

The Coordination Geometry of Np(VII) in Alkaline Solution

C. W. Williams,[†] J.-P. Blaudeau,^{*,‡,§} J. C. Sullivan,^{*,†}
Mark R. Antonio,^{*,†} B. Bursten,[§] and L. Soderholm^{*,†}

Chemistry Division, Argonne National Laboratory
Argonne Illinois 60439
Ohio Supercomputer Center, ASC-HP
2435 West 5th St., B676, WPAFB, Ohio 45433
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received September 25, 2000

The coordination environment of Np(VII) in solution remains uncertain despite numerous studies. Interest in the heptavalent Np ion is driven by the implications of the coordination environment on the basic understanding of structure/bonding relationships and its technological importance in treating nuclear waste. Initially reported by Krot and Gelman in 1967,¹ this f^0 configuration of Np is slowly reduced by H₂O in strongly alkaline solutions, and rapidly reduced in acidic media. Studies in highly basic solutions have reported various coordination geometries, including the dioxo moiety, O=Np=O, coordinated equatorially to oxo or hydroxo anions or waters,^{2,3} and a square planar tetraoxo complex with two more distant axial hydroxide ions.⁴ The latter Np(VII) coordination has precedent in the solid state.⁵ Analogies with other high-valent actinide ions, including U(VI), Np(VI), and Pu(VI), suggest that the hydroxy neptunyl ion NpO₂(OH)_n⁽³⁻ⁿ⁾(H₂O)_m is the prevalent species in solution. In contrast, the oxo anions of hexa- and heptavalent transition metals exhibit tetrahedral MO₄ⁿ⁻ coordination. We report the results of Np L₃-edge X-ray absorption spectroscopy (XAS) experiments optimized to determine the coordination environments of Np(VI) and Np(VII) in a highly basic solution. The results of these experiments, taken together with density functional theory (DFT) calculations, show Np(VII) to have a tetraoxo coordination with two additional more distant hydroxy ligands or water molecules.

An alkaline suspension of Np was prepared by precipitating Np(V) with concentrated NaOH. The resulting Np(V) hydroxide precipitate was slurried with 1 M NaOH and transferred to a purpose-built spectroelectrochemical cell equipped with Pt working and auxiliary electrodes and a Ag/AgCl reference electrode.⁶ Np(V) was oxidized, first to Np(VI) and then to Np(VII), by continuously sparging the solution with ozone while simultaneously applying an oxidizing potential of +600 mV vs Ag/AgCl. The standard reduction potential for Np(VII) under the conditions of our experiment has been previously reported as +384 mV.⁷ After several hours, the ozone was stopped and the applied potential was reduced to +500 mV. X-ray data were collected⁸ on the oxidized Np. The applied potential was reduced and data

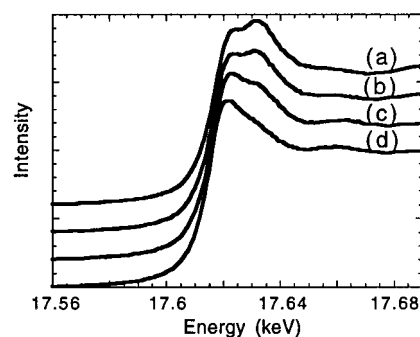


Figure 1. In situ Np L₃-edge XANES from (a) fully oxidized Np(VII), (b and c) mixtures of redox states that occur as Np(VII) is reduced, and (d) fully reduced Np(VI).

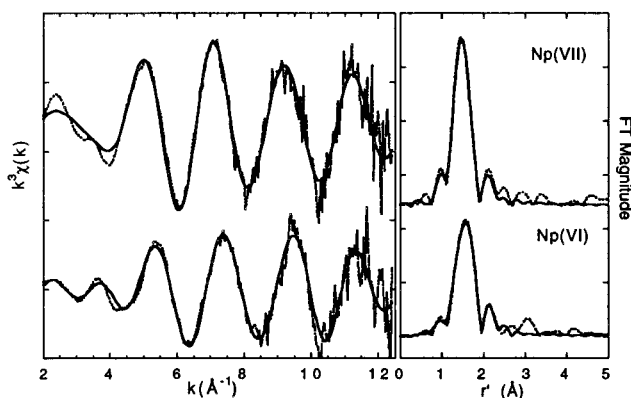


Figure 2. Left: The k^3 -weighted EXAFS of Np(VII) (top) and Np(VI) (bottom) from experiment (solid line) compared with the fit (dotted line) discussed in the text. Right: Fourier transform of the data shown on the left, which are uncorrected for phase shift as shown.

were obtained after bulk electrolysis at intermediate potentials until the solution contained only Np(VI).

The L₃-edge XANES data obtained from the 6.5 mM Np solution during and after ozonolysis and as a function of applied potential are shown in Figure 1. The Np(VI) spectrum, part d in Figure 1, exhibits the shoulder feature characteristic of an actinyl moiety,^{9,10} and is similar to the spectrum of Np(VI) and Np(V) in aqueous acidic solution.¹¹ In contrast, the spectrum of the Np(VII) species has a broader, doubled white line, thereby suggesting a change in the coordination environment from a simple O=Np=O configuration. The coordination environments of Np(VI) and Np(VII) are quantified by analyses of the EXAFS data and their Fourier transforms (FT),¹² which are shown in Figure 2. The Np(VI) coordination is consistent with 2 oxygens at 1.82(2) Å and a more distant equatorial shell of 4(1) oxo (or hydroxo) ions at a distance of 2.21(3) Å. This coordination environment about Np(VI) is consistent with the experiments

[†] Argonne National Laboratory.

[‡] Ohio Supercomputer Center.

[§] The Ohio State University.

(1) Krot, N. N.; Gelman, A. D. *Dokl. Akad. Nauk. SSSR* **1967**, *177*, 124–136.

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

(3) Clark, D. L.; Conradson, S. D.; Neu, M. P.; Palmer, P. D.; Runde, W.; Tait, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 5259–5260.

(4) Appelman, E. H.; Kostka, A. G.; Sullivan, J. C. *Inorg. Chem.* **1988**, *27*, 2002–2005.

(5) Grigor'ev, M. S.; Gulev, B. F.; Krot, N. N. *Soviet Radiochem.* **1986**, *28*, 630–633.

(6) Antonio, M. R.; Soderholm, L.; Song, I. *J. Appl. Electrochem.* **1997**, *27*, 784–792.

(7) Zielen, A. J.; Cohen, D. *J. Phys. Chem.* **1970**, *74*, 394–405.

(8) X-ray data were collected on the BESSRC CAT station 12-BM-B at the Advanced Photon Source. The monochromator, equipped with Si (111) crystals, was calibrated by setting the inflection point of the first derivative from the Zr K edge to 17 998 eV. Fluorescence data were collected using a 9 element Ge detector (Canberra).

(9) Hudson, E. A.; Rehr, J. J.; Bucher, J. J. *Phys. Rev. B* **1995**, *52* (1), 13815–13826.

(10) Ankudinov, A. L.; Conradson, S. D. *Phys. Rev. B* **1998**, *57* (1), 7518–7525.

(11) Antonio, M. R.; Soderholm, L.; Williams, C. W.; Blaudeau, J. P.; Bursten, B. E. *Radiochim. Acta* **2001**, *89*, 17–25.

(12) Data analyses were performed with WinXAS [Ressler, T. J. *Synchrotron Radiat.* **1998**, *5*, 118–122]. The $k^3\chi(k)$ EXAFS were fit using single scattering theoretical phase shifts and amplitudes calculated with FEFF8 [Rehr, J. J.; Albers, R. C. *Phys. Mod. Phys.* **2000**, *72*, 621–654]. The k range of fits was 2–12.5 Å⁻¹. (See Supporting Information.)

and theory reported for U(VI) under similar conditions.^{13,14} In contrast to the Np(VI) environment, the Np(VII) central ion is coordinated to 4(1) oxygens at a short distance of 1.87(1) Å and 2 oxygens at a distance of 2.24(4) Å. In addition to oxygen coordination, the FTs from both the Np(VI) and Np(VII) data show an additional resolved peak at an uncorrected distance of about 2.1 Å. These peaks are best fit with an additional coordination of 1–2 Na ions at an average distance of 2.33(3) Å. This determination of strong ion pairing with Na⁺ could be used to rationalize the significant dependence on the counteraction of Np(VI) solubility in basic solution.¹⁵ Finally, we see no evidence in our Np(VII) XANES or EXAFS data for the presence of dioxo species in the fully oxidized sample.¹⁶

The difference in coordination environment between the Np(VI) dioxo and the Np(VII) tetraoxo coordination does not appear to involve a significant structural rearrangement. Both ions are coordinated to a total of 6 oxygens at distances of about 1.85 and 2.22 Å, the difference being that Np(VI) has 2 short and 4 long oxygen distances, whereas Np(VII) has the reverse. This similarity in coordination is consistent with the high rate of Np(VI)–Np(VII) redox transformation that has been previously reported from kinetic studies.¹⁷ The observed Np(VII)–O bond distance of 1.87(1) Å is much longer than the 1.74–1.76 Å expected for a dioxo Np(VII); however, it is consistent with the 1.89(4) Å distance found for the Np–O tetraoxo coordination in the solid compound, Co(NH₃)₆NpO₄(OH)₂·2H₂O.⁵ The slightly shorter Np(VII)–O bonds seen in the solution over that in the solid state are consistent with the general trend toward shorter bond distances in disordered systems.

The Np(VII) coordination determined here is inconsistent with the previously suggested dioxo coordination for Np(VII).³ A comparison of our XANES data, shown in Figure 1, with those in the previous report shows that the samples are indeed different. The in situ methodology employed here for sample preparation eliminates problems of sample stability during transport that may have affected the earlier study.

Our observed coordination for Np(VII) is different from that seen for U(V) or (VI), Np(V) or (VI), or Pu(V) or (VI) in either acidic or basic solution. It is also different from the tetrahedral coordination seen for high-valent transition metal oxides. An insight into the stabilization of this unusual coordination environment has been obtained from calculations based on density functional theory methodology that include relativistic effects.¹¹ These calculations are performed with the Amsterdam Density Functional Code (ADF)¹⁸ by using the generalized gradient approximation functional of Perdew and Wang (PW91).¹⁹ Three

(13) Wahlgren, U.; Moll, H.; Grenthe, I.; Schimmelpfennig, B.; Maron, L.; Vallet, V.; Groen, O. *J. Phys. Chem. A* **1999**, *103*, 8257–8264.

(14) Clark, D. L.; Conradson, S. D.; Donohoe, R. J.; Keogh, D. W.; Morris, D. E.; Palmer, P. D.; Rogers, R. D.; Tait, C. D. *Inorg. Chem.* **1999**, *38*, 1456–1466.

(15) Cohen, D.; Fried, S. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 653–663.

(16) Conversion to Np(VII) was determined independently using both optical spectroscopy and spectrophotometrically by measuring the amount of Cr(VI) produced by the following reaction: 3Np(VII) + Cr(III) → 3Np(VI) + Cr(VI) [Thompson, R. C.; Sullivan, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 3028–3030].

(17) Shilov, V. P. *Radiochemistry*. **1998**, *40*, 12–17.

(18) Amsterdam Density Functional (ADF) code Version 2.3.0, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands.

(19) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671–6687.

different geometrical arrangements for NpO₄[−] have been compared: a tetrahedron (*T_d* symmetry) to probe the MO₄^{*n*−} geometry, a tetragonal square plane (*D_{4h}*), and a complex derived from a distorted square plane with the trans oxygen atoms either above or below the square molecular plane (*D_{2d}*). The *D_{2d}* geometry, with 4 equidistant oxygen at a calculated Np–O distance of 1.862 Å, has the lowest energy configuration, 1.76 eV lower than the tetrahedral symmetry and 0.16 eV lower than the tetragonal form. The calculated coordination compares well with our EXAFS results of 4 O at an average of 1.87(1) Å. The calculated bond angles are 169.83° for trans O–Np–O ligands and 89.11° and 90.45° for adjacent ligands. A vibrational analysis of the tetrahedron reveals two imaginary frequencies, including an E mode at 52 cm^{−1}, one component of which corresponds to an atomic displacement that leads to the *D_{2d}* arrangement. A Mulliken analysis of the charge distribution reveals significantly different f-orbital (*m_l* = ±3) populations for the *T_d* (0.31) and the *D_{2d}* (0.70) geometries. These orbitals lie in the horizontal plane, and allow for greater overlap with the ligand orbitals in the latter case. The result is that the *D_{2d}* complex has the smaller Mulliken charge on Np, and the calculated Np–O bond length is shorter (1.862 Å vs 1.919 Å). There is greater bonding and charge transfer between the actinide ion and the oxygen ligands in the *D_{2d}* than in the *T_d* complex. In contrast, in the comparison with the square-planar, *D_{4h}* complex, the increased Mulliken d-population on Np (1.67 vs 1.58) explains the greater stability of the *D_{2d}* structure. This slight distortion from *D_{4h}* has been observed in the solid state, where it was attributed to hydrogen bonding.⁵

Combining our XAS results with DFT calculations, we conclude that Np(VII) has a tetraoxo first-coordination sphere, slightly distorted from square-planar geometry with a Np–O bond distance of 1.87(1) Å. This tetraoxo coordination environment of Np(VII) is unusual. It is different from that observed for the high-valent transition-metal anions, which exhibit tetraoxo coordination with *T_d* symmetry, and high-valent actinide ions, which exhibit dioxo coordination. The Np(VII) coordination geometry appears to result from a competition for ligand electron density among Np's d- and f-orbitals of various symmetries. Increased nuclear charge is believed to stabilize the 5f with respect to 6d orbitals. DFT calculations show that the square-planar based geometry is favored by increased f-orbital participation in bonding with oxygen p-states. The slight distortion from *D_{4h}* symmetry results directly in a slightly higher Mulliken population of the d-states in *D_{2d}* symmetry. Understanding further details about the competition for charge density in systems with competing d- and f-orbitals, such as NpO₄(OH)₂^{3−}, will provide new insights into the role of bonding on structure.

Acknowledgment. The authors thank M. Denecke and S. Skanthakumar for technical assistance, and acknowledge the infrastructure support from the Actinide Facility and the BESSRC CAT. This work is supported by the U.S. DOE, BES-Chemical Sciences, and the APS is supported by the U.S. DOE, BES-Material Sciences, all under contract W-31-109-ENG-38. The authors also acknowledge the Ohio Supercomputer Center for a grant of computer time.

Supporting Information Available: Details of EXAFS data analysis and a table of metrical parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA005640G