

XAFS Structural Determination of Np(VII). Evidence for a Trans Dioxo Cation Under Alkaline Solution Conditions

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From an historical perspective, the chemistry of actinide ions under acidic conditions is relatively well-known,² and near-neutral solution chemistry has received considerable attention due to its relevance to radioactive waste isolation and disposal.³ In contrast, actinide solution chemistry under strongly alkaline conditions, such as those found in aging waste tanks within the DOE complex, is poorly understood. Alkaline conditions can stabilize high oxidation states such as V, VI, and even VII.⁴ The heptavalent oxidation state of actinide ions is rare, but has been known since the late 1960's.⁵ Single crystal X-ray structures have been determined for $\text{Na}_3\text{NpO}_4(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ⁶ and $\text{Co}(\text{NH}_3)_6\text{NpO}_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$,⁷ which display the highly unusual tetragonal bipyramidal $\text{NpO}_4(\text{OH})_2^{3-}$ central core (I) in the solid state. However, from alkaline solution, one can also isolate infinite chains such as $\text{LiCo}(\text{NH}_3)_6\text{Np}_2\text{O}_8(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (II),⁸ or layered solids such as MNpO_4 (M = Cs, K) which, based on marginal Rietveld refinement (R=12.1), is reported to contain a NpO_2^{3+} central core (III).⁹ No simple anion of formula NpO_4^- (IV), akin to MO_4^- (M = Re, Tc, Mn), has been observed. Based on the solid state structure of I, it has been argued that I must exist in alkaline solution.^{6,7} There are no data to support this claim. We report here an XAFS study to determine the structure of Np(VII) in alkaline solution.

Alkaline Np(VII) solutions (0.03 M) were prepared by bubbling O_3 through a 2.5 M NaOH solution containing $\text{NpO}_2(\text{OH})_2$,¹⁰ and the resulting dark green solution was characterized by using UV–Vis–NIR spectroscopy. Solution spectra revealed absorption maxima at 410 ($\epsilon = 1350 \text{ M}^{-1} \text{ cm}^{-1}$) and 625 nm ($\epsilon = 385 \text{ M}^{-1} \text{ cm}^{-1}$), consistent with previous reports of alkaline Np(VII) solutions.⁵ These solutions are stable for

(1) (a) LANL Mail Stop G739. (b) G. T. Seaborg Institute. (c) LANL Mail Stop D429. (d) LANL Mail Stop J514.

(2) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements*; Chapman and Hall: London, 1986.

(3) Clark, D. L.; Hobart, D. E.; Neu, M. P. *Chem. Rev.* **1995**, *95*, 25–48.

(4) Peretruchin, V. F.; Shilov, V. P.; Pikaev, A. K. Alkaline chemistry of transuranic elements and technetium and the treatment of alkaline radioactive wastes, Westinghouse Hanford Company, WHC-EP-0817, 1995.

(5) Spitsyn, V. I.; Gelman, A. D.; Krot, N. N.; Medfodiyeva, M. P.; Zakharova, F. A.; Komkov, Y. A.; Shilov, V. P.; Smirnova, M. P. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2733–2745.

(6) (a) Tomilin, S. V.; Volkov, Y. F.; Kapshukov, I. J.; Rykov, A. G. *Radiokhimiya* **1981**, *23*, 862–867; *Engl. Transl.* **1981**, *23*, 695–699. (b) *Radiokhimiya* **1981**, *23*, 704–709; *Engl. Transl.* **1981**, *23*, 570–574. (c) *Radiokhimiya* **1981**, *23*, 710–715; *Engl. Transl.* **1981**, *23*, 574–578.

(7) Grigor'ev, M. S.; Gulev, B. F.; Krot, N. N. *Radiokhimiya* **1986**, *28*, 690–694; *Engl. Transl.* **1986**, *28*, 630–634.

(8) Burns, J. H.; Baldwin, W. H.; Stokely, J. R. *Inorg. Chem.* **1973**, *12*, 466–469.

(9) Grigor'ev, M. S.; Glazunov, M. P.; Krot, N. N.; Gavrish, A. A.; Shakh, G. E. *Radiokhimiya* **1979**, *21*, 665–667; *Engl. Transl.* **1979**, *21*, 576–578.

(10) ²³⁷Np was purified with use of ion exchange chromatography of Np(IV). NpCl_6^{2-} was loaded onto the column, washed with 6 M HCl, and Np(IV) eluted with 0.5 M HCl. Purified Np(IV) was oxidized to Np(VI) by fuming HClO_4 . The Np(VI) was analyzed and quantified spectrophotometrically ($\lambda_{\text{max}} = 1200 \text{ nm}$, $\epsilon = 47 \text{ M}^{-1} \text{ cm}^{-1}$). $\text{NpO}_2(\text{OH})_2$ was precipitated with NaOH, centrifuged, and washed with distilled water.

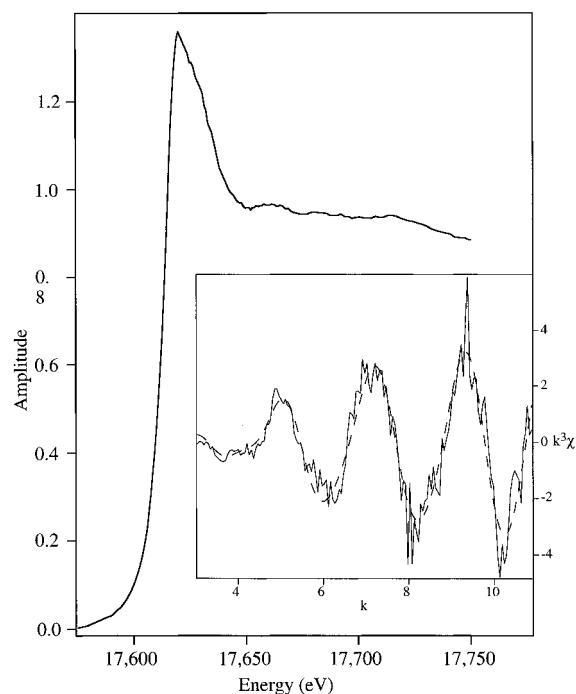
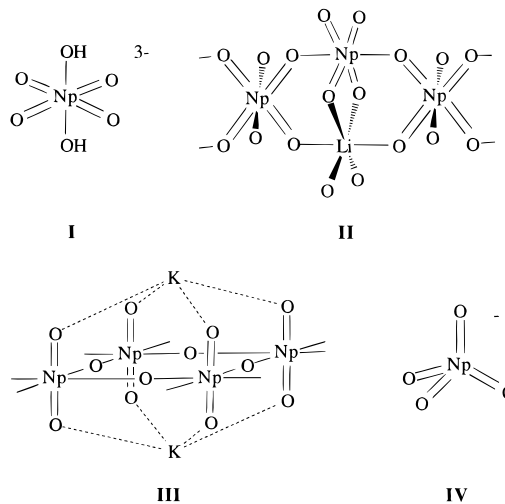


Figure 1. XANES and k^3 -weighted EXAFS (inset) spectra of Np(VII) in 2.5 M NaOH solution. For the EXAFS spectra (inset), the solid line is the data, and the dashed line is the fit.

several months when sealed under an O_3 atmosphere. X-ray absorption measurements of these Np(VII) solutions were performed at the Np L_{III} -edge,¹¹ and calibrated against a Zr foil.¹² Curve-fitting amplitudes and phases were calculated with FEFF6.¹³



The X-ray absorption near-edge structure (XANES) of the Np(VII) solution is shown in Figure 1, where it can be seen

(11) EXAFS fluorescence data were recorded at 295 K at the Stanford Synchrotron Radiation Laboratory (SSRL): unfocused beamline 4-2, Si-(220), double-crystal monochromator, 3.0 GeV, 60–100 mA. Spectra are the average of four scans collected with 7 Ge detector elements.

(12) The Np L_{III} edge spectrum was normalized by setting the value of a polynomial fit through the pre-edge region to zero and that of a polynomial fit through the EXAFS region to unity at 17700 eV. The spectrum was calibrated by setting the first inflection point in the spectrum for an external Zr foil to 17999.35 eV.

(13) (a) Rehr, J. J.; Mustre de Leon, J.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135. (b) Mustre de Leon, J.; Rehr, J. J.; Zabinsky, S. I.; Albers, R. C. *Phys. Rev. B* **1991**, *44*, 4146. ΔE_0 values, σ values, and scale factors for the different shells were fixed at values optimized from the examination of a large number of L_{III} edge spectra of Np compounds.

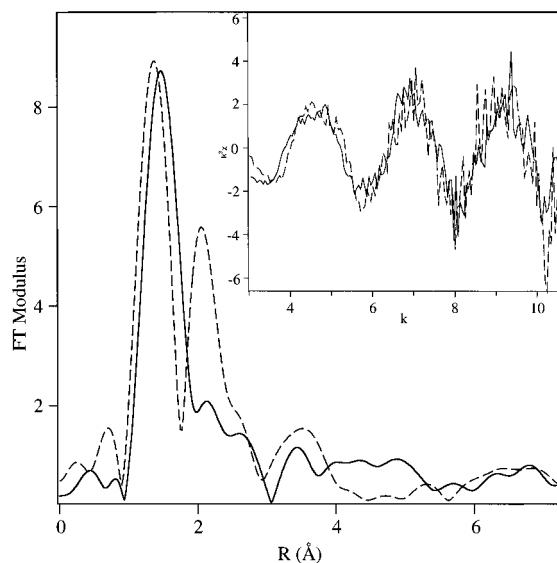


Figure 2. Background-subtracted k^3 -weighted EXAFS spectra of Np(V) tris-carbonato complex (dashed line), and Np(VII) in 2.5 M NaOH solution (solid line). The inset shows a comparison of the isolated EXAFS for the O=Np=O shell for both species; the nearly identical amplitudes are consistent with two oxo units in both species.

Table 1. Summary of EXAFS Results^a for Np(VII) Green Solution Fit to k^3 ($k = 3-11$)

bond	r (Å)	σ (Å)	n
Np=O	1.85(2)	0.03	1.8
Np—O	2.18(3)	0.08	4.1
Np—O	2.43(3)	0.001	1.0

^aUncertainties 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. ΔE_0 for all shells = -6.00 eV, scale factor for all shells = 0.85, σ was allowed to vary between different shells but held fixed for the same shell for different samples.

that the white line is uncharacteristically strong. In addition, the k^3 -weighted EXAFS (Figure 1 insert) shows a relatively flat signal at low k , which implies the presence of more than one antiphased contribution at a short bond distance around Np(VII). EXAFS Fourier transform moduli of the Np(VII) solution spectrum along with that of the well-known Np(V) tris-carbonato anion, $\text{NpO}_2(\text{CO}_3)_3^{5-}$, are shown in Figure 2. The first two peaks in the FT spectrum (Figure 2) for ($\text{NpO}_2(\text{CO}_3)_3^{5-}$) correspond to two O atoms of the dioxo unit, O=Np=O at 1.86 Å, and six O atoms of the equatorial ligands at 2.53 Å.¹⁴ Curve fitting for the Np(VII) species reveals that the first peak in the FT spectrum contains two shells with a small bond length separation generating the appearance of only a single peak. The first shell corresponds to two O atoms (Table 1) with a Np=O distance of 1.85 Å consistent with the interpretation of a dioxo ion. The second shell at 2.18 Å is best fit by four O atoms, and the third shell at 2.43 Å is consistent with a single O atom (Table 1).¹⁵ Inclusion of a O=Np=O multiple scattering (ms)

(14) Clark, D. L.; Conradson, S. D.; Ekberg, S. A.; Hess, N. J.; Neu, M. P.; Palmer, P. D.; Runde, W.; Tait, C. D. *J. Am. Chem. Soc.* **1996**, *118*, 2089.

shell (3.7 Å) was essential to the fit of Np(V) data,¹⁴ as well as other dioxo ions,¹⁶ and made contributions to the Np(VII) fits. The four short Np—O distances of 2.18 Å are consistent with expectations for terminal Np—OH bonds, of which the only reported examples are those found in the unusual structures **I** and **II** which span 2.26(4)–2.32(1) Å.^{6–9} The observed distance of 2.18 Å is more typical of related terminal An—OR distances which span 2.15–2.25 Å,¹⁷ and can be compared with 2.153(6) and 2.197(5) Å seen in $\text{UO}_2(\text{OR})_2(\text{Ph}_3\text{PO})_2$, where R = O-*t*-Bu¹⁸ and O-2,6-*i*-Pr₂C₆H₂,¹⁹ respectively. The single Np—O distance of 2.43 Å is typical of a coordinated water molecule, and can be compared to 2.42(1) Å observed in structures containing the $\text{UO}_2(\text{OH}_2)_5^{2+}$ ion.²⁰

The EXAFS data show that the Np(VII) species in alkaline solution contains a trans dioxo ion, formally based on an NpO_2^{3+} central unit, which must be coordinated to OH⁻ and possibly OH₂ ligand(s). The uncertainties for the number of O atoms in the latter two shells is roughly ± 1 , consistent with a formulation $\text{NpO}_2(\text{OH})_n(\text{OH}_2)_m^{3-n}$, where the best fit ($n = 4$, $m = 1$) is suggestive of a pentagonal bipyramidal coordination motif common to many trans dioxo actinide ions.² Our conclusion that these Np(VII) species are trans dioxo ions is unequivocally demonstrated in the amplitudes of the isolated EXAFS of the oxo shells shown in the inset to Figure 2 (obtained by subtracting the sum of the EXAFS of the other shells from the data). The amplitude of the Np(VII) oxo shell is identical with that of a bona fide dioxo ion ($\text{NpO}_2(\text{CO}_3)_3^{5-}$), confirming the assignment of only two O atoms in this shell, in contradiction to previous literature claims.^{6,7} Additional studies to determine the solid-state structure, number of equatorial ligands, and solution dynamics are in progress.

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Supporting Information Available: Figures of UV–Vis–NIR spectra, EXAFS data, and fits (4 pages). See any current masthead page for ordering and Internet access instructions.

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(15) The DW factor (Table 1) is rather small, but exclusion of this shell results in a lower quality fit. The EXAFS residual obtained by subtracting the sum of the EXAFS from the first two shells shows a significant amplitude with minimal correspondence of phase with the other two shells (Supporting Information). Thus we conclude that this shell is necessary for fitting the data, but the number of equatorial ligands is admittedly not well-defined.

(16) Allen, P. G.; Bucher, J. J.; Clark, D. L.; Edelstein, N. M.; Ekberg, S. A.; Gohdes, J. W.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Neu, M. P.; Palmer, P. D.; Reich, T.; Shuh, D. K.; Tait, C. D.; Zwick, B. D. *Inorg. Chem.* **1995**, *34*, 4797.

(17) Clark, D. L.; Sattelberger, A. P.; Van der Sluys, W. G.; Watkin, J. G. *J. Alloys Compd* **1992**, *180*, 303.

(18) Burns, C. J.; Smith, D. C.; Sattelberger, A. P.; Gray, H. B. *Inorg. Chem.* **1992**, *31*, 3724.

(19) Barnhart, D. M.; Burns, C. J.; Sauer, N. N.; Watkin, J. G. *Inorg. Chem.* **1995**, *34*, 4079.

(20) Deshayes, L.; Keller, N.; Lance, M.; Nierlich, M.; Vigner, J.-D. *Acta Crystallogr. C* **1994**, *50*, 1541. Rogers, R. D.; Kurihara, L. K.; Benning, M. M. *J. Inclusion Phenom.* **1987**, *5*, 645.