red crystals: UO~(COJ)~~, formed in the U(VI)-H2Mrbonate system, have and Pu(V1) systems have not been as extensively studied; however, electrode, a platinum-wire auxiliary electrode, and a saturated calomel
delivered twice from P2O5 under nitrogen. The supporting electrolyte, tetra-n-butylammonium perchlorate (TBAP), was recrystallized from EtOAc-hexane, dried, and stored in a desiccator.

Cyclic voltammetry. Reagent grade acetone was distilled twice from P2O5 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. Desorption 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.

Acknowledgment. Financial support from the Robert A. Welch Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank Professor John Bear and Dr. Mohammed Ashan for a generous gift of Rh2(OAc)4 and several stimulating discussions as well as the University of Houston NMR Institute for the 300-MHz NMR spectra.

Registry No. 2, 101348-67-8; 3, 101348-68-9; 4, 56644-59-8; 5, 16357-83-8; 6, 56826-69-8; 7, 529-34-0; 8, 101348-69-9; 9, 56658-47-3; 10, 101348-70-3; 11, 56644-58-7; 12, 101348-71-4; Rh2(OAc)4, 101348-72-6; Rh2(OAc)3[PF6], 101375-15-9; Rh2(OAc)3[12][PF6], 101348-75-8; Rh2(OAc)3, 15956-28-2; acetonaphthene, 98-86-2.

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

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Received November 4, 1985

The chemical composition of the trinuclear complexes (MO2)(CO3)64− and the equilibrium constants for the reaction 3MO2(CO3)3− = (MO2)(CO3)64− + 3CO2−, where M = Np or Pu, have been determined by spectrophotometric and emf methods. The values of the equilibrium constants at J = 3 M (NaClO4) and T = 22 ± 1 °C are log K3,6(Np) = −10.1 ± 0.1 and log K3,6(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 that of neptunium and plutonium, a fact that might be due to a lower stability of the limiting PuO~(COJ)~~. We have demonstrated the formation of mixed complexes of the type (M033(C03)66 and the equilibrium constants for the reaction 3M02(C03)3c = (M033(C03)66 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 UO2(CO3)64−, formed in the U(VI)-H2O-carbonate system, have been well-known for a long time.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. Simakin3 and Maya4 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 UO2(CO3)63− and the trimer6 (UO2)(CO3)64−. The trimer is strongly stabilized in solutions of high ionic strength,7 and it is this species that accounts for the very high solubility of UO2CO3(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 authors7 noticed a color change from green (the color of PuO2(CO3)63−) to red. Haag8 made similar observations on the Np(VI)-carbonate system and suggested that the red color was due to the complex NpO2(CO3)63−. Maya4 made a quantitative study of the Np(VI)-carbonate system and interpreted his data in terms of the formation of NpO2(CO3)63−, NpO2(CO3)64−, and a mixed complex (NpO23−(OH)3)2(CO3)−.

From the chemical similarities generally observed in the actinide series between elements of the same oxidation state (e.g. the

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2SSESD, CEN-FAR.

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of H*+ 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 NaClO₄ medium.

The carbonate systems were studied at constant partial pressure of CO₂(g), as described before.6 Notations

- ε is the molar absorptivity,
- a is the partial pressure of CO₂(g) in the test solutions,
- A is the optical absorption per centimeter.

Materials and Analysis. Neptunium(VI) (100% 237Np) and plutonium(VI) (isotope composition in atom %: 24Pu, 0.115; 239Pu, 76.772; 240Pu, 19.882; 241Pu, 2.508; 242Pu, 0.723) perchlorate solutions were prepared from acid stock solutions by evaporation with HClO₄ until most of the excess acid had been removed. The concentrated solution was dissolved in 0.1 M HClO₄, and this solution was immediately analyzed spectrophotometrically for Np(VI)–Np(V) or Pu(VI)–Pu(V). More than 99.7% of the actinides were in oxidation state +6. The solid carbonates MO₂CO₃(s) were then precipitated by addition of NaHCO₃ to the fresh perchlorate solutions in order to avoid reduction by water or through radiation. The precipitates, brown for Na₂U₂CO₇(s) and light tan for PuO₂CO₃(s), were washed on a filter with H₂O and then dissolved in a carbonate/bicarbonate solution of accurately known composition. The carbonate concentration was sufficiently high to obtain the limiting complex MO₂(CO₃)$- only. The total concentration of neptunium was determined spectrophotometrically after reduction to Np(V) with hydrazine,11 while the total concentration of Pu(VI) was determined by acidifying a sample with HClO₄ and measuring the light absorption at 380 nm. From the known concentrations of Np(VI) and Pu(VI) and the initial concentrations of carbonate/bicarbonate one can calculate the precise composition of the carbonate stock solutions. These can be kept for several weeks without any noticeable change in the oxidation state of the actinides. The procedure outlined above is simpler and probably more precise than the methods involving the precipitation of MO₂$+(aq) and the dissolution of this in carbonate/bicarbonate.11 Uranium(VI) solutions were prepared and analyzed as described before.9 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. CO₂(g)–N₂(g) mixtures with 100%, 30%, and 10% CO₂(g) of known analytical composition were obtained from Air Liquid. The analytical precision was ±0.6% and ±0.2% at the 10% and 100% 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 HClO₄ or 2.000 M NaClO₄. All titrations were made at known partial pressure of CO₂(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 system11 available and had instead to take out samples for the spectrophotometric measurements. We then bubbled CO₂(g) through the cuvettes for a few minutes, in order to resaturate the solutions with CO₂, 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 TCBCl11/HS/ta, 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 NaClO₄. The glass electrode was calibrated in concentration units by using solutions of accurately known hydrogen ion concentration, either a 10.00 M HClO₄ + 2.990 M NaClO₄ solution or a 5.000 mM NaHCO₃ + 2.950 M NaClO₄ solution. The latter was used with CO₂(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 0.5–1.0 mV. The errors in the Np system tend to be lower due to 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 PuO₂CO₃(s), and most of the tests 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 H+ and M(VI) ions, which could be determined directly, due to the early precipitation of PuO₂CO₃(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.9 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 1000 M HClO₄ + 2.000 M NaClO₄ solution at pCO₂ = 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(V) and U(VI)–Pu(V) complexes were studied by spectrophotometric titrations of test solutions of the following compositions: [UO₂(CO₃)₃]$4- = 23.96 mM, [NpO₂(CO₃)₃]$4- = 4.52 mM, [HCO₃]- = 120.06 mM and [UO₂(CO₃)₃]$4- = 25.46 mM, [PuO₂(CO₃)₃]$4- = 1.02 mM, [HCO₃]- = 122.2 mM; with 1.000 M HClO₄ + 2.000 M NaClO₄. 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 polymeric 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 MO₂$+ per two UO₂$+. By making a spectrophotometric titration on a solution of known composition of U(VI) and M(VI), we can easily detect the formation of bimetallic complexes. If the log (A/B) vs. log (a/A) 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 (MO₂)₃(CO₃)₆$- and (UO₂)₃(MO₂)₃(CO₃)₆$- 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 the colored species. The molar absorptivity A/B was found to be a function of a/h² (cf. Figures 3 and 4), which indicates that the complexes formed

Metal-Carbonate Complexes

Figure 1. Absorption spectra of Np(VI)-carbonate solutions at varying concentrations of HCO₃⁻.

\[ A = 16.78 \text{ mM}; \log \alpha h² = 13.804; 100\% \text{ CO}_2 \]
\[ B = 8.50 \text{ mM}; \log \alpha h² = 14.154; 100\% \text{ CO}_2 \]
\[ C = 8.50 \text{ mM}; \log \alpha h² = 14.666; 30\% \text{ CO}_2 \]
\[ D = 1.02 \text{ mM} \text{ and } 1.02 \text{ mM} \text{ respectively} \]

Figure 2. Absorption spectra of Pu(VI)-carbonate solutions and a U(VI)-Pu(VI)-carbonate solution, where the predominant Pu species is \((\text{UO}_2)_2(\text{PuO}_2)(\text{CO}_3)_6^{8-}\).

Figure 3. Experimental value of \( \log (A/B) \) vs. \( \log (\alpha/h²) \) 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 with \( L = c_2/c_1 = 1.0 \). The equilibrium constant \( K = 42.8 \pm 0.1 \).

\[ \log (A/B) = \beta_{1,6,3,12} \alpha h² \]
\[ \log (\alpha/h²) = \beta_{1,6,3,12} \alpha h² \]

Figure 4. Experimental values of \( \log (A/B) \) vs. \( \log (\alpha/h²) \) at 700 nm for the Np(VI)-carbonate system.

Figure 5. Experimental values of \( \log (A/B) \) vs. \( \log (\alpha/h²) \) 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 \( L = c_2/c_1 = 1.0 \). The equilibrium constant \( K = 45.4 \pm 0.2 \).

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 1. The displacement toward higher values of \( \log (\alpha/h²) \) 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 1.

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

\[ B = \beta_{1,6,3,12} \alpha h² + 3\beta_{1,6,3,12} \alpha h² \]
\[ A = \epsilon_3 \beta_{1,6,3,12} \alpha h² + \epsilon_6 \beta_{1,6,3,12} \alpha h² \]
**Table I. Equilibrium Constants and Molar Absorptivities for Complexes in the U(VI)–Np(VI)–Pu(VI)–H₂O–Carbonate System**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
<th>U(VI)</th>
<th>Np(VI)</th>
<th>Pu(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3MO₄(CO₃)₄⁶⁺ + 6H⁺</td>
<td>41.5 ± 0.1</td>
<td>42.8 ± 0.1</td>
<td>45.4 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>(MO₄)₂(CO₃)₆⁺ + 3CO₂(g) + 3H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3MO₄(CO₃)₄⁺ = (MO₄)₂(CO₃)₆⁺ + 3CO₂</td>
<td>-11.3 ± 0.1</td>
<td>-10.0 ± 0.1</td>
<td>-7.4 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>2UO₂(CO₃)₃⁻ + MO₄(CO₃)₆⁺ = (UO₂)(MO₄)(CO₃)₆⁻ + 3CO₂</td>
<td>-11.3 ± 0.1</td>
<td>-10.0 ± 0.1</td>
<td>-8.8</td>
<td></td>
</tr>
</tbody>
</table>

*All data refer to a temperature of 22 ± 1 °C and a 3.00 M NaClO₄ medium. The equilibrium constants involving carbonate ions were calculated by using log K = -17.61 for the reaction CO₂(g) + H₂O ↔ CO₃⁻ + 2H⁺.

After introduction of the normalized variables u and v (cf. ref 10), where u = β₁₆₈₄(b/a²) and v = β₁₂₁₃b²(a/h²), we obtain

\[
\frac{\log A}{B} = \log \varepsilon_1 + \log \frac{u + L_0}{u + 3v} = \log \varepsilon_1 + Y
\]

where L = ε₂/ε₁. Elimination of b from the expressions for u and v gives

\[
u = \frac{\beta_{1213}}{\beta_{1684}} \left( \frac{a}{h²} \right)^{-3}
\]

i.e.

\[
\log \left( \frac{a}{h²} \right) = 0.5 \log K + \log u - 0.5 \log v = 0.5 \log K + X
\]

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/h²), we can easily determine whether the proposed model is correct and also the position of the best fit. The log (a/h²) value corresponding to X = 0 then gives log K = 3 log (a/h²); cf. eq 4.

**The Neptunium(VI)–Carbonate System.** There are pronounced changes in the absorption spectrum of Np(VI) in the [HCO₃]⁻ range 5–100 mM; cf. Figure 1. On decrease of [HCO₃]⁻ 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.³ This color is probably due to the formation of colloidal NpO₂CO₃, 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. NpO₂CO₃(s) is more soluble than PuO₂CO₃(s), and it was possible to obtain good direct determinations of ε₁ and ε₂ (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 (Pco₂/H²⁺) is slightly better at 700 nm, possibly being due to the presence of a small quantity of colloidal NpO₂CO₃(s), which will affect the data at lower wavelengths more than at higher. Both wavelengths gave the same value, log K = 42.8 ± 0.1, for the equilibrium constant for the reaction

\[
3\text{NpO}_2(\text{CO}_3)_3^{6-} + 6\text{H}^+ = (\text{NpO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_2(g) + 3\text{H}_2\text{O}
\]

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

**The Plutonium(VI)–Carbonate System.** PuO₂CO₃(s) is much less soluble than NpO₂CO₃(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 ε₁ could be determined directly, while ε₂ had to be estimated from the curve shape by calculating normalized curves with various values of ε. This procedure was not very precise, and the first curve fitting gave log K = 45.2 ± 0.2, and ε₂ = 0.75 ± 0.25.

From the presence of an isosbestic point, the curve shape, and the data obtained at different partial pressures of CO₂(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 ε₁, we measured the absorption spectrum in a solution where 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

\[
\frac{A}{B} = \varepsilon_1 (n - 2) + \varepsilon_2 \frac{3}{3} (3 - n)
\]

where n = Z/2 is the average number of bonded carbonate ligands per Pu(VI). We obtain ε₁ = 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 ± 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 experiments. This is due both to the larger errors in the log [H⁺] measurements and to a somewhat larger error in the absorbivity 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

\[
3\text{PuO}_2(\text{CO}_3)_3^{6-} = (\text{PuO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_2^{2-}
\]

\[
k_{3,6} = \frac{3 - \varepsilon_1}{(n - 2)^3}
\]

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

The average value of log K₃,₆ is equal to −7.6 ± 0.3, which corresponds to log K = 45.2 ± 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/h²) and Z (or n). An error of ±0.1 in log [H⁺] will typically cause an error in Z around ±40.16. 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 λ > 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/h²), 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/h²); 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/h²), 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 (NpO₂)(CO₃)₆⁻ (ε₁/3 = 46.0 ± 0.1) and (PuO₂)(CO₃)₆⁻ (ε₁/3 = 56.0 ± 0.1), indicating a composition (UO₂)(MO₂)(CO₃)₆⁻ for the bimetallic complexes. This hypothesis was tested by calculating the equilibrium constant for the reaction

\[
2\text{UO}_2(\text{CO}_3)_3^{6-} + \text{MO}_2(\text{CO}_3)_3^{6-} = (\text{UO}_2)(\text{MO}_2)(\text{CO}_3)_6^{6-} + 3\text{CO}_2^{2-}
\]
Figure 6. Normalized curves for five different two-complex models: 
NpO₂(NO₃)₃⁴⁻ and (NP0₂)₃(CO₃)₆⁶⁻; (NP0₂)₃(NO₃)₆⁶⁻; (NP0₂)₅-
(CO₃)₁₀⁻; (NP0₂)₃(OH)CO₃⁻; NpO₂(NO₃)₅⁻. X and Y denote functions
defined by the normalized variable u = w and the total metal ion
concentration B. For the MO₂(CO₃)₄⁻(MO₂)₃(CO₃)₆⁶⁻ model we have Y = log [(n + Lu)/(u + 3c)] 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'/h², and the
known equilibrium constants for the U(VI)–carbonate system.
We have

\[ B_u = [UO₂(CO₃)₅⁻] + 3[UO₂(CO₃)₆⁶⁻] + 2[UO₂(MO₂(CO₃)₆⁶⁻] \]
\[ B_M = [MO₂(CO₃)₄⁻] + [UO₂(MO₂(CO₃)₆⁶⁻] \]
\[ A = (UO₂(MO₂(CO₃)₆⁶⁻)] + [UO₂(MO₂(CO₃)₆⁶⁻] \]

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 ± 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 MO₂(CO₃)₆⁶⁻ and (MO₂)₃-
(CO₃)₆⁶⁻ with M = Np or Pu. There are no indications of the
formation of ternary complexes containing both hydroxide and
carbonate as previously suggested by Maya⁴ in the Np(VI)–
carbonate system or hydroxide and bicarbonate as suggested by
Sullivan et al.⁴ 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.⁵,¹⁰ Figure 6 shows normalized curves for some of the
chemical models tested and it is obvious that the curve shapes
are very different for (MO₂)₃(CO₃)₆⁶⁻, (MO₂)₃(OH)CO₃⁻, and
MO₂(CO₃)₅⁻. 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 K₁ = 4.64 for the reaction

\[ \text{NpO₂(CO₃)₅⁻ + CO₃}^2- \rightarrow \text{NpO₂(CO₃)₆⁶⁻} \]

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,
ref 2); we obtain log K₁ = 4.63. By combination of this value
with the equilibrium constant for the reaction

\[ 3\text{NpO₂(CO₃)₅⁻} + C0₃^2- \rightarrow (\text{NpO₂})₄(CO₃)₆⁶⁻ + 3\text{CO₃}^2- \]

we obtain log K = 3.9 for the reaction

\[ 3\text{NpO₂(CO₃)₅⁻} + C0₃^2- \rightarrow (\text{NpO₂})₄(CO₃)₆⁶⁻ + 3\text{CO₃}^2- \]

From these data, we can calculate that NpO₂(CO₃)₅⁻ would
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 tri-
nuclear complexes are predominating.

Maya has used data covering only two different Np(VI) con-
centrations (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 1), 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 (UO₂)(MO₂(CO₃)₆⁶⁻
complexes; vide infra.

The formation of bimetallic carbonate complexes is not sur-
prising 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 (NP0₂)(CO₃)₆⁶⁻ and
(UO₂)(NP0₂(CO₃)₆⁶⁻. This reflects, no doubt, the identical
nearest-neighbor configurations around Np(VI) in the two com-
plexes. We could not record the spectrum of (PuO₂)(CO₃)₆⁶⁻
because of precipitation. However, the complex (PuO₂)₃-
(PuO₂)(CO₃)₆⁶⁻ does not precipitate at the concentrations we have
used, and its spectrum is given in Figure 2. We propose that the
spectrum of (PuO₂)(CO₃)₆⁶⁻ is very nearly the same.

There is no doubt that also other types of mixed complexes of
the type (MO₂)₃-M'(MO₂)(CO₃)₆⁶⁻ (x = 1, 2) can be prepared.
By using equal amounts of U(VI) and Np(VI) both in 10⁻²-fold
excess over Pu(VI), one should obtain (UO₂)(NP0₂(PuO₂-
(CO₃)₆⁶⁻ as the predominant Pu(VI) species.
The ratio \[ [UO₂(MO₂)(CO₃)₆⁶⁻]/[MO₂(CO₃)₆⁶⁻] = K
[UO₂(CO₃)₅⁻]/[CO₃] \] 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 pCO₃ = 5, a
value reasonable for a natural water system, and \[ [UO₂(CO₃)₅⁻] = 10⁻³ M, \]
we find that 60% of Pu(VI) is present as (PuO₂)₃-
(PuO₂)(CO₃)₆⁶⁻, 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 (PuO₂)(CO₃)₆⁶⁻
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

\[ 2\text{UO₂(CO₃)₅⁻ + UO₂(CO₃)₅⁻ ↔ UO₂(CO₃)₆⁶⁻ + 3CO₃}^2- \]

\[ log K = -11.63 \]

\[ 2\text{UO₂(CO₃)₅⁻ + NpO₂(CO₃)₅⁻ ↔ (UO₂)₄(NpO₂(CO₃)₆⁶⁻ + 3CO₃}^2- \]

\[ log K = -10.0 \]

\[ 2\text{UO₂(CO₃)₅⁻ + PuO₂(CO₃)₅⁻ ↔ (UO₂)₄(PuO₂(CO₃)₆⁶⁻ + 3CO₃}^2- \]

\[ log K = -8.8 \]
Synthesis and Spectral Characterization of Tetracyanoferrate(II) and Tetracyanoferrate(III) Chelates with 1,3-Diamines

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Received March 4, 1985

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 (2R,4R)-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-ptn)]⁺ 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 skew-boat conformation. A CD spectrum of [Fe(CN)₄(R-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 ¹³C 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 but for the ¹H NMR and 210 and -50 ppm for the ¹³C 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 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). Structural studies of the chelates have been carried out with several 1,2-diamines by using electronic, CD, and ¹H and ¹³C NMR spectroscopy. These chelates exhibit an interesting chemical reactivity of an oxidative ligand dehydrogenation. 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-diamine)ferrate(II), respectively.

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-diamine)ferrate(II). 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-diamine.

Low-spin tetracyanoferroferrate(II) chelates have been known with aromatic diimines, such as bipyridine (bpy) and 1,10-phenanthroline (phen), and ¹H and ¹³C NMR studies of 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.