the stability constant was made in 1M HNO_3, where hydrolysis would be negligible. The approximate value thus obtained, 1.6×10^{24}, is more plausible than those at pH 3.30, and undoubtedly represents formation of the unhydrolyzed complex[98], PuY.

In these calculations the basic properties of EDTA in acidic solutions were not considered. It has been pointed out that in acidic solutions the two nitrogen atoms of EDTA, each with an unshared electron pair, can react with H^+ ions to form the protonated species[103] H_5Y^+ and H_6Y^{2+}. On the assumption that H_6Y^{2+} is the principal species, the stability constant of PuY was calculated to be 1.38×10^{26}. This value is apparently in error also, because the ionic strength was allowed to vary, and also because of the incorrect assumption regarding the preponderance of H_6Y^{2+}. Krot and co-workers[104] have determined the dissociation constants of H_5Y^+ and H_6Y^{2+}, and have concluded from solubility studies of EDTA that below $[H^+] = 0.16M$, H_5Y^+ is the principal species, with H_6Y^{2+} becoming important at acidities above this value. Using the dissociation constants for H_5Y^+ and H_6Y^{2+}, the authors recalculated the spectrophotometric data of Foreman and Smith[98] and obtained a value of 5.7×10^{25} for the stability constant of PuY at $I = 1M$. This value appears to be the best currently available.

As explained in the discussion of Pu^{III}–EDTA chelates, the high stability of these complexes is primarily due to an increase in the entropy term[98]. Likewise, the spectrum of PuY (Fig. 10) is more intense than that of aquo Pu^{IV} for the reasons stated in the discussion of the Pu^{III} chelates.

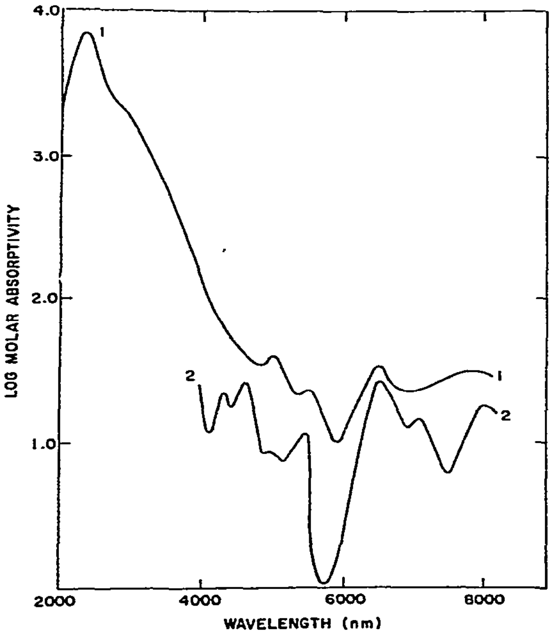


Fig. 10. (1) 1:1 EDTA chelate of plutonium(IV) at pH 4.7; (2) unchelated plutonium(IV) at pH 1.0; from Ref. 98, p. 1759.

(iii) Plutonyl(V)

The EDTA complexes have received more study than any other plutonyl(V) system. High-frequency titration of plutonyl(V) solutions with Na_2H[illegible] solution indicated that two complexes were formed with PuO_2/Y ratios of 1 and 0.5, respectively[105]. Potentiometric titration with NaOH solution established the identity of the lower complex as PuO_2Y^{3-}, with $\log K_1 = 12.9 \pm 0.1$, but the composition of the second species was not determined. The reported formation of the complex at pH values as low as three is in disagreement with the results of Gel'man and co-workers[106], who observed no complexation below pH 4. The latter investigators measured the distribution of plutonyl (V) from Na_2H_2Y solution onto cation-exchange resin as a function of pH, and concluded that PuO_2Y^{3-} begins to form at about pH 4, and becomes the predominant species at pH values above five. The stability constant of this species in the pH 4–5 range was calculated to be 1.5×10^{10}. The cause for the discrepancy between this value and that derived by potentiometric titration is unexplained.

(iv) Plutonyl(VI)

Plutonyl(VI), like Pu^{III} and Pu^{IV}, forms a stable 1/1 chelate with EDTA; in contrast to the lower-valent ions, however, it does not form a binuclear complex, since basic titration of solutions with plutonyl(VI)/H_2Y^{2-} ratios greater than unity results in precipitation[97] at about pH 10. The stability constant of PuO_2Y^{2-} has been determined both by cation exchange[97] and spectrophotometric[98] methods, the respective values being 2.5×10^{16} and 1.1×10^{16}, at 20.0 ± 0.2° and $I = 0.1M$. As in the case of the Pu^{III} and Pu^{IV} chelates, the high stability is primarily due to the increase in entropy.

In spite of the high stability constant, the plutonyl(VI) chelate is not stabilized against reduction, since the EDTA chelates with lower oxidation states of plutonium also are highly stable; in fact, reduction of plutonyl(VI) by EDTA itself has been observed. After standing for six days, a plutonyl(VI)–EDTA solution increased in pH from 6.5 to 9.1, and the color changed from violet-blue to pale yellow; the spectrum indicated the presence[98] of both Pu^{IV} and plutonyl(VI). A detailed investigation of the reduction in the pH 3–5 range indicated the plutonyl(V) or the Pu^{IV} chelate can be the reduction product, the latter resulting when an excess of EDTA is present[107]. One EDTA molecule can reduce six plutonyl(VI) ions to plutonyl(V), and in so doing three of the four acetic acid groups on the EDTA molecule are oxidized to methanol groups, with the evolution of three molecules of CO_2. The rate of reduction is proportional to the first power of both the plutonyl(VI) and the EDTA concentrations, and the rate constant at room temperature (apparently 25°) was reported to be $(2.5 \pm 1.0) \times 10^2\ M^{-1}\ min^{-1}$.

T. THIOCYANATE COMPLEXES

The Pu^{III}–thiocyanate system is the only one to receive study; Choppin and Ketels[108] investigated it with a solvent extraction technique employing bis(2-ethyl hexyl)orthophosphoric acid (D2EHPA). From the variation in extraction of Pu^{III} with thiocyanate concentration, the stepwise formation constants for $Pu(SCN)^{2+}$ and $Pu(SCN)_2{}^+$ were calculated to be 2.90 ± 0.31 and 1.95 ± 0.29, respectively, at 25 ± 0.1° and $I = 1.00M$. Anion and cation exchange have also been used to investigate this system, and yielded values in rather poor agreement with those reported above; ion-exchange distribution measurements as a function of thiocyanate concentration resulted in the following stepwise stability constants[109] at 25° and $I = 3M$; $Pu(SCN)^{2+}$, $K_1 = 1.1$: $Pu(SCN)_2{}^+$, $K_2 = 0.73$; $Pu(SCN)_3$, $K_3 \simeq 0.25$. The discrepancy may be partly due to the difference in ionic strength employed in the two investigations; in any case, the values for the higher complexes — particularly K_3 — should be accepted cautiously. Paper electrophoresis and paper anion-exchange chromatography at pH 2 indicated the presence of anionic complexes at thiocyanate concentrations above 6.5M.

Values for $\Delta H°$ and $\Delta S°$ of complexation indicated that the monothiocyanate complex is an outer-sphere ion-pair in which there is an inner hydration layer between ligand and cation[108]. The situation is similar to that described for the Pu^{III}–chloride system, although the ranges of stability differ; Pu^{III}–SCN ion-pairs become inner-sphere complexes at thiocyanate concentrations above 1M, while in the chloride system the conversion to inner-sphere complexes does not occur until the chloride concentration reaches 4.5–5M.

U. ACETYLACETONE COMPLEXES

Rydberg[110] has used an extraction method to investigate the acetylacetone complexes of Pu^{IV}, the only system studied to date. From the distribution of Pu^{IV} between aqueous acetylacetone solutions and benzene, the following stepwise stability constants at 25° and $I = 0.1M$ were determined: $\log K_1 = 10.5 \pm 1$; $\log K_2 = 9.2 \pm 0.5$; $\log K_3 = 8.4 \pm 0.5$; $\log K_4 = 6.0 \pm 0.4$. Since each acetylacetone group is bidentate (coordinating through both carbonyl oxygens to form a six-membered chelate ring), the maximum coordination number of Pu^{IV} in these complexes is eight.

V. COMPLEXES WITH 8-HYDROXYQUINOLINE DERIVATIVES

Onley plutonyl(V) complexes of this type have been reported. Keller and Eberle[111] have investigated complexing with two sulfonic acid derivatives of 8-

hydroxyquinoline by a cation exchange method. 8-Hydroxyquinoline-5-sulfonic acid was found to form a single complex with plutonyl(V), with log $K_1 = 5.7 \pm 0.05$ at 25.0 ± 0.1° and $I = 1$M; at the same temperature and ionic strength 7-iodo-8-hydroxyquinoline-5-sulfonic acid formed two complexes, with log $K_1 = 5.08 \pm 0.04$ and log $\beta_2 \simeq 9.1$.

W. MISCELLANEOUS COMPLEXES

(i) Plutonium(III)

The existence of carbonate complexes of Pu^{III} has been suggested by the solubility of $Pu(OH)_3$ in 45% K_2CO_3 to form a blue solution[112], and of Pu^{III} oxalate in carbonate solution[113], but no quantitative data on their identities and stabilities have been published. Further investigation of the coordination chemistry of Pu^{III} has undoubtedly been discouraged by the difficulty of maintaining this oxidation state in the presence of complexing agents (which favor oxidation to Pu^{IV}), and by the relative insensitivity of the Pu^{III} electronic spectrum to complex formation.

(ii) Plutonium(IV)

It is probably safe to say that Pu^{IV} is appreciably complexed by the anions of all weak acids. In fact, even strong acid anions form complexes of not insignificant stability; the chloride, bromide, nitrate, and sulfate complexes have been described above, and even perchlorate complexes are believed to exist at high anion concentrations. Those systems that have been investigated more thoroughly have been discussed above; there are a number of other cases where complex formation has been observed but not studied in detail, and these will be mentioned briefly.

The Pu^{IV}-benzohydroxamic acid system has been investigated by a technique involving equilibration of a thenoyltrifluoroacetone–toluene solution containing Pu^{IV} with various concentrations of benzohydroxamic acid[114] in 1M $HClO_4$. From these data the stability constant of $Pu(C_6H_5CONHO)^{3+}$ was calculated: $K_1 = (5.4 \pm 0.2) \times 10^{12}$ at 25° and $I = 1$M.

From data on the extraction of Pu^{IV} from nitrate solutions (with a correction applied for nitrate complexing) into benzene containing various concentrations of N-benzoylphenylhydroxylamine ($C_{13}H_{11}O_2N$), it was concluded that complexes of the type $Pu(C_{13}H_{10}O_2N)_n^{(4-n)+}$, containing up to four ligands, are formed[115]. Since the ligands are bidentate, the maximum coordination number of Pu^{IV} is eight. The following stability constants at ~22° and $I = 1$M were calculated from the data: $K_1 = 3.13 \times 10^{11}$; $K_2 = 2.80 \times 10^{11}$; $K_3 = 7.39 \times 10^9$; $K_4 = 3.44 \times 10^9$.

The readiness with which plutonium peroxide can be dissolved in ammonium sulfite solution (without gas evolution) has been interpreted to indicate the existence of sulfite complexes, and variations in the visible absorption spectrum with sulfite concentration suggested the formation of at least two different complexes[116]. Quantitative stability data were not obtained, but it was inferred that the sulfite complexes are intermediate in stability between the sulfate and carbonate complexes.

Salicylate complexes of Pu^{IV} have been reported in alkaline salicylate solutions[117], and one such complex was found to be extractable into amyl acetate (Ref. 118). Complexes with several disulfonic acids have been prepared, and appear to be stable over a limited pH range. A blue-violet 1/1 complex is formed[119] with 2-(*o*-arsonophenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonic acid (uranol) in HNO_3 at pH 0.95–1.35, while 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (thoronol) also forms a 1/1 complex in HNO_3 solutions of the same pH range[120]; the estimated stability constants of these two complexes are 5.5×10^6 and 3.3×10^6, respectively. Benzene-2-(arsonic acid)-2,2′-azo-1′,8′-dihydroxynaphthalene-3′,6′-disulfonic acid (arseneazo, represented below as H_6R) forms a blue 1/1 complex that is thought to be[121] either $Pu(H_3R)^+$, with a calculated stability constant of 4.8×10^7, or $Pu(OH)(H_4R)^+$, with a stability constant of 3.6×10^6. The reaction in HCl is most complete at pH 2.20, but is sufficiently complete at pH 2–5 to merit its suggested use for the spectrophotometric determination of plutonium in this pH range.

(iii) Plutonyl(V)

Relatively few plutonyl(V) complexes have been reported, and there are some surprising omissions. The absence of nitrato complexes is particularly noteworthy; the constancy of the plutonyl(V) spectrum in HNO_3 solutions in the pH 2–6 range[122] and in 1–10M NH_4NO_3 solutions[23] has been interpreted to indicate the absence of complexation. Whether this conclusion is strictly true is debatable, but it does seem safe to say that nitrate complexes, if they exist, are very unstable.

(iv) Plutonyl(VI)

Several other plutonyl(VI) complexes have been reported, but they have been less thoroughly investigated than those described above. Eberle and Schaefer[123] have established by a spectrophotometric method that plutonyl(VI) forms two complexes with glycolate ion, *viz.* $PuO_2(C_2H_3O_3)^+$ and $PuO_2(C_2H_3O_3)_2$, with overall stability constants of 267 ± 9 and 6110 ± 270, respectively, at $I = 0.1M$ and $25.0 \pm 0.2°$.

A brief spectrophotometric study has indicated the existence of two salicylate complexes, $PuO_2(C_7H_4O_3)$ and $PuO_2(C_7H_4O_3)_2{}^{2-}$, with stability constants of $(3.2 \pm 0.8) \times 10^{15}$ and $(1.4 \pm 0.1) \times 10^{11}$, respectively, at $25 \pm 2°$ (ionic strength not specified)[124]. In these complexes both the hydroxyl-hydrogen and the carboxyl-hydrogen are removed from the salicylic acid molecule, forming a bidentate ligand with a 2^- charge.

Mention of sulfato complexes has been deferred until last, since no quantitative data have been reported. Even in 0.1M H_2SO_4 there are changes in the plutonyl(VI) absorption spectrum that indicate complex formation[125], and electromigration studies suggest that the majority of the plutonyl(VI) is present as an anionic complex[26]. In 1M H_2SO_4 anionic complexes are present almost exclusively. Similar results were obtained in an investigation involving both spectrophotometry and electrophoresis at various H_2SO_4 and $(NH_4)_2SO_4$ concentrations[27]. It was found that complexing is more complete in solutions of the salt than in acid solutions. Concentration ranges of acid and salt for formation of the various complexes were reported as follows: $PuO_2(SO_4)$, 0.1M H_2SO_4 or $(NH_4)_2SO_4$; $PuO_2(SO_4)_2{}^{2-}$, 0.1–4.5M acid, or 0.1–1.4M salt; $PuO_2(SO_4)_3{}^{4-}$, >4.5M acid, or 1.4–1.84M salt. The fourth complex, $PuO_2(SO_4)_4{}^{6-}$, is not formed to an appreciable extent in H_2SO_4 solution, but exists in $(NH_4)_2SO_4$ solutions above 1.84M. These conclusions, based on changes in the absorption spectrum, clearly need confirmation by independent methods before they can be accepted unequivocally.

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