Actinide Chemistry

DOI: 10.1002/ange.200501281

Optical Absorption and Structure of a Highly Symmetrical Neptunium(V) Diamide Complex[**]

*Guoxin Tian, Jide Xu, and Linfeng Rao**

The neptunium(V) cation, NpO_2^+, contains Np in its most stable oxidation state under a wide range of conditions in aqueous media. Because of its low positive charge, NpO_2^+ does not form strong complexes with ligands so it is difficult to separate neptunium from high-level nuclear wastes by using traditional extracting agents that are effective for separating other actinides.[1] Also, the low tendency of NpO_2^+ to undergo hydrolysis and sorption makes it highly mobile in the subsurface, raising concern in the migration of this radionuclide in the environment.[2]

The absorption spectrum of NpO_2^+ is dominated by a band in the near-IR region with a fairly high intensity ($\varepsilon \approx 390\,\text{M}^{-1}\,\text{cm}^{-1}$ at 980.2 nm). This band, as well as a weaker band at 1024 nm, follows Beer–Lambert behavior and is often used to quantitatively determine the concentration of NpO_2^+ in solution.[3] The position and intensity of these bands are also affected by the coordination environment of NpO_2^+ and are frequently used to study the complexation behavior of NpO_2^+.[4,5] The absorption band of the free $[NpO_2(H_2O)_n]^+$ ion at 980.2 nm is usually shifted to longer wavelengths when NpO_2^+ forms complexes with ligands that replace the water molecules in the primary hydration sphere. For a series of structurally related ligands, the magnitude of the shifts in the wavelength appears to increase as the binding strength of the ligand is increased. For example, in the 1:1 complexes of NpO_2^+ with dicarboxylates, the stability constants and the shifts in wavelength (logβ and $\Delta\lambda$ in nm) are 1.29 and 3.7 for glutarate,[6] 1.47 and 4.5 for succinate,[6] 2.63 and 7.2 for malonate,[7] and 3.79 and 8.4 for oxalate.[7] Formation of 1:2 complexes with these ligands shifts the absorption band to even longer wavelengths.[4,6,7] The molar absorptivities of the bands vary in the range from 250 to $390\,\text{M}^{-1}\,\text{cm}^{-1}$.[4,6,7] The underlying mechanism that allows the transitions and the origin of the intensities remain unclear. Theoretical calculations suggest that the absorption band at 980 nm is a 5f→5f electric-dipole transition, which is forbidden by Laporte's rule, and that the intensity of the transition depends on the symmetry of the Np^V species.[8] The results of theoretical calculations are enlightening but need to be tested by comparison with experimentally observed spectra of Np^V complexes with different ligands.

In an effort to develop efficient extractants for the separation of actinide ions including Np^V, we have found that tetraalkyl-3-oxa-glutaramide, L^1, displays a good ability to extract Np^V ions.[9] To obtain insight into the complexation of Np^V with diamide ligands, a simple water-soluble homologue of L^1, tetramethyl-3-oxa-glutaramide (L^2), was synthesized and studied by optical absorption spectroscopy in aqueous solution.

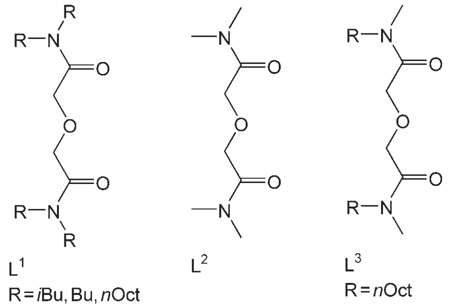

Figure 1 a shows the absorption spectra obtained during spectrophotometric titrations of Np^V with L^2. As the concentration of L^2 was increased, the intensities of the absorption bands at 980 and 1024 nm that belong to the free NpO_2^+ cation decreased and new bands appeared at 987 and 1037 nm, which correspond to the formation of a 1:1 complex of Np^V with L^2, $[NpO_2(L^2)^+]$. As the concentration of L^2 was further increased, the intensities at 987 and 1037 nm decreased but no new absorption peaks appeared at longer wavelengths. These changes in the spectra are different from those for Np^V complexes with many other ligands for which the decrease of the absorbance of the first complex is accompanied by the appearance of new absorption band(s) of successive complexes at longer wavelengths.

The variation of the spectra in Figure 1 a is interpreted with the assumption that two complexes of Np^V with L^2 form in solution successively but that the second complex, $[NpO_2(L^2)_2{}^+]$, does not absorb in that wavelength region. This assumption is consistent with the factor analysis of the spectra using the Hyperquad2000 program;[10] the formation constants of the $[NpO_2(L^2)]^+$ and $[NpO_2(L^2)_2]^+$ complexes are calculated to be $23.7 \pm 0.5\,\text{M}^{-1}$ and $295 \pm 6\,\text{M}^{-2}$, respectively. The deconvoluted spectra for free NpO_2^+ and the $[NpO_2(L^2)]^+$ complex are shown in Figure 1 b.

The $[NpO_2(H_2O)_n]^+$ ion also has absorption bands of much lower intensity in the visible region that render its usual green-blue color. Figure 2 shows that the intensities of the bands at 430, 476, and 616 nm decrease and the spectra tend to become flat and featureless as the concentration of L^2 increases, which suggests that the $[NpO_2(L^2)_2]^+$ complex does

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[*] Dr. G. Tian, Dr. L. Rao
Lawrence Berkeley National Laboratory
Berkeley, California 94720 (USA)
Fax: (+1) 510-486-5596
E-mail: lrao@lbl.gov
Dr. J. Xu
Department of Chemistry, University of California
Berkeley, California 94720 (USA)

[**] This work was supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH 11231 at the Lawrence Berkeley National Laboratory (LBNL). The Advanced Light Source (ALS) is operated by LBNL for the DOE. The authors thank Drs. D. Shuh and A. Gordon for developing the procedures for handling small crystals of actinides at Beamline 11.3.1 of the ALS, and Dr. Allen Oliver for collecting the X-ray diffraction data at the ALS.

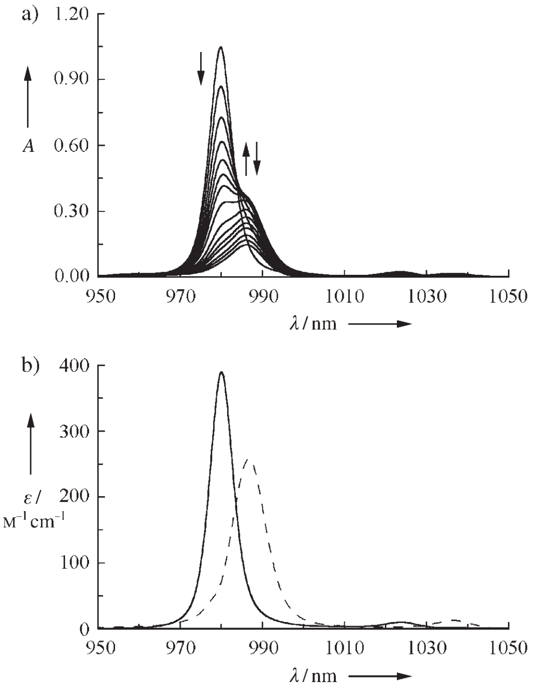


Figure 1. a) Spectrophotometric titrations in the near-IR region of Np^V with L^2. [Np] = 2.66 mM; [L^2] = 0–336 mM; optical path: 1.0 cm. b) Deconvoluted absorption spectra of NpO_2^+ (——) and the $[NpO_2(L^2)]^+$ complex (-----); $[NpO_2(L^2)_2]^+$ does not absorb in this region.

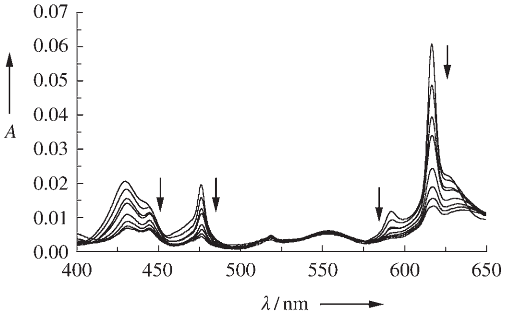
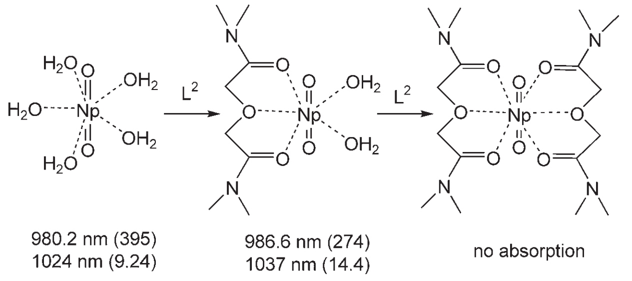


Figure 2. Spectrophotometric titrations of Np^V with L^2 in the visible region. [Np] = 2.66 mM; [L^2] = 0–336 mM; optical path: 1.0 cm.

not absorb in the visible region. In fact, the initial green-blue color of the solution of $[NpO_2(H_2O)_n]^+$ gradually faded as the concentration of L^2 was increased and became almost colorless at the end of titration.

These results are consistent with the theoretical calculations by Matsika et al.[8] For the f^2 electronic configuration of NpO_2^+, all of the excited states up to 23000 cm^{-1} (corresponding to $\lambda \approx 430$ nm) contain two f electrons and display the gerade parity in the ground state.[8] Thus, all the excitations at low energies should be electric-dipole forbidden by Laporte's rule. This rule is followed if NpO_2^+ is in a coordination environment where a center of inversion exists. However, if the ligands that surround the NpO_2^+ are arranged so that the center of inversion is destroyed, Laporte's rule does not apply and the f→f transitions are allowed. The successive complexation of Np^V with L^2 and the accompanying changes in symmetry and absorption spectra are best illustrated by Scheme 1.

The free NpO_2^+ cation contains five molecules of H_2O in the equatorial plane[11] to result in a structure without a center of inversion. As a result, the f→f transitions are allowed and absorption bands at 980 and 1024 nm are observed. For the same reason of absence of a center of inversion, the first complex, $[NpO_2(L^2)]^+$, does absorb light, but the energies of the absorption bands are red-shifted (987 and 1037 nm). However, the second complex, $[NpO_2(L^2)_2]^+$, could be highly symmetrical with a center of inversion, wherein each L^2 ligand supplies three oxygen atoms to coordinate NpO_2^+ in the equatorial plane. This complex is expected to display no absorption in the near-IR region (Figure 1). The same discussions apply to the change of absorption bands in the visible region (Figure 2) because all the bands up to 23000 cm^{-1} originate from f→f transitions as shown by the theoretical calculations by Matsika et al.[8]



Scheme 1. Successive complexation of $[Np^VO_2(H_2O)_5]^+$ with L^2 and the accompanying changes in symmetry and absorption bands (corresponding ε values in $M^{-1}cm^{-1}$ are given in parentheses).

A comparison of the absorption spectra between the complexes of Np^V and L^2 (Figures 1 and 2) and those between Np^V and oxalate ($C_2O_4^{2-}$) complexes (Figure 3) further demonstrates the dependence of f→f transitions on the symmetry of the coordination environment of Np^V. It is known that the Np^V oxalate complexes, $[NpO_2(C_2O_4)]^-$ and $[NpO_2(C_2O_4)_2]^{3-}$, with a coordination number of five in the equatorial plane of NpO_2^+, do not have inversion centers.[12] There are three water molecules and one bidentate oxalate ligand in $[NpO_2(C_2O_4)]^-$, and one water molecule and two bidentate oxalate ligands in $[NpO_2(C_2O_4)_2]^{3-}$. As a result, the f→f transitions in both complexes should be allowed. This is indeed the case as shown by the absorption spectra in Figure 3. For the spectra in both the near-IR and visible regions, distinctive absorption bands are seen for $[NpO_2(H_2O)_n]^+$, $[NpO_2(C_2O_4)]^-$, and $[NpO_2(C_2O_4)_2]^{3-}$. The successive complexation of Np^V ion with oxalate ion and the accompanying changes in symmetry and absorption spectra are illustrated in Scheme 2.

To obtain structural information for the $[NpO_2(L^2)_2]^+$ complex and test the assumption based on the theoretical calculations discussed above, single crystals of the complex were prepared from solution and X-ray diffraction data were collected (Figure 4).[13] The perchlorate salt, $[NpO_2(L^2)_2]ClO_4$, crystallized in a highly symmetrical tetragonal space group, *I4/mcm*. The neptunium atom sits at the crossover

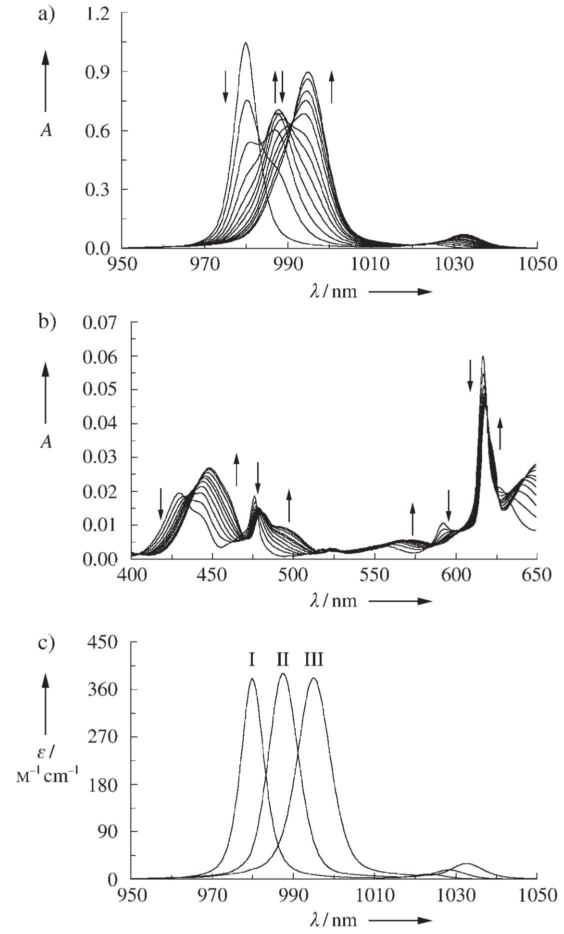
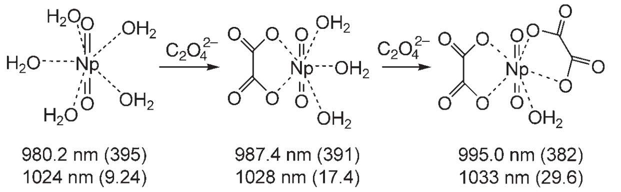


Figure 3. Spectrophotometric titrations of Np^V with oxalate ($[Np] = 2.66$ mM; $[C_2O_4^{2-}] = 0$–28.6 mM; optical path: 1.0 cm): a) in the near-IR region and b) in the visible region. c) Deconvoluted absorption spectra of $[NpO_2(H_2O)_5]^+$ (I), $[NpO_2(C_2O_4)]^-$ (II), and $[NpO_2(C_2O_4)_2]^{3-}$ (III).



Scheme 2. Successive complexation of $[Np^VO_2(H_2O)_5]^+$ with oxalate ion and the accompanying changes in symmetry and absorption bands (corresponding ε values in $M^{-1}cm^{-1}$ are given in parentheses).

point of three mirror planes that lie perpendicular to each other. The two L^2 ligands are coplanar and are mirror images of each other. The O=Np=O moiety is perfectly linear and symmetrical, with an angle of 180° and Np=O distances of 1.729 Å. The f→f transition in this highly symmetrical complex with a center of inversion is forbidden according to the theoretical calculations. In fact, the crystals and solutions of $[NpO_2(L^2)_2]ClO_4$ are almost colorless, drastically different from the green-blue colors of most reported Np^V compounds. We believe that the $[NpO_2(L^2)_2]^+$ complex in solution has the structure shown in Figure 4. Attempts to collect the diffuse reflectance spectra of $[NpO_2(L^2)_2]ClO_4$ in the solid state were unsuccessful owing to the limited availability of the solids and the complications involved in the experimental setup for handling the transuranic elements.

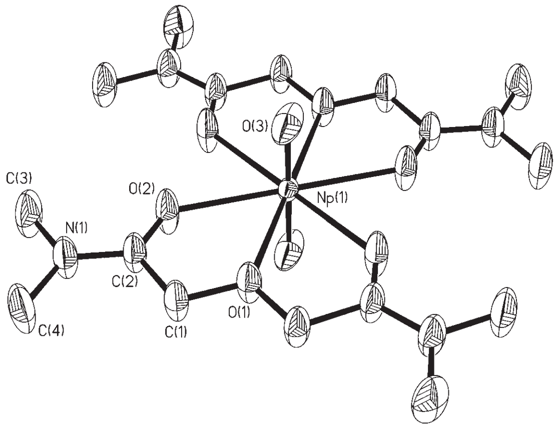


Figure 4. ORTEP drawing (30% probability ellipsoids) of $[NpO_2(L^2)_2]^+$. For clarity, the perchlorate anion is not shown.

The structure of $[NpO_2(L^2)_2]^+$ (Figure 4) provides guidance in the design of better ligands to complex Np^V. The distance between the two carbon atoms of the terminal methyl groups is 4.01 Å, implying that significant steric hindrance would be present if the methyl groups are replaced by bigger and/or bulkier alkyl groups such as the octyl or *iso*-butyl groups in L^1, which is used as an extractant for the separation of actinides. The bigger alkyl groups in L^1 are mainly for enhancing its solubility in organic solvents. However, the structure of $[NpO_2(L^2)_2]^+$ suggests that asymmetric amide groups such as *N*-methyl-*N*-octyl (L^3) could be used, guaranteeing the solubility of the ligand in organic solvents as well as improving the complexation and thus the extraction of Np^V by reducing the steric hindrance in the Np^V complex. Also, the structural parameters of $[NpO_2(L^2)_2]^+$ help with the design of hexadentate amide ligands with a rigid backbone connecting the diamide ligands. Complexation of such ligands with Np^V should be enhanced due to a lower preorganization energy and a larger entropy effect.

In conclusion, we have synthesized, studied the optical absorption properties, and characterized the molecular structure of a highly symmetrical Np^V diamide complex, $[NpO_2(L^2)]_2^+$. This is the first neptunium complex that has been characterized by single-crystal X-ray diffraction with a synchrotron radiation source. The correlation between the optical absorption properties and the symmetry of Np^V complexes in solution was experimentally demonstrated and confirms the theoretical calculations of the optical spectra of 5f elements. The identified structure of $[NpO_2(L^2)_2]^+$, while helping to interpret the optical absorption spectra also suggests approaches for the rational design of ligands to improve the binding ability with Np^V and the separation of neptunium from nuclear wastes.

Experimental Section

Spectrophotometric titrations were performed on a Cary 5G UV-Vis-NIR spectrophotometer (Varian). Initial solutions of $(NpO_2)(ClO_4)$ ($V_0 = 2.50$ mL, $[Np] = 0.5$–3 mM, $I = 1$ M NaClO$_4$, pH 5–7) in a 1-cm quartz cuvette were titrated with solutions of L^2 or oxalate ion (0.2–1 M). After each addition of the titrant (0.05–0.140 mL), the absorption spectrum was collected from $\lambda = 400$–1150 nm at 0.2-nm intervals.

Single crystals of $[NpO_2(L^2)_2]ClO_4$ were prepared from 0.05 M $(NpO_2)(ClO_4)$ (0.2 mL) and 0.5 M L^2 by slow evaporation in a hood. A small crystal (20–80 μm) was immerged in Paratone-N oil and sealed inside a quartz capillary (i.d. = 0.3 mm). Precautions, including coating the capillary with a thin layer of protective resin, were taken to ensure the containment of radioactive neptunium. The capillary was mounted in a brass pin on the goniometer, which was then transported from the radiochemistry laboratory in a closed container to the Advanced Light Source (ALS), thus minimizing the amount of alignment required once at the diffractometer. Crystallographic data were collected at 255 K in less than one hour using a Bruker Platinum 200 detector at the Small-Crystal Crystallographic Beamline 11.3.1 at the ALS of Lawrence Berkeley National Laboratory.

Received: April 12, 2005
Revised: June 24, 2005

Keywords: absorption · amides · coordination modes · neptunium · X-ray diffraction

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[13] Crystal data: $NpC_{16}H_{32}ClN_4O_{12}$, $M_r = 744.91$, crystal dimensions $0.25 \times 0.20 \times 0.16$ mm^3, tetragonal, $I4/mcm$, $a = 11.1785(16)$, $b = 11.1785(16)$, $c = 24.6937(81)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 3085.7(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.603$ g cm^{-3}, $2\theta_{max} = 62.20°$, $T = 255$ K, 8874 reflections collected, 1053 independent ($I > 2.00\sigma(I)$), $R_{int} = 0.0407$, $\mu = 5.856$ mm^{-1}, absorption correction with SADABS,[14] refinement against $|F^2|$, data/restrains/parameters of 1053/4/72, $R_1 = 0.0215$ ($wR_2 = 0.0671$, $I > 2\sigma(I)$), $R_1 = 0.0294$ ($wR_2 = 0.0910$, all data), GoF = 1.096, shift/esd in final cycle = 0.00, largest difference peaks 1.150/−0.646 e Å^{-3}. Crystallographic data were collected using a Bruker Platinum 200 detector at the Small-Crystal Crystallographic Beamline 11.3.1 at a wavelength of 0.77490 Å at the ALS of LBNL. The goniometer was mounted vertically and has a chi angle of 54.7 degrees. Intensity data were collected in less than one hour using Bruker Apex II software.[15] Intensity data integrations, cell refinement, and data reduction were performed using the Bruker SAINT software package.[16] Dispersion factors (f and f) at 16 keV for C, N, O, and Cl atoms were included using values from CROMER for Windows. Dispersion factors for Np were interpolated and imported for use in SHELXS using reported data.[17] No decay corrections were applied. The structure was solved with direct methods using SHELXS[18] and expanded using Fourier techniques.[19] Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculation positions but not refined. All calculations were performed using SHELXL-97,[19] the crystallographic software package of Bruker Analytical X-ray System. CCDC 268309 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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