135.2, 131.9, 131.8, 130.5, 127.4, 119.8, 29.8, 28.5, 26.8, 26.6; thermospray mass spectrum, m/e 716.

$Rh_2(OAc)_3$(12)[PF_6]. By the procedure described above, 17 mg (55 μmol) of **12** and 24.5 mg (55 μmol) of $Rh_2(OAc)_4$ gave a complex that was recrystallized from acetonitrile–water to afford 36 mg (78%) of dark red crystals: ^1H NMR (300 MHz, CD_3CN)[11] δ 9.27 (dd, H_2, $J_{2,3}$ = 5.1 Hz, $J_{2,4}$ = 2.3 Hz), 8.67 (d, H_{10} (2 H), J = 4.6 Hz), 8.54 (d, H_6, $J_{6,6a}$ = 8.4 Hz), 8.44 (s, H_5), 8.26 (d, H_4, J = 7.9 Hz), 8.12–7.96 (m, H_{6a}, H_3, H_7, H_8, H_9), 3.49 (s, $-CH_2-$), 2.14 (s, 3 H, axial OAc), 1.55 (s, 6 H, equatorial OAc); thermospray mass spectrum, m/e 692.

Cyclic Voltammetry. Reagent grade acetonitrile was distilled twice from P_2O_5 under nitrogen. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was recrystallized from EtOAc–hexane, dried, and stored in a desiccator.

Cyclic voltammograms were recorded with a PAR Model 174A polarographic analyzer, PAR Model 175 universal programmer, and a Houston Instruments Omnigraphic 2000 X-Y recorder. A three-electrode system was employed consisting of a platinum-button working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was separated from the bulk of the solution by a cracked-glass bridge filled with 0.1 M TBAP in acetonitrile. Deaeration of all solutions was performed by passing high-purity nitrogen through the solution for 5 min and maintaining a blanket of nitrogen over the solution while making measurements.

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Studies of Metal–Carbonate Complexes. 14. Composition and Equilibria of Trinuclear Neptunium(VI)- and Plutonium(VI)-Carbonate Complexes

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The chemical composition of the trinuclear complexes $(MO_2)_3(CO_3)_6^{6-}$ and the equilibrium constants for the reaction $3MO_2(CO_3)_3^{4-} \rightleftharpoons (MO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$, where M = Np or Pu, have been determined by spectrophotometric and emf methods. The values of the equilibrium constants at I = 3 M ($NaClO_4$) and T = 22 ± 1 °C are log $K_{3,6}$(Np) = −10.1 ± 0.1 and log $K_{3,6}$(Pu) = −7.4 ± 0.2; the constant for U determined previously is −11.3 ± 0.1. The range of stability of the trinuclear plutonium complex is much larger than those of uranium and neptunium, a fact that might be due to a lower stability of the limiting $PuO_2(CO_3)_3^{4-}$ complex. We have demonstrated the formation of mixed complexes of the type $(MO_2)_x(M'O_2)_{3-x}(CO_3)_6^{6-}$ in the U(VI)–Np(VI)–Pu(VI)–carbonate system, formed by the isomorphic substitution of U(VI) by another actinide. Spectral characteristics and estimated stabilities are given for $(UO_2)_2(MO_2)(CO_3)_6^{6-}$ (M = Np, Pu). The equilibrium constants for the reaction $2UO_2(CO_3)_3^{4-} + MO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_2(MO_2)(CO_3)_6^{6-} + 3CO_3^{2-}$, where M = Np or Pu, are equal to log K(Np) = −10.0 ± 0.1 and log K(Pu) = −8.8.

The structure and compositions of the limiting complex $UO_2(CO_3)_3^{4-}$, formed in the U(VI)–H_2O–carbonate system, have been well-known for a long time.[1,2] The corresponding Np(VI) and Pu(VI) systems have not been as extensively studied; however, several investigations indicate that the limiting complexes have the same stoichiometry as found in the uranium system. Simakin[3] and Maya[4] used solubility and emf techniques to establish this fact for the neptunium system, while Sullivan et al.[5] used a spectrophotometric technique in a study of the corresponding plutonium carbonates.

There is less agreement about the composition of the precursor to the limiting complex. We have previously established the formation of $UO_2(CO_3)_2^{2-}$ and the trimer[2,6] $(UO_2)_3(CO_3)_6^{6-}$. The trimer is strongly stabilized in solutions of high ionic strength,[2] and it is this species that accounts for the very high solubility of UO_2CO_3(s) in carbonate solutions. Gel'man et al.[7] noticed a similar high solubility of ammonium diplutonate in ammonium carbonate solutions (solubilities up to 22.7 g of Pu/L). With increasing total concentration of plutonium, the authors[5] noticed a color change from green (the color of $PuO_2(CO_3)_3^{4-}$) to red. Haag[8] made similar observations on the Np(VI)–carbonate system and suggested that the red color was due to the complex $NpO_2(CO_3)_2^{2-}$. Maya[4] made a quantitative study of the Np(VI)–carbonate system and interpreted his data in terms of the formation of $NpO_2(CO_3)_2^{2-}$, $NpO_2(CO_3)_3^{4-}$, and a mixed complex $(NpO_2)_2(OH)_3(CO_3)^-$.

From the chemical similarities generally observed in the actinide series between elements of the same oxidation state (e.g. the solubilities in actinide(VI)–carbonate systems) one expects to find chemical species of the same composition and with only minor variations in chemical properties (apart from their redox potentials). The variations of properties are of great chemical interest and can be correlated with the size of the central ion or with the f-electron configuration, as is often done when chemical variations through the lanthanide group are interpreted.

The $(MO_2)_3(CO_3)_6^{6-}$ structure[9] is extremely well adapted to the steric requirements of both the MO_2^{2+} and the CO_3^{2-} ions, and it seems very likely that one or more MO_2^{2+} ions can be replaced by another actinoid(VI) ion. One of the themes of this communication will be to demonstrate the formation of such heterometallic complexes.

We have previously described two different experimental techniques, viz. potentiometric measurements of the concentration

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of H^+[6] and spectrophotometry,[10] which are suitable for the treatment of the problem. The potentiometric method requires high precision in the emf measurements in order to establish a precise chemical model. This is often difficult to achieve when the experimental work has to be done in a plastic glovebox, as in this study.

On the other hand, the pronounced color changes observed when the total concentration of carbonate is varied indicates that spectrophotometry might provide accurate information on the concentrations of the different complexes. We have therefore chosen spectrophotometry as the main experimental technique, the details of which will be discussed in the Experimental Section. The experiments have been made at "room temperature", 22 ± 1 °C, in a 3 M $NaClO_4$ medium.

The carbonate systems have been studied at constant partial pressure of $CO_2(g)$, as described before.[6]

Notations

h	concentration of H^+
H	analytical concentration excess of H^+ over H_2O and CO_2
b, B	concentrations of MO_2^{2+} and total concentrations of M(VI), respectively
a	P_{CO_2}, partial pressure of $CO_2(g)$ in the test solutions
A	optical absorbance per centimeter
$\epsilon_1\epsilon_2$	molar absorption coefficients of $MO_2(CO_3)_3^{4-}$ and $(MO_2)_3(CO_3)_6^{6-}$, respectively
$\beta_{1,6,3}$	equilibrium constant for $MO_2^{2+} + 3CO_2(g) + 3H_2O \rightleftharpoons MO_2(CO_3)_3^{4-} + 6H^+$
$\beta_{3,12,6}$	equilibrium constant for $3MO_2^{2+} + 6CO_2(g) + 6H_2O \rightleftharpoons (MO_2)_3(CO_3)_6^{6-} + 12H^+$
K	$\beta_{3,12,6}/\beta_{1,6,3}^3$ = equilibrium constant for $3MO_2(CO_3)_3^{4-} + 6H^+ \rightleftharpoons (MO_2)_3(CO_3)_6^{6-} + 3CO_2(g) + 3H_2O$
Z	$(h - H - [HCO_3^-] - 2[CO_3^{2-}])/B$ = average number of H^+ ions split off per MO_2^{2+} during complex formation

Experimental Section

Materials and Analysis. Neptunium(VI) (100% ^{237}Np) and plutonium(VI) (isotope composition in atom %: ^{238}Pu, 0.115; ^{239}Pu, 76.772; ^{240}Pu, 19.882; ^{241}Pu, 2.508; ^{242}Pu, 0.723) **perchlorate** solutions were prepared from acid stock solutions by evaporation with $HClO_4$ until most of the excess acid had been removed. The concentrated solution was dissolved in 0.1 M $HClO_4$, and this solution was immediately analyzed spectrophotometrically for Np(VI)–Np(V) or Pu(VI)–Pu(IV). More than 99.7% of the actinides were in oxidation state +6. The solid carbonates $MO_2CO_3(s)$ were then precipitated by addition of $NaHCO_3$ to the fresh perchlorate solutions in order to avoid reduction by water or through radiolysis. The precipitates, brown for $NpO_2CO_3(s)$ and light tan for $PuO_2CO_3(s)$, were washed on a filter with H_2O and then dissolved in a carbonate/bicarbonate solution of accurately known composition. The carbonate concentration was sufficiently high to obtain the limiting complex $MO_2(CO_3)_3^{4-}$ only. The total concentration of neptunium was determined spectrophotometrically after reduction to Np(V) with hydrazine,[11] while the total concentration of Pu(VI) was determined by acidifying a sample with $HClO_4$ and measuring the light absorption at 830 nm. From the known concentrations of Np(VI) and Pu(VI) and the initial concentrations of carbonate/bicarbonate one can calculate the precise composition of the carbonate stock solutions. These can be kept for several weeks without any noticeable change in the oxidation state of the actinides.[5] The procedure outlined above is simpler and probably more precise than the methods involving the precipitation of $MO_2(OH)_2(s)$ and the dissolution of this in carbonate/bicarbonate.[12] **Uranium(VI)** solutions were prepared and analyzed as described before.[6]

Perchloric acid, sodium bicarbonate and **sodium perchlorate** were all of analytical grade. Stock solutions were prepared and analyzed by using standard methods.

Sodium hydroxide (ampules containing a known quantity of analytical grade NaOH) was used to prepare the sodium carbonate/sodium bicarbonate stock solutions. **$CO_2(g)$–$N_2(g)$ mixtures** with 100%, 30%, and 10% $CO_2(g)$ of known analytical composition were obtained from Air Liquide. The analytical precision was ±0.6% and ±0.2% at the 30% and 10% levels, respectively.

Measurements. All measurements were made in gloveboxes at ambient temperature (22 ± 1 °C). The spectrophotometric measurements were made by using a Cary 17 D instrument. The experiments were made as titrations, where an initial solution of accurately known total concentrations of M(VI) and carbonate/bicarbonate was titrated with a solution of 3.000 M $HClO_4$ or 1.000 M $HClO_4$ + 2.000 M $NaClO_4$. All titrations were made at known partial pressure of $CO_2(g)$. The addition of titrant caused a slight change in the total concentrations of Np(VI) and Pu(VI) throughout the titrations. This was taken into account where the molar absorptivities were calculated. The variation in concentration was often so small that the position of the normalized curves did not change; vide infra. We did not have flow-through cells with a circulation system[13] available and had instead to take out samples for the spectrophotometric measurements. We then bubbled $CO_2(g)$ through the curvettes for a few minutes, in order to resaturate the solutions with CO_2, closed the cuvette, and recorded the spectrum. The spectra did not change if the cuvette was left open for a few minutes.

The free hydrogen ion concentration was determined potentiometrically by using a combined glass electrode (Tacussel TCBC11/HS/sm, with an Ag–AgCl reference half-cell). The original reference solution was replaced with a solution of the composition 0.0100 M NaCl + 2.990 M $NaClO_4$. The glass electrode was calibrated in concentration units by using solutions of accurately known hydrogen ion concentration, either a 10.00 mM $HClO_4$ + 2.990 M $NaClO_4$ solution or a 50.00 mM $NaHCO_3$ + 2.950 M $NaClO_4$ solution. The latter was used with $CO_2(g)$ of known partial pressure. The emf was measured by using a Tacussel ISIS 20 000 pH-meter.

We had great difficulties in making precise emf measurements, particularly in the Pu glovebox, and we estimate the errors to be in the range 0.6–1.0 mV. The errors in the Np system tend to lie at the low end of this range, and the errors in the Pu system, at the high end.

The glass electrode was standardized several times a day, and the calibration values were in general constant within 1 mV.

The Pu(VI) measurements were complicated by the precipitation of $PuO_2CO_3(s)$, and most of the test solutions were supersaturated with respect to this solid. When a precipitate formed, we filtered the solution and tried to continue the titration, now at a somewhat lower total concentration of M(VI). The precipitation showed up very clearly in the absorption spectra, particularly in the lower wavelength region. In the Np(VI) system this complication was less important, and we could obtain good direct measurements of both ϵ_1 and ϵ_2, while in the Pu(VI) system only ϵ_1 could be determined directly, due to the early precipitation of $PuO_2CO_3(s)$. In order to obtain an unambiguous interpretation of the Pu(VI) system, we therefore found it necessary to make an independent measurement of $Z(-\log [H^+])$, by using the technique described before.[6]

We made two series of titrations at different total concentrations of Pu(VI): 19.34 and 11.26 mM. Test solutions with known total concentrations of Pu(VI) and H were titrated with a 1.000 M $HClO_4$ + 2.000 M $NaClO_4$ solution at p_{CO_2} = 1 atm. The additions of titrant were made by using calibrated Eppendorf pipettes. The relative merits of the two methods will be discussed in a following section.

Mixed U(VI)–Np(VI) and U(VI)–Pu(VI) complexes were studied by spectrophotometric titrations of test solutions of the following compositions: $[UO_2(CO_3)_3^{4-}]$ = 23.96 mM, $[NpO_2(CO_3)_3^{4-}]$ = 4.52 mM, $[HCO_3^-]$ = 120.06 mM and $[UO_2(CO_3)_3^{4-}]$ = 25.46 mM, $[PuO_2(CO_3)_3^{4-}]$ = 1.02 mM, $[HCO_3^-]$ = 122.2 mM; with 1.000 M $HClO_4$ + 2.000 M $NaClO_4$. Uranium(VI) does not absorb above 500 nm; hence, the interesting parts of the Np(VI) and Pu(VI) spectra could be studied without interference of uranium.

The values of log K are sufficiently similar for the U(VI) and M(VI) systems, for the polynuclear complexes to be formed in the same concentration range. By using an excess of U(VI), we have tried to ensure that the possible mixed complexes only contain one MO_2^{2+} per two UO_2^{2+}. By making a spectrophotometric titration on a solution of known concentrations of U(VI) and M(VI), we can easily detect the formation of bimetallic complexes. If the log (A/B) vs. log (a/h^2) data are displaced from the position given by log K for the M(VI) system, we have direct evidence for the formation of a mixed complex, even if the spectral characteristics of $(MO_2)_3(CO_3)_6^{6-}$ and $(UO_2)_{3-x}(MO_2)_x(CO_3)_6^{6-}$ are very nearly the same, as they in fact turn out to be; cf. Results.

Treatment of the Data and Results

The absorption spectra of Np(VI) and Pu(VI) vary strongly with the total concentrations of metal ion and carbonate; cf. Figures 1–5. The presence of isosbestic points is a strong indication that we have an equilibrium between two colored species. The molar absorptivity A/B was found to be a function of a/h^2 (cf. Figures 3 and 4), which indicates that the complexes formed

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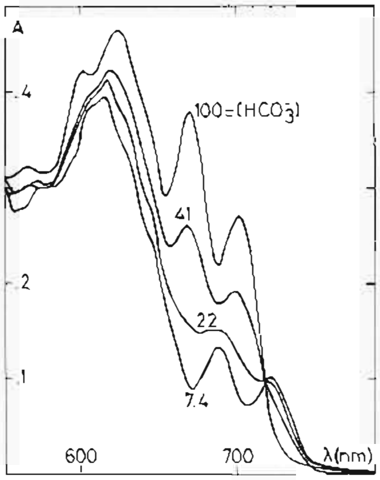

Figure 1. Absorption spectra of Np(VI)–carbonate solutions at varying concentrations of HCO_3^-.

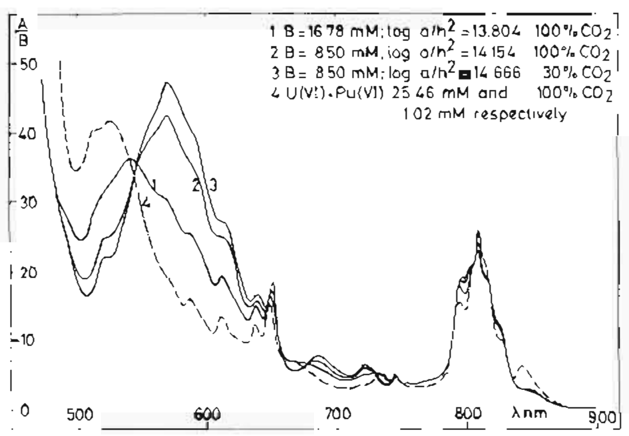

Figure 2. Absorption spectra of Pu(VI)–carbonate solutions and a U(VI)–Pu(VI)–carbonate solution, where the predominant Pu species is $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$.

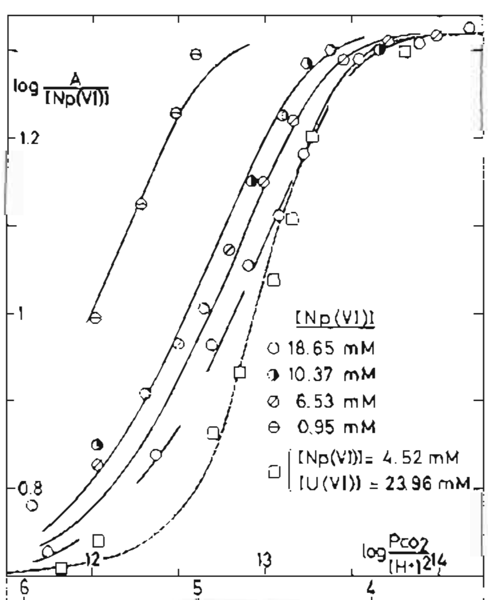

Figure 3. Experimental value of log (A/B) vs. log (a/h^2) for the Np(VI)–carbonate system. The data refer to $\lambda = 670$ nm, and the full-drawn curves are the normalized curves for the proposed model at the position of best fit. This corresponds to log $K = 42.8 \pm 0.1$. The experimental data for the measurements in the U(VI)–Np(VI)–carbonate system are also included. The displacement toward higher values of log (a/h^2) for the given value of B, as compared to the data in the binary Np(VI)–carbonate system indicates that mixed complexes are formed. The dashed curve has been calculated by using the parameters given in the supplementary material and in Table I.

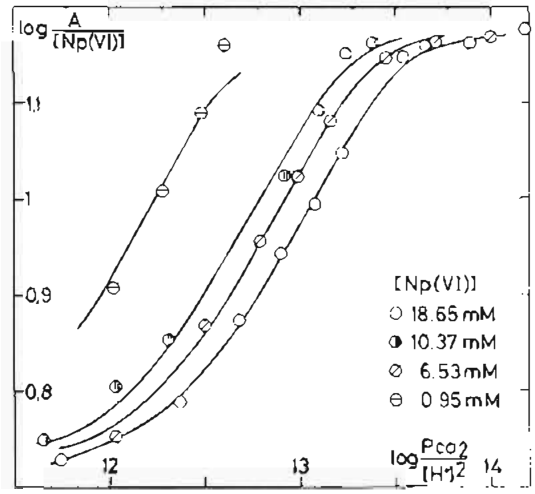

Figure 4. Experimental values of log (A/B) vs. log (a/h^2) at 700 nm for the Np(VI)–carbonate system.

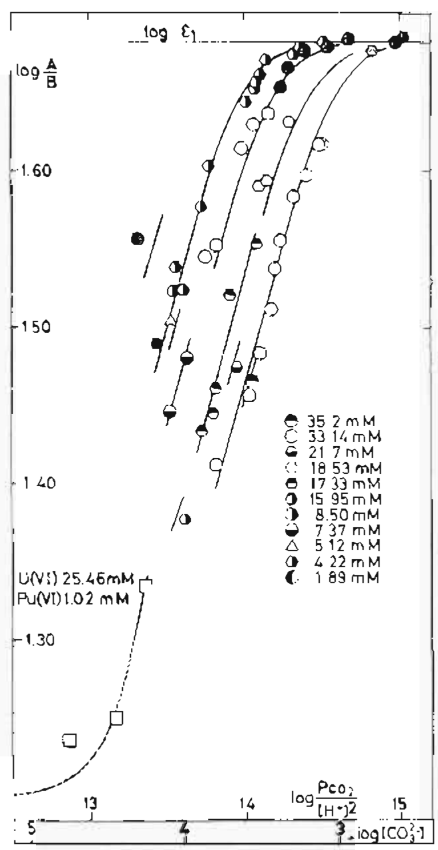

Figure 5. Experimental values of log (A/B) vs. log (a/h^2) at 570 nm for the Pu(VI)–carbonate system and for the ternary U(VI)–Pu(VI)–carbonate system. The full-drawn normalized curves correspond to the position of best fit with $L = \epsilon_2/\epsilon_1 = 1.0$. The equilibrium constant log $K = 45.4 \pm 0.2$. The dashed curve for the mixed U(VI)–Pu(VI)–carbonate system has been calculated by using the parameters given in the supplementary material and in Table I.

only contain carbonate as the ligand; i.e., mixed hydroxide/carbonate complexes are not present in significant concentrations. The dependence on B indicates that polynuclear complexes are formed. In view of these observations, it seems reasonable to test the U(VI) polynuclear model also on the Np(VI)– and Pu(VI)–carbonate systems.

For the mass balance for M(VI) and the measured absorptivity A, we obtain

$$B = \beta_{1,6,3}b(a/h^2)^3 + 3\beta_{3,12,6}b^3(a/h^2)^6 \quad (1)$$

$$A = \epsilon_1\beta_{1,6,3}b(a/h^2)^3 + \epsilon_2\beta_{3,12,6}b^3(a/h^2)^6 \quad (2)$$

Table I. Equilibrium Constants and Molar Absorptivities for Complexes in the U(VI)–Np(VI)–Pu(VI)–H_2O–Carbonate System[a]

reaction	log K		
	U(VI)	Np(VI)	Pu(VI)
$3MO_2(CO_3)_3^{4-} + 6H^+ \rightleftarrows (MO_2)_3(CO_3)_6^{6-} + 3CO_2(g) + 3H_2O$	41.5 ± 0.1	42.8 ± 0.1	45.4 ± 0.2
$3MO_2(CO_3)_3^{4-} \rightleftarrows (MO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$	−11.3 ± 0.1	−10.0 ± 0.1	−7.4 ± 0.2
$2UO_2(CO_3)_3^{4-} + MO_2(CO_3)_3^{4-} \rightleftarrows (UO_2)_2(MO_2)(CO_3)_6^{6-} + 3CO_3^{2-}$	−11.3 ± 0.1	−10.0 ± 0.1	−8.8

complex	ϵ_{670}(Np)	ϵ_{700}(Np)	ϵ_{570}(Pu)
$MO_2(CO_3)_3^{4-}$	20.8 ± 0.2	15.2 ± 0.2	48.0 ± 0.2
$(MO_2)_3(CO_3)_6^{6-}$	14.4 ± 0.3	14.8 ± 0.3	47.4 ± 0.5
$(UO_2)_2(MO_2)(CO_3)_6^{6-}$	5.0 ± 0.4		15.8 ± 0.2

[a] All data refer to a temperature of 22 ± 1 °C and a 3.00 M Na(ClO$_4$) medium. The equilibrium constants involving carbonate ions were calculated by using log $K = -17.61$ for the reaction $CO_2(g) + H_2O \rightleftarrows CO_3^{2-} + 2H^+$.

After introduction of the normalized variables u and v (cf. ref 10), where $u = \beta_{1,6,3}b(a/h^2)^3$ and $v = \beta_{3,12,6}b^3(a/h^2)^6$, we obtain

$$\log \frac{A}{B} = \log \epsilon_1 + \log \frac{u + Lv}{u + 3v} = \log \epsilon_1 + Y \qquad (3)$$

where $L = \epsilon_2/\epsilon_1$. Elimination of b from the expressions for u and v gives

$$\frac{v}{u^3} = \frac{\beta_{3,12,6}}{\beta_{1,6,3}{}^3}\left(\frac{a}{h^2}\right)^{-3}$$

i.e.

$$\log (a/h^2) = \tfrac{1}{3} \log K + \log u - \tfrac{1}{3} \log v = \tfrac{1}{3} \log K + X \quad (4)$$

Normalized curves $Y(X)$, were calculated for each value of B, usually the average value in a titration series, provided that B did not vary more than a few percent. By superposition of these curves on the experimental data plotted as log (A/B) vs. log (a/h^2), we can easily determine whether the proposed model is correct and also the position of the best fit. The log (a/h^2) value corresponding to $X = 0$ then gives log $K = 3$ log (a/h^2); cf. eq 4.

The Neptunium(VI)–Carbonate System. There are pronounced changes in the absorption spectrum of Np(VI) in the $[HCO_3^-]$ range 5–100 mM; cf. Figure 1. On decrease of $[HCO_3^-]$ the original green solution turns brownish at the highest, or yellow at the lowest, metal ion concentrations. Immediately before the precipitation, the solution turns red-brown; cf. the observation of Haag.[8] This color is probably due to the formation of colloidal NpO_2CO_3, as judged from the practically featureless absorption spectrum with a base line that rises with decreasing wave length and a slow sedimentation of a very fine precipitate. NpO_2CO_3(s) is more soluble than PuO_2CO_3(s), and it was possible to obtain good direct determinations of ϵ_1 and ϵ_2 (cf. Table I), just as in the uranium system.[10]

The curve fitting was made by using data at two different wavelengths, 670 and 700 nm; cf. Figures 3 and 4. The fit at the lowest values of log $(p_{CO_2}/[H^+]^2)$ is slightly better at 700 nm, possibly being due to the presence of a small quantity of colloidal NpO_2CO_3(s), which will affect the data at lower wavelengths more than those at higher. Both wavelengths gave the same value, log $K = 42.8 \pm 0.1$, for the equilibrium constant for the reaction

$$3NpO_2(CO_3)_3^{4-} + 6H^+ \rightleftarrows (NpO_2)_3(CO_3)_6^{6-} + 3CO_2(g) + 3H_2O$$

The experimental data are given as supplementary material (Table Ia).

The Plutonium(VI)–Carbonate System. $PuO_2(CO_3)$(s) is much less soluble than NpO_2CO_3(s), and it was not possible to study the carbonate complex formation over such a large carbonate concentration range as in the Np(VI) system. Only ϵ_1 could be determined directly, while ϵ_2 had to be estimated from the curve shape by calculating normalized curves with various values of L. This procedure was not very precise, and the first curve fitting gave log $K = 45.2$ and $L = 0.75 \pm 0.25$.

From the presence of an isosbestic point, the curve shape, and the data obtained at different partial pressures of CO_2(g), it is clear that the same predominant complexes are formed as in the corresponding U(VI)- and Np(VI)–carbonate systems.

In order to get a better estimate of ϵ_2, we measured the absorption spectrum in a solution were Z was known from a potentiometric measurement. At $Z = 4.82$, we measured $A/B = 29.0$. As the first normalized curve fit indicated that only two Pu(VI) complexes are present in solution, we can write

$$\frac{A}{B} = \epsilon_1(\bar{n} - 2) + \frac{\epsilon_2}{3}(3 - \bar{n})$$

where $\bar{n} = Z/2$ is the average number of bonded carbonate ligands per Pu(VI). We obtain $\epsilon_2 = 47.4$; i.e., $L = 1.0$. This value is more precise than the estimate $L = 0.75$ and was therefore used in the final curve fitting of the experimental data; cf. Figure 5. The value of log $K = 45.4 \pm 0.2$ was obtained from the position of best fit.

The experimental data for the spectrophotometric measurements are given as supplementary material (Table Ib).

The precision is lower in the Pu(VI) system than in the corresponding Np(VI) study. This is due both to the larger errors in the log $[H^+]$ measurements and to a somewhat larger error in the absorptivity measurements; the latter are mainly due to analytical errors when the Pu(VI) concentration had to be reanalyzed after precipitations in the titration experiments.

The spectrophotometric titrations were rather time-consuming, and we therefore decided to perform some direct emf measurements of $Z = f(\log [H^+])$ and to calculate the equilibrium constant from these data. By using the appropriate mass balance and equilibrium conditions, we obtain the following expression for the equilibrium constant for the reaction

$$3PuO_2(CO_3)_3^{4-} \rightleftarrows (PuO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$$

$$K_{3,6} = \frac{3 - \bar{n}}{(\bar{n} - 2)^3} \frac{[CO_3^{2-}]^3}{3B^2}$$

The experimental data $Z = f(-\log [H^+])$ are given as supplementary material (Table Ic).

The average value of log $K_{3,6}$ is equal to −7.6 ± 0.3, which corresponds to log $K = 45.2 \pm 0.3$, a value that is in good agreement with the spectrophotometric value; however, the error limits are somewhat larger. This is due to errors in the log $[H^+]$ measurements, which in the potentiometric method influence both log (a/h^2) *and* Z (or $\bar{n}$). An error of ±0.01 in log $[H^+]$ will typically cause an error in Z around ±0.16. In the spectrophotometric measurement A/B, which is a function equivalent to Z, is independent of errors in $-\log [H^+]$.

Evidence for the Formation of Mixed U(VI)–Np(VI)- and U(VI)–Pu(VI)–Carbonate Complexes. The absorption spectra of Np(VI) and Pu(VI) in the ternary systems at $\lambda > 500$ nm turned out to be very similar to the absorption spectra of the binary systems. However, by plotting log (A/B) vs. log (a/h^2), we found that the experimental data (given as supplementary material (Table Id) and in Figures 3 and 5) for a given value of the concentration of Np(VI) (or Pu(VI)) are displaced toward higher values of log (a/h^2); cf. Figures 3 and 5. This fact indicates that ternary bimetallic complexes are formed in the U(VI)–M(VI)–carbonate systems. By decreasing the value of log (a/h^2), we found that the molar absorptivities approaches constant values, which were 5.0 ± 0.4 at λ = 670 nm for Np(VI) and 15.8 ± 0.1 at λ 570 nm for Pu(VI). These values are very nearly one-third of the previously measured molar absorptivities of $(NpO_2)_3(CO_3)_6^{6-}$ ($\epsilon_2/3 = 4.6 \pm 0.1$) and $(PuO_2)_3(CO_3)_6^{6-}$ ($\epsilon_2/3 = 15.6 \pm 0.1$), indicating a composition $(UO_2)_2(MO_2)(CO_3)_6^{6-}$ for the bimetallic complexes. This hypothesis was tested by calculating the equilibrium constant for the reaction

$$2UO_2(CO_3)_3^{4-} + MO_2(CO_3)_3^{4-} \rightleftarrows (UO_2)_2(MO_2)(CO_3)_6^{6-} + 3CO_3^{3-} \quad (5)$$

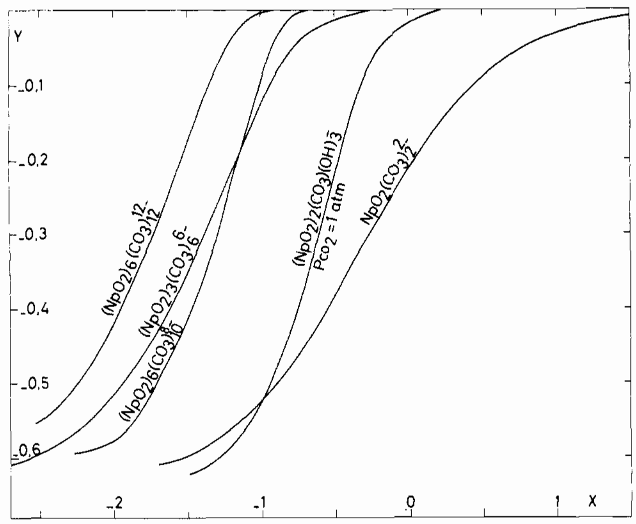

Figure 6. Normalized curves for five different two-complex models: $NpO_2(CO_3)_3^{4-}$ and $(NpO_2)_6(CO_3)_{12}^{12-}$; $(NpO_2)_3(CO_3)_6^{6-}$; $(NpO_2)_6(CO_3)_{10}^{8-}$; $(NpO_2)_2(OH)CO_3^-$; $NpO_2(CO_3)_2^{2-}$. X and Y denote functions defined by the normalized variables u and v and the total metal ion concentration B. For the $MO_2(CO_3)_3^{4-}$–$(MO_2)_3(CO_3)_6^{6-}$ model we have $Y = \log [(n + Lv)/(u + 3v)]$ and $X = \log u - {}^1/_3 \log v$ (eq 3 and 4).

The concentrations of all species were obtained from the mass balance conditions, the measured values of A/B vs. a/h^2, and the known equilibrium constants for the U(VI)–carbonate system. We have

$$B_U = [UO_2(CO_3)_3^{4-}] + 3[(UO_2)_3(CO_3)_6^{6-}] + 2[(UO_2)_2(MO_2)(CO_3)_6^{6-}]$$

$$B_M = [MO_2(CO_3)_3^{4-}] + [(UO_2)_2(MO_2)(CO_3)_6^{6-}]$$

$$A = \epsilon_1[MO_2(CO_3)_3^{4-}] + (\epsilon_2/3)[(UO_2)_2(MO_2)(CO_3)_6^{6-}]$$

In order to get a precise value of the equilibrium constant, one must use experimental data where the concentrations of the species appearing in (5) have a sufficiently high analytical accuracy. Seven of the experimental points in the U(VI)–Np(VI) system could be used and gave $\log K = -9.95 \pm 0.06$ for reaction 5. In the U(VI)–Pu(VI) system only two experimental points could be used and both gave $\log K = -8.8$. We have not made an estimate of the error in this quantity because of the scarcity of data.

Discussion

The predominant complexes in the metal carbonate ion concentration ranges investigated are $MO_2(CO_3)_3^{4-}$ and $(MO_2)_3(CO_3)_6^{6-}$ with M = Np or Pu. There are no indications of the formation of ternary complexes containing both hydroxide and carbonate as previously suggested by Maya[4] in the Np(VI)–carbonate system or hydroxide and bicarbonate as suggested by Sullivan et al.[14] for the Pu(VI)–carbonate system. On the other hand, it is difficult to establish the presence of *minor* species from the data of moderate precision obtained in our study. However, it is comforting that we have found the same chemical model as for the corresponding U(VI) system, where data of high precision are available.[6,10] Figure 6 shows normalized curves for some of the chemical models tested and it is obvious that the curve shapes are very different for $(MO_2)_3(CO_3)_6^{6-}$, $(MO_2)_2(OH)_3(CO_3)^-$, and $MO_2(CO_3)_2^{2-}$. The two latter species have been proposed by Maya for M = U and Np and they cannot explain our data.

Maya proposed a value $\log K_3 = 4.64$ for the reaction

$$NpO_2(CO_3)_2^{2-} + CO_3^{2-} \rightleftarrows NpO_2(CO_3)_3^{4-}$$

at $I = 1.0$ M. By using the specific-ion interaction theory and the interaction coefficients for the corresponding U(VI) complexes we can recalculate this value to $I = 3.0$ M (for the procedure, cf. ref 2); we obtain $\log K_3 = 4.63$. By combination of this value with the equilibrium constant for the reaction

$$3NpO_2(CO_3)_3^{4-} \rightleftarrows (NpO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$$

we obtain $\log K = 3.9$ for the reaction

$$3NpO_2(CO_3)_2^{2-} \rightleftarrows (NpO_2)_3(CO_3)_6^{6-}$$

From these data, we can calculate that $NpO_2(CO_3)_2^{2-}$ should predominate under the experimental conditions we have used (the degree of dissociation of the trinuclear complex is 98% and 61% at $B = 10^{-3}$ and 10^{-2} M, respectively), of Maya's constants are correct. It is obvious from our experimental data that the trinuclear complexes are predominating.

Maya has used data covering only two different Np(VI) concentrations (1.12 and 1.24 mM). By using such a small variation in the metal ion concentration, it is difficult to establish a unique chemical model in systems where polynuclear species are formed. For this reason we suggest that both the chemical interpretation and the numerical values of the equilibrium constants given by Maya are in error.

From the values of $\log K$ (cf. Table I), it is obvious that the stability range for the trinuclear complex increases in the order Pu(VI) > Np(VI) > U(VI); a similar conclusion can be drawn for the stability of the corresponding $(UO_2)_2(MO_2)(CO_3)_6^{6-}$ complexes; vide infra.

The formation of bimetallic carbonato complexes is not surprising in view of the chemical similarities of the three M(VI) ions. However, we were surprised to find that the Np(VI) parts of the spectra were practically identical for $(NpO_2)_3(CO_3)_6^{6-}$ and $(UO_2)_2(NpO_2)(CO_3)_6^{6-}$. This reflects, no doubt, the identical nearest-neighbor configurations around Np(VI) in the two complexes. We could not record the spectrum of $(PuO_2)_3(CO_3)_6^{6-}$ because of precipitation. However, the complex $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$ does not precipitate at the concentrations we have used, and its spectrum is given in Figure 2. We propose that the spectrum of $(PuO_2)_3(CO_3)_6^{6-}$ is very nearly the same.

There is no doubt that also other types of mixed complexes of the type $(MO_2)_{3-x}(M'O_2)_x(CO_3)_6^{6-}$ (x = 1, 2) can be prepared. By using equal amounts of U(VI) and Np(VI) both in 10–20-fold excess over Pu(VI), one should obtain $(UO_2)(NpO_2)(PuO_2)(CO_3)_6^{6-}$ as the predominant Pu(VI) species.

The ratio $[(UO_2)_2(MO_2)(CO_3)_6^{6-}]/[MO_2(CO_3)_3^{4-}] = K[UO_2(CO_3)_3]^2/[CO_3^{2-}]^3$ is independent of the total concentration of M(VI). This means that U(VI) may act as a very efficient solution "carrier" of M(VI) in the uranium concentration range where polynuclear complexes are formed. E.g., at $p_{CO_3^{2-}} = 5$, a value reasonable for a natural water system, and $[UO_2(CO_3)_3^{4-}] = 10^{-3}$ M, we find that 60% of Pu(VI) is present as $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$, independent of the total concentration of Pu(VI), provided U(VI) ≫ Pu(VI). Polynuclear uranium complexes should not be present in undisturbed natural water systems. The situation may be different in a repository for spent nuclear fuel, where one has a large source of uranium and possibly also an oxidizing near field region, due to radiolysis. When modeling the migration of actinides in such systems, it seems advisable to give some consideration to this "carrier" action.

It is obvious from the equilibrium data that the $(PuO_2)_3(CO_3)_6^{6-}$ complex has the broadest range of stability of the investigated M(VI) ions. The ability of Pu(VI) to stabilize the trinuclear structure can also be demonstrated by comparing the equilibrium constants for the reactions

$$2UO_2(CO_3)_3^{4-} + UO_2(CO_3)_3^{4-} \rightarrow (UO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-} \quad \log K = -11.63$$

$$2UO_2(CO_3)_3^{4-} + NpO_2(CO_3)_3^{4-} \rightleftarrows (UO_2)_2(NpO_2)(CO_3)_6^{6-} + 3CO_3^{2-} \quad \log K = -10.0$$

$$2UO_2(CO_3)_3^{4-} + PuO_2(CO_3)_3^{4-} \rightleftarrows (UO_2)_2(PuO_2)(CO_3)_6^{6-} + 3CO_3^{2-} \quad \log K = -8.8$$

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Supplementary Material Available: Tables Ia–Ie, giving primary experimental data for the spectrophotometric and potentiometric measurements (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectral Characterization of Tetracyanoferrate(II) and Tetracyanoferrate(III) Chelates with 1,3-Diamines

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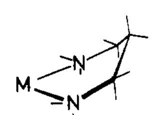
Low-spin tetracyano(diamine)ferrate(II) chelates and the corresponding Fe(III) chelates were prepared with four 1,3-diamines: 1,3-diaminopropane (tn), 1,3-diaminobutane (bn), *meso*-2,4-diaminopentane (*meso*-ptn), and (2*R*,4*R*)-diaminopentane (*R*-ptn). The Fe(III) chelates were prepared by oxidation of the Fe(II) chelates under acidic conditions. A CD spectrum of $[Fe(CN)_4(R\text{-ptn})]^{2-}$ showed two CD components of opposite signs at 22 200 and 26 000 cm^{-1} in the region of the first absorption band, which are ascribed to a λ-skew-boat conformation. A CD spectrum of $[Fe(CN)_4(R\text{-ptn})]^-$ is different from those of 1,2-diamine chelates in the CN → metal charge-transfer region but an MCD spectrum is analogous to those of 1,2-diamine chelates. ^1H and ^{13}C NMR of the Fe(II) chelates showed the preference of the chair conformation for the tn, bn, and *meso*-ptn chelates. Well-resolved signals were observed for the Fe(III) chelates in the regions between 40 and −10 ppm for the ^1H NMR and 210 and −50 ppm for the ^{13}C NMR spectra. The isotropic shifts are different from those found for Ni(II) chelates. The analysis of the isotropic shifts leads to an estimation of 50:50 contribution of λ-skew-boat and chair conformations for the *R*-ptn chelates.

Substitution of tris(diamine)iron(II) with strong coordination ligands, four cyano anions, leads to the formation of a low-spin Fe(II) chelate, tetracyano(diamine)ferrate(II).[1-3] Structural studies of the chelates have been carried out with several 1,2-diamines by using electronic, CD,[2,3] and ^1H and ^{13}C NMR spectroscopy.[4] These chelates exhibit an interesting chemical reactivity of an oxidative ligand dehydrogenation.[1] The oxidation under acidic and basic conditions leads to the corresponding metal-oxidized tetracyano(1,2-diamine)ferrate(III) and the ligand-oxidized tetracyano(1,2-diimine)ferrate(II), respectively.[1,3] A redox reaction of tetracyano(1,2-diamine)ferrate(III) takes place in basic solution and results in simultaneous formations of metal-reduced tetracyano(1,2-diamine)ferrate(II) and ligand-oxidized Fe(II) chelates, predominantly tetracyano(1,2-diimine)ferrate(II).[5,6] Different chemical behavior is expected for the oxidation of the 1,3-diamine chelates, because the dehydrogenation of a 1,3-diamine coordinated to a metal ion will yield a nonconjugative 1,3-diimine.

Low-spin tetracyanoferrate(II) chelates have been known with aromatic diimines, such as bipyridine (bpy) and 1,10-phenanthroline (phen),[7] and α-amino acids,[8] as well as 1,2-diamines. Studies on the 1,3-diamine chelates are desirable to extend the chemistry of this class of compounds.

The conformation of the six-membered chelate rings formed by 1,3-diamines has been the subject of many investigations. The geometry of the six-membered chelate rings is different from that of cyclohexane in the long metal–nitrogen bond length and the reduced nitrogen–metal–nitrogen bond angle. Four conformers, **1**–**4**, are conceivable for 1,3-diaminopropane (tn) chelates.



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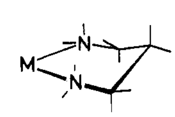

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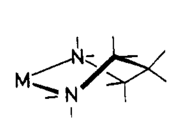

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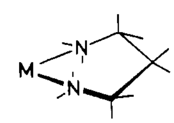

4

The boat form, **1**, suffers considerable steric repulsion between hydrogens of the masthead carbon atom and the apical ligand and has not been reported for the formation. The chair form, **2**, is the most sterically unhindered on a molecular force field calculation.[9] The skew-boat conformers, **3** and **4**, are chiral and are reported to be at slightly higher energy (6.7 kJ mol^{-1}) than the chair form.[9] Though the counterparts for cyclohexanes rarely exist, the occurrence of the skew-boat conformation has been demonstrated by the crystal structural analysis of $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$, where one of the three tn chelate rings takes a skew-boat and the other two take a chair conformation.[10]

Substitution of hydrogen atoms with methyl groups introduces steric interactions between the methyl groups and other atoms within the complex ion molecule. The methyl group equatorial to the chelate ring is sterically less hindered than the axial group. The chelate ring of *meso*-2,4-diaminopentane (*meso*-ptn) takes exclusively a chair form in which both methyl groups are equatorial. But for a chelate ring of *rac*-2,4-diaminopentane (*rac*-ptn), the preference of a chair form is incompatible with the preference of the equatorial orientation of a methyl group, because one of the two methyl groups should take an axial orientation in a chair form. Therefore a skew-boat is possible in which both the methyl groups take the equatorial orientation. The preference between

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