Inorganic Chemistry
Article
pubs.acs.org/IC

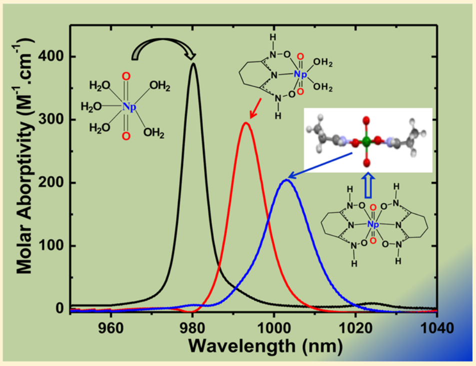
Complexation of Neptunium(V) with Glutaroimide Dioxime: A Study by Absorption Spectroscopy, Microcalorimetry, and Density Functional Theory Calculations

Seraj A. Ansari,[†,‡] Arunasis Bhattacharyya,[‡] Zhicheng Zhang,[†] and Linfeng Rao*[,†]

[†]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
[‡]Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Supporting Information

ABSTRACT: Complexation of NpO_2^+ ions with glutaroimide dioxime (H_2L), a cyclic imide dioxime ligand that has been shown to form strong complexes with UO_2^{2+} in aqueous solutions, was studied by absorption spectroscopy and microcalorimetry in 1.0 M $NaClO_4$ aqueous solutions. NpO_2^+ forms two successive complexes, $NpO_2(HL)(aq)$ and $NpO_2(HL)_2^-$ (where HL^- stands for the partially deprotonated glutaroimide dioxime ligand), with stability constants of $\log \beta_{111} = 17.8 \pm 0.1$ and $\log \beta_{122} = 33.0 \pm 0.2$, respectively. The complexation is both enthalpy- and entropy-driven, with negative enthalpies ($\Delta H_{111} = -52.3 \pm 1.0$ kJ/mol and $\Delta H_{122} = -96.1 \pm 1.4$ kJ/mol) and positive entropies ($\Delta S_{111} = 164 \pm 3$ J/mol/K and $\Delta S_{122} = 310 \pm 4$ J/mol/K). The thermodynamic parameters suggest that, similar to complexation of UO_2^{2+}, the ligand coordinates with NpO_2^+ in a tridentate mode, via the two oxygen atoms of the oxime groups and the nitrogen atom of the imide group. Density functional theory calculations have helped to interpret the optical absorption properties of the $NpO_2(HL)_2^-$ complex, by showing that the cis and trans configurations of the complex have very similar energies so that both configurations could be present in the aqueous solutions. It is the noncentrosymmetric cis configuration that makes the 5f → 5f transition allowable so that the $NpO_2(HL)_2^-$ complex absorbs in the near-IR region.



INTRODUCTION

^{237}Np is formed in significant quantities in nuclear reactors (pressurized water reactors as well as fast reactors) through the successive neutron captures of ^{235}U followed by the β decay of ^{237}U.[1,2] It is also an α-decay product of ^{241}Am. Neptunium is considered to be a problematic element in the spent nuclear fuel (SNF) reprocessing as well as in the environmental management of nuclear wastes, mainly for three reasons: (1) neptunium can exist in multiple oxidation states (III, IV, V, and VI) and precise control of its chemical behavior in the SNF reprocessing processes is difficult; (2) ^{237}Np has a long half-life (2×10^6 years) so that the nuclear wastes containing ^{237}Np will remain hazardous for a very long time (it is predicted that ^{237}Np will become a major hazard, contributing 67% of the total radiation dose from high-level nuclear wastes after 75000 years[3]); (3) the most stable oxidation state of neptunium, Np^V as NpO_2^+, has very high mobility in the geological environment because of its weak tendencies toward hydrolysis, precipitation, or sorption by the geomedia.

To achieve precise control over the chemical behavior of neptunium in the separation processes of SNF reprocessing, numerous studies have been conducted to understand the interactions, including complexation and redox reactions, of neptunium with organic ligands including carboxylic acids,[4,5] amides,[6,7] and hydroxamic acids.[8−10] Some ligands, especially those containing both oxygen and nitrogen donors [e.g., 1,10-phenanthroline-2,9-dicarboxylic acid,[11] N-methyliminodiacetic acid (MIDA),[12] and dipicolinic acid (DPA)[13]], form fairly strong complexes with neptunium(V) and have the potential to be used as efficient complexants for neptunium. Other ligands, such as acetohydroxamic acid and formohydroxamic acid, exhibit redox capabilities of adjusting the oxidation states of neptunium to facilitate its separation from other metal ions.[8−10]

A tridentate ligand containing both oxygen and nitrogen donors, glutaroimide dioxime (Figure 1), has recently been shown to form strong complexes with UO_2^{2+}, an actinyl cation with a linear dioxo configuration analogous to NpO_2^+.[14,15] We hypothesize that this ligand, with a tridentate chelation mode similar to that of MIDA and DPA, could form fairly strong

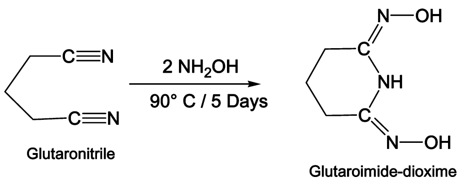


Figure 1. Scheme for synthesizing glutaroimide dioxime (H_2L).

Received: June 11, 2015
Published: August 11, 2015

DOI: 10.1021/acs.inorgchem.5b01319
Inorg. Chem. 2015, 54, 8693−8698

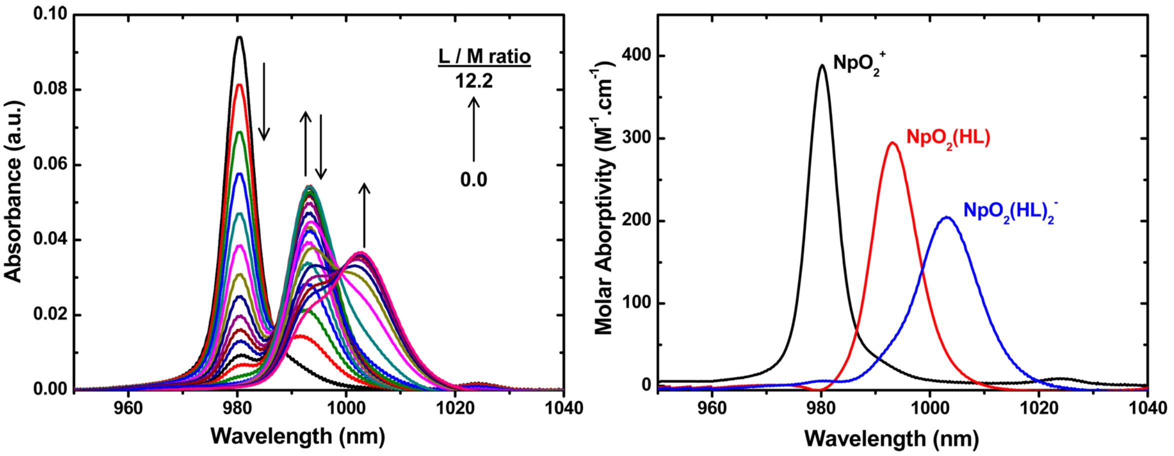


Figure 2. Spectrophotometric titration of $NpO_2(ClO_4)$ with glutaroimide dioxime (left) and calculated molar absorptivities of NpO_2^+ and two complexes (right). Cuvette solution: 0.24 mM $NpO_2(ClO_4)$ at pH ~ 7. Titrant: C_L = 20 mM; C_H = 10 mM. Ionic strength: 1 M $NaClO_4$.

complex(es) with NpO_2^+ and that, with oxime groups similar to those in hydroxamic acids, this ligand could play a role in the redox reactions of neptunium in acidic solutions. The validity of both hypotheses are of potential importance in determining the chemical behavior of neptunium in the separation processes. Therefore, the present study was conducted to quantify the stability constants and enthalpy of complexation for the neptunium(V)/glutaroimide dioxime complexes in neutral solutions, where redox reactions between neptunium(V) and the ligand probably do not occur. The thermodynamic results, in conjunction with density functional theory (DFT) calculations, provide insight into the energetics of the complexation and the coordination modes in the complex. Furthermore, the thermodynamic data on the complexation are expected to help in understanding the mechanisms of the possible redox reactions in acidic solutions because the redox reactions between neptunium and organic ligands could proceed through the formation of an intermediate complex, as shown in a previous study.[16] The redox behavior of neptunium in the presence of glutaroimide dioxime will be the subject of future studies.

■ EXPERIMENTAL SECTION

Chemicals and Reagents. Glutaroimide dioxime, denoted as H_2L in this paper, was synthesized by reacting glutaronitrile and hydroxylamine (1:2 mole ratio) in a 1:1 ethanol/water mixture at 80−90 °C (Figure 1). Detailed procedures for the synthesis were described elsewhere.[14] Stirring the reaction mixture at 80−90 °C for 5 days resulted in the formation of H_2L, a white solid with >90% yield. The resultant material was purified by recrystallization and subsequently characterized by ^1H NMR and potentiometric titration.[17]

The neptunium(V) stock solution was prepared by dissolving solid neptunium oxide (NpO_2) in concentrated HCl, followed by $HClO_4$ fuming to remove the excess HCl and oxidize the neptunium to neptunium(VI). (***Caution!*** *(1) Extreme precautions must be taken in handling* ^{237}Np *beause of the high radiation hazards from* α *radioactivity. (2) Extreme precautions must be taken to ensure the absence of any organic matter in the container before concentrated* $HClO_4$ *fuming. The presence of organic matter in the* $HClO_4$ *fuming process could lead to explosion.*) To the obtained pink solution of neptunium(VI) was added a small amount of $NaNO_2$ to reduce it to neptunium(V), resulting in a green solution. Neptunium(V) was then precipitated as hydroxide with 1 M NaOH, filtered, washed with deionized water to remove the excess NaOH, and finally dissolved in 1 M $HClO_4$ to obtain a stock solution of neptunium(V). The oxidation state and the concentration of neptunium(V) in the stock were confirmed by absorption spectra at 980.2 nm (ε = 395 M^{-1} cm^{-1}).[18] The free acid concentration in the neptunium(V) stock solution was determined by Gran titration.[19] Milli-Q water (resistivity ≈ 18.2 MΩ·cm^2/cm at 25 °C) was used for the preparation of all solutions. The ionic strength of all working solutions was maintained at 1 M $NaClO_4$ (25 °C).

Spectrophotometry. The absorption spectra of the NpO_2^+ solutions was collected in the wavelength region 950−1050 nm (0.1 nm interval) on a double-beam Varian Cary 6000i spectrophotometer using 10-mm-path-length quartz cells. The temperatures of the sample and reference cell holders were controlled by a Peltier device coupled with cooling water circulation from a water bath. The NpO_2^+ solution in the cuvette was titrated with a buffered (half-neutralized) solution of glutaroimide dioxime. In each titration, appropriate aliquots of the titrant were added into the cell and mixed thoroughly for about 2 min before the spectrum was recorded. The mixing time was found to be sufficient to complete the complexation reaction. Usually 15−20 spectra were recorded in each set of titrations. The stability constants (β_{ijk}) of the NpO_2^+/H_2L complexes were calculated by nonlinear least-squares regression analysis using the *HypSpec* program.[20]

Microcalorimetry. Microcalorimetric titrations were performed on an isothermal titration microcalorimeter (ITC-4200). Both electrical and chemical calibrations were performed to validate the performance of the instrument. The chemical calibration was carried out by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane at 25 °C, and the obtained enthalpy of protonation (−47.6 ± 0.3 kJ/mol) was in good agreement with the literature data.[21] The titration was performed by adding the solution of glutaroimide dioxime into the reaction vessel containing NpO_2^+. About 50 additions of the titrant (5 μL per addition) were made in each titration. The overall heat generated after each addition was measured. The dilution heat, obtained from a blank titration in separate experiments, was subtracted from the overall heat to obtain the net heat of reaction. Multiple titrations using different concentrations of neptunium, ligand, and proton (denoted as C_M, C_L, and C_H) were performed to reduce the uncertainty of the results. The reaction heat measured by microcalorimetry was used, in conjunction with the equilibrium constants obtained by spectrophotometry, to calculate the enthalpy of complexation with the *HypDeltaH* program.[22]

Computational Studies. The geometries of the neptunium complexes in the gas phase were optimized at the generalized gradient approximation level of DFT by using Becke's exchange functional,[23] in conjunction with Perdew's correlation functional (BP86),[24] where 60-electron-core pseudopotentials along with the corresponding def-SV(P) basis set were selected for the neptunium ion, and all other lighter atoms were treated at the all-electron level. The geometries of the complexes in the aqueous medium were also optimized using the conductor-like screening model (COSMO) approach[25] with the *TURBOMOLE* program package[26,27] at the DFT level using the hybrid

Table 1. Thermodynamic Data for the Complexation of NpO_2^+ and UO_2^{2+} with Glutaroimide Dioxime (H_2L) at 25 °C

reaction	medium	log β	ΔH (kJ/mol)	ΔS (J/mol/K)	ref
$H^+ + L^{2-} \rightarrow HL^-$	0.5 M NaCl	12.27 ± 0.03	−36.1 ± 0.5	110 ± 2	14, 17
$2H^+ + L^{2-} \rightarrow H_2L$	0.5 M NaCl	23.15 ± 0.12	−69.7 ± 0.9	202 ± 3	14, 17
$3H^+ + L^{2-} \rightarrow H_3L^+$	0.5 M NaCl	25.67 ± 0.12	−77.0 ± 6.0	218 ± 14	14, 17
$NpO_2^+ + H^+ + L^{2-} \rightarrow NpO_2(HL)(aq)$	1 M $NaClO_4$	17.8 ± 0.1	−52.3 ± 1.0	164 ± 3	p.w.
$NpO_2^+ + 2H^+ + 2L^{2-} \rightarrow NpO_2(HL)_2^-$	1 M $NaClO_4$	33.0 ± 0.2	−96.1 ± 1.4	310 ± 4	p.w.
$NpO_2^+ + HL^- \rightarrow NpO_2(HL)(aq)$	1 M $NaClO_4$	5.3 ± 0.1[a]			p.w.
$NpO_2^+ + 2HL^- \rightarrow NpO_2(HL)_2^-$	1 M $NaClO_4$	8.5 ± 0.2[a]			p.w.
$UO_2^{2+} + H^+ + L^{2-} \rightarrow UO_2(HL)^+$	0.5 M NaCl	22.7 ± 1.3	−71.0 ± 6.0	197 ± 14	14
$UO_2^{2+} + 2H^+ + 2L^{2-} \rightarrow UO_2(HL)_2(aq)$	0.5 M NaCl	43.0 ± 1.1	−154 ± 25	307 ± 59	14
$UO_2^{2+} + HL^- \rightarrow UO_2(HL)^+$	0.5 M NaCl	10.4 ± 1.3[a]			14
$UO_2^{2+} + 2HL^- \rightarrow UO_2(HL)_2(aq)$	0.5 M NaCl	18.5 ± 1.1[a]			14

[a] Calculated by using the protonation constant of HL^- in 0.5 M NaCl from ref 17.

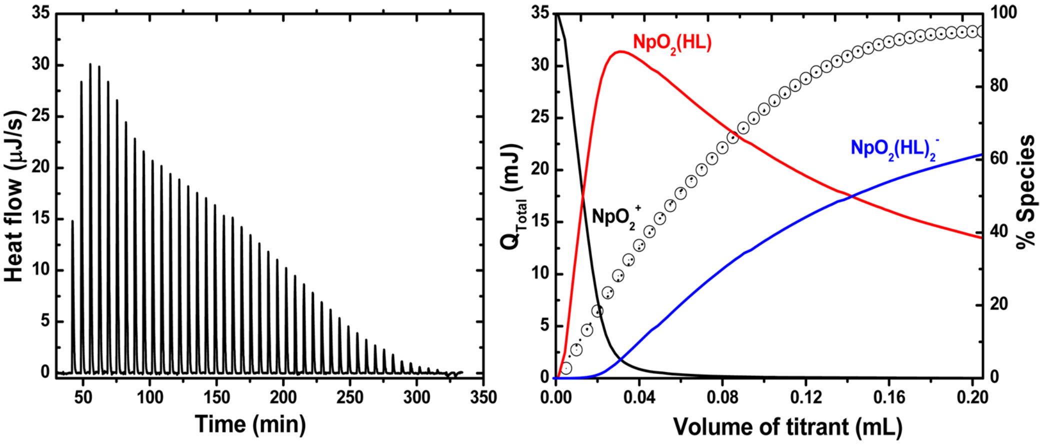


Figure 3. Calorimetric titration of NpO_2^+ with glutaroimide dioxime at 25 °C. (Left) Thermograms (uncorrected for dilution heat). (Right) Cumulative heat (left y axis; circles, experimental; dotted line, fit) and speciation of NpO_2^+ (right y axis) as a function of the titrant volume. Initial cup solution (0.90 mL): 0.224 μmol of $NpO_2(ClO_4)$ and 0.246 μmol of H^+. Titrant: 12.8 mM ligand (half-neutralized). Ionic strength: 1 M $NaClO_4$.

exchange correlation functional (B3LYP)[23,28,29] with the same pseudopotentials and basis sets as those used in the gas-phase calculation. The dielectric constant (ε) of water was considered as 80.2. For cavity generation, the following atomic radii were used in COSMO calculations: H, 1.30 Å; O, 1.72 Å; Np, 1.80 Å.[30]

RESULTS

Absorption Spectroscopy. Figure 2 shows the representative spectrophotometric titration of NpO_2^+ ions with H_2L in the near-IR region. Under the experimental conditions, no reduction of neptunium(V) by the ligand was observed. As the concentration of the ligand was increased, the intensity of the absorption band of free NpO_2^+ at 980.2 nm decreased and a new absorption band appeared at 993.4 nm. As the titration proceeded, the intensity of the absorption band at 993.4 nm reached a maximum at $C_L/C_M \sim 4$ and then started to decrease with the concomitant appearance of another absorption band at a longer wavelength (1002.9 nm). Factor analysis of the absorption spectra by the *HypSpec* program indicated the presence of three absorbing species, i.e., the free NpO_2^+ and two successive NpO_2^+/H_2L complexes. Various models including a variety of NpO_2^+/H_2L complexes were tested, and the best fit was achieved by using the model including the successive formation of the (1, 1, 1) and (1, 2, 2) complexes, i.e., $NpO_2(HL)(aq)$ and $NpO_2(HL)_2^-$, as represented by eqs 1 and 2.

$$NpO_2^+ + H^+ + L^{2-} = NpO_2(HL)(aq)$$

$$\beta_{111} = [NpO_2(HL)(aq)]/([NpO_2^+][H^+][L^{2-}]) \quad (1)$$

$$NpO_2^+ + 2H^+ + 2L^{2-} = NpO_2(HL)_2^-$$

$$\beta_{122} = [NpO_2(HL)_2^-]/([NpO_2^+][H^+]^2[L^{2-}]^2) \quad (2)$$

where L^{2-} represents the doubly deprotonated form of glutaroimide dioxime ($H_2L \rightarrow 2H^+ + L^{2-}$). The calculated molar absorptivities of $NpO_2(HL)(aq)$ and $NpO_2(HL)_2^-$ complexes are shown in Figure 2, while the stability constants of these complexes (log β_{111} and log β_{122}) are summarized in Table 1.

Microcalorimetry. Figure 3 shows a representative calorimetric titration of NpO_2^+ with glutaroimide dioxime. Positive spikes in the thermogram (left figure) represent exothermic reaction heat. The right side of the figure shows the accumulated reaction heat and the distribution of neptunium(V) species as a function of the volume of titrant added. The calculated enthalpies and entropies of complexation at 25 °C are summarized in Table 1.

DISCUSSION

Comparison between the NpO_2^+ and UO_2^{2+} Complexes with Glutaroimide Dioxime. Table 1 shows a comparison of the thermodynamic parameters between the corresponding glutaroimide dioxime complexes of NpO_2^+ and UO_2^{2+}. The complexation reactions of glutaroimide dioxime with neptunium(V) and uranium(VI) are all exothermic accompanied by large entropies of complexation. The enthalpies and entropies of complexation for the two systems are comparable in their trends and magnitudes, suggesting that the coordination modes in the glutaroimide dioxime complexes with NpO_2^+ and UO_2^{2+} are probably similar.

Attempts to prepare crystals of the neptunium(V)/glutaroimide dioxime complexes from the working solutions were not successful. Future attempts may include using different countercation(s) and/or raising the solution pH, based on the suggestions from an anonymous reviewer. However, in the absence of the experimentally obtained structure of the neptunium(V) complex, the crystal structure of the $UO_2(HL)_2$ complex previously identified by single-crystal X-ray diffractometry[14] could provide insight into the structure of the analogous neptunium(V) complex. In the $UO_2(HL)_2$ complex (Figure 4), the middle imide group (−CH*N*HCH−) of the ligand is deprotonated, while the protons of both oxime groups (−CH=NO*H*) are rearranged from the oxygen atom to the nitrogen atom. The electron density of the resulting HL^- ligand is delocalized on − O−N−C−N−C−N−O−, forming a conjugated system that coordinates to UO_2^{2+}. As shown by Figure 4, the structure of $UO_2(HA)_2$ is centrosymmetric, with the two HL^- ligands in the equatorial plane of UO_2^{2+}, and the uranium atom is located at the inversion center. On the basis of the similarity in the thermodynamic parameters for the complexation of glutaroimide dioxime with neptunium(V) and uranium(VI), it is reasonable to assume that the HL^- ligand also coordinates to NpO_2^+ via the equatorial plane in a tridentate mode and the analogous $NpO_2(HL)_2^-$ complex possesses a structure similar to that of the $UO_2(HL)_2$ complex.

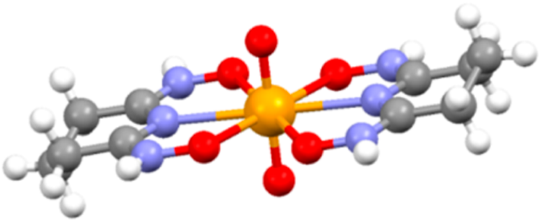


Figure 4. Crystal structure of $UO_2(HA)_2$.[14] Color code: U, gold; O, red; N, purple; C, gray; H, white.

As shown in Table 1, the NpO_2^+/H_2L complexes are weaker than the corresponding UO_2^{2+}/H_2L complexes (Table 1). For the purpose of comparison, formation of the $NpO_2(HL)(aq)$ and $NpO_2(HL)^-$ complexes could be expressed as reactions (3) and (4), with the equilibrium constants of $\beta_{1(11)}$ and $\beta_{1(22)}$, respectively.

$$NpO_2^+ + HL^- = NpO_2(HL)(aq)$$
$$\beta_{1(11)} = [NpO_2(HL)(aq)]/([NpO_2^+][HL^-]) \tag{3}$$

$$NpO_2^+ + 2HL^- = NpO_2(HL)_2^-$$
$$\beta_{1(22)} = [NpO_2(HL)_2^-]/([NpO_2^+][HL^-]^2) \tag{4}$$

The values of log $\beta_{1(11)}$ and log $\beta_{1(22)}$ can be obtained by taking into consideration the first protonation reaction of glutaroimide dioxime ($H^+ + L^{2-} \rightarrow HL^-$). Table 1 shows that the values of log $\beta_{1(11)}$ and log $\beta_{1(22)}$ for the NpO_2^+/H_2L complexes are 5.3 ± 0.1 and 8.5 ± 0.2, respectively. In comparison, the corresponding UO_2^{2+}/H_2L complexes are stronger with log $\beta_{1(11)} = 10.4 \pm 1.3$ and log $\beta_{1(22)} = 18.5 \pm 1.1$. The difference in the stability constants between neptunium(V) and uranium(VI) complexes reflects the difference in the effective cationic charges of NpO_2^+ ($Z_{eff} = +2.2$) and UO_2^{2+} ($Z_{eff} = +3.2$).[31]

Optical Properties and the Symmetry of Neptunium(V) Species. It is known that the absorption bands of neptunium(V) in the near-IR region originate from the f → f transitions, which are electric-dipole-forbidden by Laporte's rule.[32,33] Therefore, the intensities of the bands are sensitive to the symmetry of the coordination environment of neptunium(V), as extensively studied for a number of NpO_2^+ complexes by Krot and co-workers[34,35] and summarized recently.[36] If the neptunium(V) complex is centrosymmetric and the neptunium atom is at the inversion center, the f → f transitions of neptunium(V) are completely forbidden and the near-IR absorption bands will be "silent". Only if the arrangement of ligands around NpO_2^+ destroys the center of inversion are absorption bands of neptunium(V) observed.

For the system in this study, the optical absorption properties and schematic structures of the neptunium(V) species [free aquo NpO_2^+ ion, $NpO_2(HL)(aq)$, and $NpO_2(HL)_2^-$] are shown in Figure 5. The free aquo NpO_2^+ ion, $NpO_2(HL)(aq)$, and $NpO_2(HL)_2^-$ species show optical absorption bands at 980.2, 993.4, and 1002.9 nm, respectively, implying that none of the three species is centrosymmetric. This is easy to understand for the free aquo NpO_2^+ ion and $NpO_2(HL)(aq)$ species, as shown in Figure 5. The free aquo NpO_2^+ ion is not centrosymmetric because it has five water molecules in the equatorial plane, as determined by X-ray absorption studies.[37] Obviously, the 1:1 complex, $NpO_2(HL)(aq)$, cannot be centrosymmetric either, because its equatorial plane consists of one tridentate ligand and two water molecules. However, a question arises as to the optical absorption of the $NpO_2(HL)_2^-$ species: if we assume the $NpO_2(HL)_2^-$ complex possesses a structure similar to that of the $UO_2(HA)_2$ complex that is centrosymmetric (Figure 4), why does it show fairly strong optical absorption ($\varepsilon = 206\ M^{-1}\ cm^{-1}$) at 1002.9 nm? The

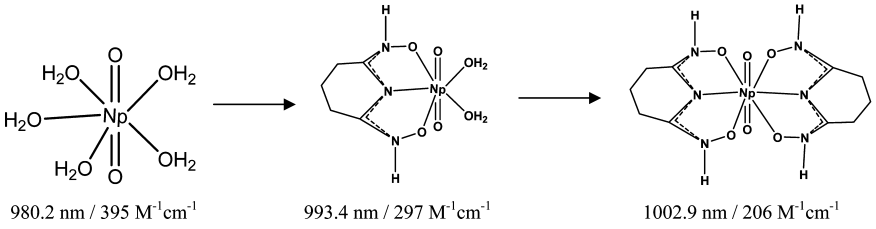


Figure 5. Stepwise formation of NpO_2^+/glutaroimide dioxime complexes and their optical absorption properties (band position/molar absorptivity).

Figure 6. Calculated cis (left) and trans (right) isomers of the 1:2 NpO_2^+/glutaroimide dioxime complex $NpO_2(HL)_2^-$. Color code: Np, green; O, red; N, purple; C, gray; H, white.

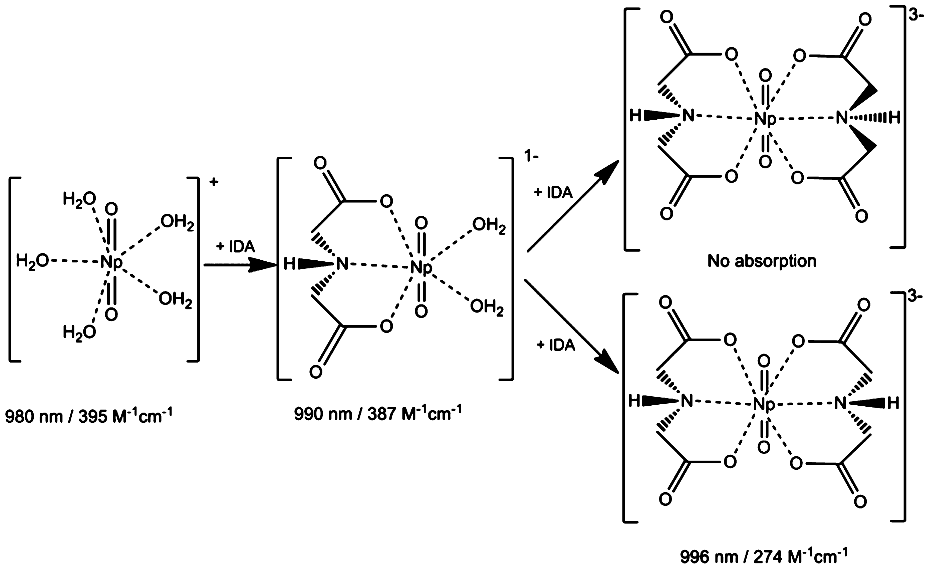


Figure 7. Stepwise formation of NpO_2^+/iminodiacetate complexes and their optical absorption properties (band position/molar absorptivity).[36]

discussions on the configurational isomers and the results of DFT calculations presented in the next section help to answer this question.

Molecular Modeling (DFT Calculations). Similar to cyclohexane, the six-membered piperidine ring in the glutaroimide dioxime ligand prefers a chair conformation.[38,39] In the $NpO_2(HL)_2^-$ complex shown in Figure 5, depending on the orientation of the chair conformation, the $NpO_2(HL)_2^-$ complex could possess a cis or trans configuration relative to the equatorial plane of the NpO_2^+ ion: the cis isomer has both "chairs" pointing toward the same direction, while the trans isomer has the two "chairs" pointing toward opposite directions (Figure 6). The cis isomer should have optical absorption bands due to the f → f transition because it does not possess an inversion center. On the contrary, the trans isomer would be "silent" in optical absorption because it is centrosymmetric. (It should also be noted that, as an anonymous reviewer pointed out, the electronic states are not pure 5f and a small amount of covalence would make it electric-dipole-transition-allowed. Various effects could "relax" Laporte's rule, including the vibrational modes of odd parity, dynamic movements of counterions and molecules breaking the inversion symmetry, and contributions from electric quadrupole and magnetic dipole moments and other higher-order mechanisms.)

We hypothesize that the cis and trans isomers of the $NpO_2(HL)_2^-$ complex probably coexist in solution and it is the cis isomer that makes the absorption band at 1002.9 nm active (Figures 2 and 5). DFT calculations were performed to test this hypothesis. The geometries of the cis and trans isomers of $NpO_2(HL)_2^-$ were optimized, and the energies were calculated in the gas phase as well as in the aqueous medium using COSMO, as implemented in *TURBOMOLE*. The results show that the two configurations possess very similar energies in both the gas and solution phases (Tables S1 and S2 in the Supporting Information). In the gas phase, the energy of the cis isomer is 2.23 kcal/mol lower than that of the trans isomer. However, in the aqueous medium, the energy of the cis isomer is 0.19 kcal/mol higher than that of the trans isomer. Such a small difference in energy suggests that the energy barrier for the configurational change from trans to cis (or vice versa) is very low and the two configurations could indeed coexist in solution. It is the presence of the noncentrosymmetric cis isomer that renders the absorption bands at 1002.9 nm. A similar observation has been reported for the complexation of NpO_2^+ with iminodiacetic acid (IDA),[36] in which cis and trans isomers of $NpO_2(IDA)_2^{3-}$ coexist, and the $NpO_2(IDA)_2^{3-}$ species absorbs at 996 nm, as shown in Figure 7. Detailed information on the DFT calculations is provided in the Supporting Information.

■ CONCLUSIONS

NpO_2^+ forms moderately strong 1:1 and 1:2 complexes with glutaroimide dioxime (H_2L) in aqueous solutions, $NpO_2(HL)(aq)$, and $NpO_2(HL)_2^-$. No reduction of neptunium(V) was observed under the experimental conditions. The complexation of NpO_2^+ with glutaroimide dioxime is driven by both exothermic enthalpies and positive entropies of complexation. The results of DFT calculations validated the hypothesis that the cis and trans isomers of $NpO_2(HL)_2^-$ could coexist in solutions, and it is the presence of the nonsymmetric cis isomer that makes the f → f transitions allowable so that the $NpO_2(HL)_2^-$ complex shows optical absorption in the near-IR region.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01319.

Tables S1 and S2 containing calculated energies of cis and trans isomers in gas and solvent phases and major bond distances in the $NpO_2(HL)_2^-$ complex (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: LRao@lbl.gov.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

All experimental work was conducted at Lawrence Berkeley National Laboratory (LBNL) and supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-05CH11231 at LBNL. S.A.A. acknowledges the Indo−U.S. Science & Technology Forum (IUSSTF) for awarding a fellowship to support his visit to LBNL. The DFT computation was performed by A.B. at Bhabha Atomic Research Centre, Mumbai, India. The authors thank C. J. Leggett of LBNL for synthesizing and checking the purity of the glutaroimide dioxime ligand.

■ REFERENCES

(1) Fried, S. Neptunium. In *The Actinide Elements*; Seaborg, G. T., Katz, J. J., Eds.; McGraw-Hill: New York, 1954; p 471.

(2) Yoshida, Z.; Johnson, S. G.; Kimura, T.; Krsul, J. R. Neptunium. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp 699−812.

(3) *Yucca Mountain Science and Engineering Report*, revision 1; U.S. Department of Energy: North Las Vegas, NV, 2002.

(4) Martell, A. E., Smith, R. M., Eds. *Critical Stability Constant Database 46*; National Institute of Science and Technology (NIST): Gaithersburg, MD, 2003.

(5) Hummel, W.; Anderegg, G.; Puigdomènech, I.; Rao, L.; Tochiyama, O. In *Chemical Thermodynamics of Compounds and Complexes of: U, Np, Pu, Am, Tc, Zr, Ni and Se with Selected Organic Ligands*; Mompean, F. J., Illemassene, M., Perrone, J., Eds.; Elsevier BV: Amsterdam, The Netherlands, 2005.

(6) Rao, L.; Tian, G. Complexation of actinides with derivatives of oxydiacetic acid. In *Actinides 2005—Basic Science, Applications and Technology: Proceedings of the Materials Research Society Symposium*; Sarrao, J. L., Schwartz, A. J., et al., Eds.; MRS: Warrendale, PA, 2006; Vol. *893*; Paper 0893-JJ08-06.

(7) Rao, L.; Tian, T.; Teat, S. J. *Dalton Trans.* **2010**, *39*, 3326−3330.

(8) May, I.; Taylor, R. J.; Denniss, I. S.; Brown, G.; Wallwork, A. L.; Hill, N. H.; Rawson, J. M.; Less, R. *J. Alloys Compd.* **1998**, *275*−*277*, 769−772.

(9) Colston, B. J.; Choppin, G. R.; Taylor, R. J. *Radiochim. Acta* **2000**, *88*, 329−334.

(10) Sinkov, S. I.; Choppin, G. R.; Taylor, R. J. Complexation and redox chemistry of U(VI), Np(V) and Pu(VI) with acetohydroxamic acid. *Abstract of Papers of the American Chemical Society*; American Chemical Society: Washington, DC, 2006; Vol. *232*, pp 853−853; Meeting Abstract 173-IEC.

(11) Yang, Y.; Zhang, Z.; Luo, S.; Rao, L. *Eur. J. Inorg. Chem.* **2014**, *2014*, 5561−5566.

(12) Tian, G.; Rao, L. *Dalton Trans.* **2010**, *39*, 9866−9871.

(13) Tian, G.; Rao, L.; Teat, S. J. *Inorg. Chem.* **2009**, *48*, 10158−10164.

(14) Tian, G.; Teat, S. J.; Zhang, Z.; Rao, L. *Dalton Trans.* **2012**, *41*, 11579−11586.

(15) Sun, X.; Tian, G.; Xu, C.; Rao, L.; Vukovic, S.; Kang, S. O.; Hay, B. P. *Dalton Trans.* **2014**, *43*, 551−557.

(16) Rao, L.; Choppin, G. R. *Inorg. Chem.* **1984**, *23*, 2351−2354.

(17) Leggett, C. J.; Rao, L. *Polyhedron* **2015**, *95*, 54−59.

(18) Rao, L.; Srinivasan, T. G.; Garnov, A. Y.; Zanonato, G. P.; Di Bernardo, P.; Bismondo, A. *Geochim. Cosmochim. Acta* **2004**, *68*, 4821−4830.

(19) Gran, G. *Analyst* **1952**, *77*, 661−671.

(20) Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739−1753.

(21) Wilson, E. W.; Smith, D. F. *Anal. Chem.* **1969**, *41*, 1903−1903.

(22) Gans, P.; Sabatini, A.; Vacca, A. *J. Solution Chem.* **2008**, *37*, 467−476.

(23) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098−3100.

(24) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822−8824.

(25) Klamt, A.; Schuurmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, *2*, 799−805.

(26) *TURBOMOLE* is a program package developed by the Quantum Chemistry Group at the University of Karlsruhe, Karlsruhe, Germany, in 1988.

(27) Ahlrichs, R.; Bar, M.; Haser, M.; Horn, H.; Kolmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.

(29) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(30) Shamov, G. A.; Schreckenbach, G. *J. Am. Chem. Soc.* **2008**, *130*, 13735−13744.

(31) Choppin, G. R.; Rao, L. *Radiochim. Acta* **1984**, *37*, 143−146.

(32) Matsika, S.; Pitzer, R. M. *J. Phys. Chem. A* **2000**, *104*, 4064−4068.

(33) Matsika, S.; Pitzer, R. M.; Reed, D. T. *J. Phys. Chem. A* **2000**, *104*, 11983−11992.

(34) Bessonov, A. A.; Afonaseva, T. V.; Krot, N. N. *Soviet Radiochemistry* **1991**, *33*, 245−250.

(35) Grigorev, M. S.; Baturin, N. A.; Bessonov, A. A.; Krot, N. N. *Radiochemistry* **1995**, *37*, 12−14.

(36) Rao, L.; Tian, G. *Symmetry* **2009**, *2*, 1−14.

(37) Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Edelstein, N. M.; Reich, T. *Inorg. Chem.* **1997**, *36*, 4676−4683.

(38) Carballeira, L.; Perez-Juste, I. *J. Comput. Chem.* **1998**, *19*, 961−976.

(39) Blackburne, I. D.; Katritzky, A. R.; Takeuchi, Y. *Acc. Chem. Res.* **1975**, *8*, 300−306.