EXAFS Studies of Pentavalent Neptunium Carbonato Complexes. Structural Elucidation of the Principal Constituents of Neptunium in Groundwater Environments

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The vast majority of transuranic elements are produced in commercial nuclear reactors utilizing uranium-based fuels, and the spent fuel and decay products are expected to be stored in deep geologic repositories.[2] Neptunium is the most problematic actinide element with respect to environmental migration[2,3] because its solubility under typical groundwater conditions is expected to be high enough to be of radiological concern,[4] and its sorption on common minerals is expected to be relatively low.[5] Under most environmental conditions, Np will be present as the pentavalent trans dioxo (i.e., neptunyl) cation, NpO_2^+.[6] Carbonate is an important natural ligand because of its relatively high concentration[3,6] and strong actinide-complexing ability.[3,6,7] Therefore, carbonato complexes of Np(V) are expected to play an important role in the fate and transport of Np in natural aquatic environments.

Neptunium solubility in carbonate solutions is controlled by the formation of solids of general formula $M_{2n-1}NpO_2(CO_3)_n$,[8] whose features have been reviewed.[6] The limited solubilities (10^{-4}−10^{-7} M)[9,10] of these phases make the solution species in equilibrium with the solids very difficult to study using common structural methods. We find that alkali metal free synthesis employing the tetrabutylammonium (TBA)[11] cation provides 10^{-3} M solutions of $NpO_2(CO_3)^-$ and $NpO_2(CO_3)_2^{3-}$.[12] These relatively high solubilities are unprecedented and afford the opportunity to determine the molecular structures of these environmentally important complexes employing EXAFS spectroscopy. The near-IR absorption spectra of NpO_2^+, $NpO_2(CO_3)^-$ (**I**), $NpO_2(CO_3)_2^{3-}$ (**II**), and $NpO_2(CO_3)_3^{5-}$ (**III**) in $NaClO_4$[10,13] and $TBA(NO_3)$ electrolyte solutions are nearly identical, indicating that the same species are present in both solutions. Known thermodynamic constants were used to prepare single-component solutions,[10] and near-IR spectra were measured both before and after EXAFS analysis to confirm that each solution sample contained a single, pure neptunyl carbonato species.

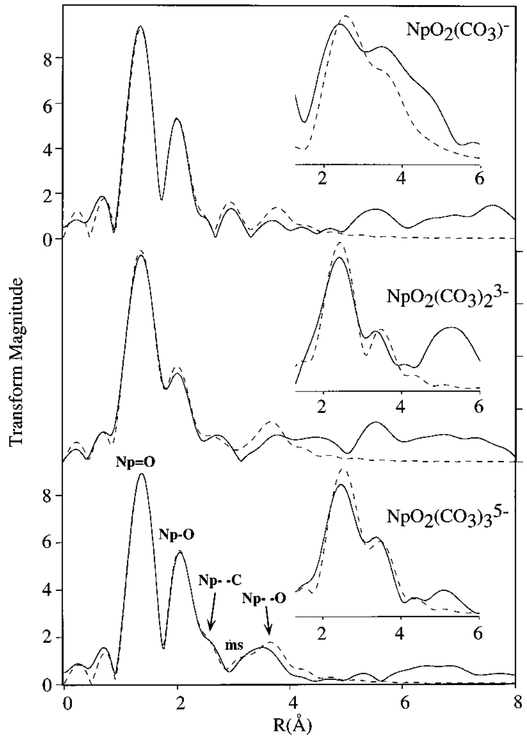

Figure 1. Comparison of the Fourier transforms of the experimental data (solid line) with those of the theoretical signal (dashed line) for $NpO_2(CO_3)^-$ and $NpO_2(CO_3)_2^{3-}$ in $TBA_2(CO_3)$ solution and $NpO_2(CO_3)_3^{5-}$ in $Na_2(CO_3)$ solution. Insets for all spectra show data (solid line) and fits (dashed line) after subtraction of the strong O═Np═O and equatorial Np—O shells.

X-ray absorption measurements of 0.001 M Np solutions were performed at the Np L_{III} edge.[14] The absorption edge and E_0 of all spectra were assigned to 17 616.16 and 17 625 eV on the basis of calibration against a Zr foil.[15] EXAFS Fourier transforms (not phase shift corrected) for **I**−**III** are shown in Figure 1. Curve-fitting amplitudes and phases were calculated using FEFF6.[16] To maximize and conserve the significance of

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[11] $^{13}CO_2$ (6.0 g, 0.136 mol) was slowly transferred into 150 mL (0.231 mol) of aqueous 40% tetrabutylammonium hydroxide at −78 °C in an evacuated vessel and stirred for 12 h. The solvent was removed under vacuum and the product isolated by triturating the residue with ethyl acetate and recrystallizing from ethyl acetate.

[12] Np was purified using ion chromatography of Np(IV) in 9 M HCl ($NpCl_6^{2-}$) and eluted using 0.5 M HCl. Purified Np(IV) was oxidized to Np(VI) in fuming $HClO_4$ and electrochemically reduced to Np(V). The Np(V) was analyzed spectrophotometrically (A_{max}) and the Np(V) concentration determined at 980 nm (ϵ = 395 M^{-1} cm^{-1}). Np(V) was precipitated using TBA(OH), centrifuged, and washed with distilled water. The hydroxide was dissolved using HNO_3. The precipitation/dissolution process was repeated three times to produce a sodium-free Np(V) solution.

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[14] EXAFS fluorescence data (295 K) were recorded at the Stanford Synchrotron Radiation Laboratory (SSRL): unfocused beamline 4-2, Si(220) double-crystal monochromator, 3.0 GeV, 60−100 mA. EXAFS signals for each of the two-body and three-body configurations were calculated on the basis of crystallographic distances and angles. Individual signals with significant contributions (see text) were summed to generate the total theoretical EXAFS signal, which was then fitted to the experimental data by varying distances, angles, Debye−Waller factors, and nonstructural parameters.

[15] Spectra are the averages of four scans collected with 7 Ge detector elements (Canberra). χ was calculated as the difference between a spectrum and a two-region polynomial spline fit from ca. 30 eV to 10.7 $Å^{-1}$ above E_0.

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Table 1. Summary of EXAFS Results[a] for $NpO_2(CO_3)_n^{(2n-1)-}$ Fitted to k^3

	$NpO_2(CO_3)_3^{5-}$			$NpO_2(CO_3)_2^{3-}$			$NpO_2(CO_3)^-$		
bond	r (Å)	σ (Å)	n	r (Å)	σ (Å)	n	r (Å)	σ (Å)	n
Np═O	1.86(2)	0.03(2)	2[b]	1.85(2)	0.05(2)	2[b]	1.84(2)	0.03(2)	2[b]
Np—O	2.53(3)	0.116	6−7[b]	2.48(3)	0.133	6−7[b]	2.49(3)	0.089	4−5[b]
Np- -C	2.98(3)	0.02[b]	2.7(0.6)	2.93(3)	na[c]	<2.5	2.94(3)	na	<2
Np- -O	4.22(3)	na	3(0.6)	4.18(3)	na	1.5(0.6)	4.24(3)	na	na

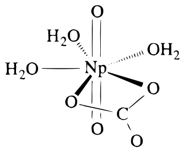
[a] ΔE_0 for Np═O = −3.0 eV ± 4.8 eV; Np—O = 1.5 eV ± 2.3 eV; Np- -C = 2.0 eV ± 3.0 eV; Np- -O = −2.5 eV ± 2.4 eV. Uncertainties were calculated as the change in the parameter from the reported value that results in a 10% decrease in the quality of the fit based on the contribution for that shell. [b] Fixed at this value. [c] Not applicable.

individual waves, structural parameters (Table 1) were obtained by fitting from $k = 2.5$ to 10.5 $Å^{-1}$ for the NpO_2^+ moiety, 2.5 to 8.8 $Å^{-1}$ for the equatorial O, and 2.5 to 8.0 $Å^{-1}$ for the C and distal O, subtracting out the contribution from each shell as the range was decreased. Curve-fitting was complicated by noise resulting from measuring dilute solutions enclosed in several layers of radiological containment, and the proximity of the equatorial and distal O and C shells to the O═Np═O multiple-scattering (ms) shell.

For the tris complex $NpO_2(CO_3)_3^{5-}$ (**III**) (Figure 1, bottom), assignment of shells corresponding to a hexagonal bipyramidal coordination of the NpO_2^+ ion is straightforward. The first shell, at 1.86 Å, corresponds to two trans neptunyl O atoms (Table 1), while the second shell, at 2.53 Å, arises from six O atoms in the equatorial plane. The three C and distal O atoms give rise to the third and fourth shells, at 2.98 and 4.22 Å. Inclusion of an O═Np═O ms shell (3.7 Å) was essential to the fit as observed in uranyl systems.[17] It was previously suggested that the carbonate ligands in **III** were coordinated in a monodentate fashion.[18] The EXAFS data, however, show unequivocally that the carbonate ligands must be coordinated in a bidentate fashion based on the combination of six Np—O and three Np- -C distances of 2.53 and 2.98 Å, respectively. The Np═O distance of 1.86 Å is in agreement with that observed (1.85 Å) in EXAFS studies of the NpO_2^+ aquo ion.[19] The Np—O, Np- -C, and Np- -O distances (Table 1) compare favorably to 2.55, 2.97, and 4.29 Å seen in the solid state structure of $K_3NpO_2(CO_3)_2$, where hexagonal bipyramidal coordination and bidentate carbonate ligation were observed.[8d]

Fitting the bis- and monocarbonato complexes proved more difficult. Np═O shells at 1.85 and 1.84 Å were observed along with equatorial Np—O shells of 2.48 and 2.49 Å (Table 1). Of significance is a distinct change in coordination geometry about the neptunyl ion, from six O atoms in the tris- and biscarbonato complexes, to five O atoms in the monocarbonato complex (Table 1). Based on the ubiquitous dioxo unit, the number of neptunyl O atoms was fixed at 2 and the Debye−Waller factor allowed to vary. Coordination numbers (cn) were obtained by comparisons in R space of the data and models, fixing cn's at integers between 4 and 7 and allowing the Debye−Waller factor to vary, and selecting those showing the best correspondence between data and model. These assignments were corroborated by observation of a relatively low amplitude of the equatorial oxygen wave **I** and equal amplitudes for **II** and **III** at low k. Fits to the C and distal O atoms in these complexes were less accurate, but phases matching those expected for third and fourth shells at chemically reasonable distances were always found (Figure 1). This was confirmed by direct comparison in both k and R space of the fit for each shell with the residual EXAFS after subtraction of the other components (Figure 1 insets). A match between the phase of the model and the residual spectrum was always observed, and the resulting distances were reported (Table 1). Amplitude information was not reported in cases where the amplitude was questionable. Consistent with the lower amplitude of the C and distal O features, the certainty of these results is greatest for **III**, poorest for **I**.

Thermodynamic data establish the stoichiometry of **I**−**III**,[10] near-IR spectra verify that individual EXAFS solutions of **I**−**III** contain a single species, and EXAFS spectra provide structural details. The change in coordination number in the equatorial plane in **I** relative to **II** and **III** is not expected, yet reasonable. Bidentate carbonate ligation is indicated by the Np- -C distances of 2.93−2.98 Å (Table 1). Finally, with two O per bidentate carbonate ligand, the remainder of O atoms in the equatorial plane of Np must correspond to H_2O molecules, yielding our proposed molecular structures for **I**−**III**.



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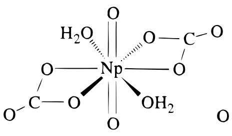
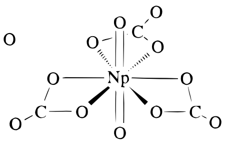


II



III

These carbonato complexes of Np(V) have been known for over a decade,[6] and this work represents the first elucidation of the molecular structures of these environmentally important compounds in solution. The structural information reported here may enable more accurate modeling of neptunyl carbonate reactivity and provides structural models with which to study the sorption and transport properties of Np(V) at the water−mineral interface. Research on the corresponding pentavalent plutonium system is in progress.

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Supporting Information Available: Figures of near-IR spectra, FEFF6 fits, and experimental data (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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