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Complexation-Assisted Reduction: Complexes of Glutaroimide-dioxime with Tetravalent Actinides (Np(IV) and Th(IV))

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Abstract

Glutaroimide-dioxime forms strong complexes with tetravalent Th(IV) and Np(IV) in aqueous solution. In conjunction with literature data on the complexation of glutaroimide-dioxime with other metal ions, It was found that the complexes becomes weaker as the effective charge density on the metal ions decreases: $V^{+5} > Th^{4+} \approx Fe^{3+} > UO_2^{2+} > Eu^{3+}/Nd^{3+} > Cu^{2+} > Pb^{2+} > NpO_2^+ > Ca^{2+}/Mg^{2+}$. In the glutaroimide-dioxime complexes with Th(IV) and Np(IV), deprotonation of the imide group and relocation of the two hydrogen atoms from oxygen to nitrogen of the oxime groups result in a large conjugated system (–O-N-C-N-C-N-O-) that coordinates strongly to the metal center in a tridentate mode *via* the central imide nitrogen atom and the two oxime oxygen atoms. Because the stability of glutaroimide-dioxime complexes with Np(IV) is much higher than those with Np(V), the redox potential of the Np(V)/Np(IV) couple is expected to be shifted significantly. As a result, crystals of glutaroimide-dioxime complexes with Np(IV) were readily obtained from initial solutions containing Np(V). A mechanism of complexation-assisted reduction integrating the thermodynamic and structural data from this work is discussed.

Key Words: Complexation-assisted reduction, tetravalent neptunium, thorium, glutaroimide-dioxime, crystal structure

1. Introduction

In recent years, the complexation of glutaroimide-dioxime (Figure 1, denoted as H_3L in this work) has been studied with a number of metal ions, including hexavalent UO_2^{2+}, pentavalent NpO_2^+ and VO_2^+, trivalent Fe^{3+} and Nd^{3+}/Eu^{3+}, and divalent Cu^{2+}, Ni^{2+}, Pb^{2+}, Ca^{2+}, and Mg^{2+}.[1,2,3,4,5,6,7] Equilibrium constants were determined for these metal complexes and crystal structures for some of them were obtained. In all the complexes, glutaroimide-dioxime coordinates to the metal center via the two oxygen atoms of the oxime groups and the nitrogen atom of the amido group in a tridentate fashion.

In studies of complexation of glutaroimide-dioxime with pentavalent vanadium (starting as the vanadyl species VO_2^+),[4,5,8] it was found that a non-oxido V(V) complex, VL_2^-, forms in and crystallizes from aqueous solution.[4] The VL_2^- complex is extremely strong because the glutaroimide-dioxime ligand interacts with a "bare" V^{5+} center instead of the oxido VO_2^+ ion (the V=O oxido bonds in VO_2^+ were replaced by V-O and V-N bonds where the donor atoms O and N were from glutaroimide-dioxime). In fact, the stability constant of VL_2^- is the highest among the studied metal/glutaroimide-dioxime complexes. In general, the stability constants follow the order: $V^{+5} > Fe^{3+} > UO_2^{2+} > Eu^{3+}/Nd^{3+} > Cu^{2+} > Pb^{2+} > NpO_2^+ > Ca^{2+}/Mg^{2+}$, roughly the same order of the effective charge density on the metal ions. Until now, no thermodynamic equilibrium constants for the complexes between glutaroimide-dioxime and tetravalent metal ions have been reported. To fill this gap, the equilibrium constants for the complexation of glutaroimide-dioxime with a representative tetravalent ion, Th(IV), were experimentally determined.
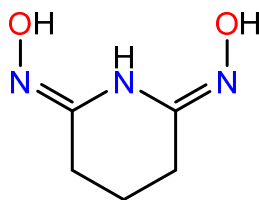
Figure 1 Glutaroimide-dioxime (donated as H_3L in this paper).

The formation of non-oxido vanadium(V) complex with glutaroimide-dioxime[4] is particularly interesting because non-oxido vanadium(V) species are very rare and, to our best knowledge, no "bare" V^{5+} complexes had been directly synthesized from oxido V(V) species (VO_2^+ or vanadates) and crystallized from aqueous solution until that study.[4] It had been reported that one non-oxido V^{5+} complex, $[PPh_4][\Delta-V((S,S)\text{-HIDPA})_2] \cdot H_2O$ (HIDPA^{3-} = fully-deprotonated 2,2'-(hydroxyimino)dipropionic acid, H_3HIDPA), was crystallized as the oxidized analogue of the naturally-existing Amavadin[19–23(CS)] from aqueous solution through the oxidation of a V(IV) complex by Ce(IV).[24 of CS] In addition, there had only been suggestions that non-oxido V^{5+} complexes could be formed in aqueous solutions via the displacement of the oxido V=O bonds by chelating ligands (e.g., the trishydroxamate derivative deferoxamine[25 of CS]), but such formation had not been confirmed.

The observation of non-oxido V(V)/glutaroimide-dioxime complex[4] stimulated our interest in synthesizing non-oxido Np(V) species in and from aqueous solution through complexation of NpO_2^+ with glutaroimide-dioxime. Despite a previous study[2] that demonstrated NpO_2^+ could form glutaroimide-dioxime complexes in the forms of protonated $NpO_2(H_2L)$ and $NpO_2(H_2L)_2^-$ species (in which the ligand is not fully de-protonated and the oxido Np=O bonds remain intact), we were still interested in exploring the possibilities of preparing non-oxido Np(V)/glutaroimide-dioxime complexes. However, after making various attempts to do so by

adjusting experimental conditions such as acidity, ligand/metal ratios, and background ionic media (perchlorate *vs.* chloride), we have not succeeded in preparing non-oxido Np(V) complexes with glutaroimide-dioxime in the present work. Instead, it was found that Np(V) was slowly reduced to Np(IV) in solutions containing glutaroimide-dioxime and crystals of Np(IV)/glutaroimide-dioxime complexes were obtained from the aqueous solution.

This paper summarizes the thermodynamic data for the complexation of glutaroimide-dioxime with Th(IV), the structural data for the glutaroimide-dioxime complexes with Np(IV), and describes a mechanism of complexation-assisted reduction that we postulate to be responsible for the formation of Np(IV)/glutaroimide-dioxime complexes from Np(V).

2. Experimental

2.1 Chemicals

Freshly boiled and cooled MilliQ water was used in preparations of all aqueous solutions. Glutaroimide-dioxime, denoted as H_3L in this paper (Figure 1), was synthesized by mixing and stirring glutaronitrile (Aldrich, 99%) and hydroxylamine (Sigma-Aldrich, 99%) at a 1:2 mole ratio in a 1:1 ethanol/water mixture at 80 – 90°C for five days. H_3L was obtained as white solids upon cooling to room temperature with > 90% yield. The resultant material was purified by recrystallization twice from methanol, and subsequently characterized by ^{1}H-NMR and potentiometric titration.[3,4,8] Stock solutions of Np(V) in perchloric and hydrochloric acids are taken from the laboratory stock solutions, preparations of which were described in the literature.[2,9] The radioisotopic purity ([237]Np) and oxidation state (Np(V)) of the stock solutions were confirmed by α-spectroscopy and optical absorption spectroscopy, respectively. The concentration of Np(V) was determined by the absorbance at 980.4 nm ($\varepsilon = 394$ $(\text{mol·L}^{-1})^{-1}\text{cm}^{-1}$).

A stock solution of Th(IV) perchlorate (for potentiometric titrations) was prepared by dissolving Th(NO$_3$)$_4$·xH$_2$O (Sigma-Aldrich, 99%) in water and precipitating Th(IV) as Th(OH)$_{4(s)}$ from the solution. The precipitate was then centrifuged, washed thoroughly with water, and re-dissolved with a moderate excess of HClO$_4$. The precipitation and dissolution were repeated three times. The Th(IV) and free H$^+$ concentrations in the stock solution were determined, respectively, by complexometry,[10] and Gran's potentiometric method.[11] All potentiometric titrations were conducted at (25.0 $\pm$ 0.1)^{o}C. The ionic strength of all working solutions used for the potentiometric experiments was adjusted to 1.00 mol dm^{-3} NaClO$_4$ by adding appropriate amounts of NaClO$_4$. Common chemicals used in this work, including NaClO$_4$, HClO$_4$, HCl, NaOH, methanol, and ethanol, are all of reagent grade and obtained from Sigma-Aldrich.

2.2 Potentiometry

The potentiometric titration system consists of a glass titration cell, a Metrohm dosimat (Model 765), a Metrohm pH meter (Model 713) equipped with a Ross combination pH electrode (Orion Model 8102), and a computer. The temperature of the titration cell was maintained at (25.0 $\pm$ 0.1)^{o}C by an external circulating water bath. A constant flow of argon over the solution in the cell protected the solution from the contamination of CO$_2$. The original inner solution of the electrode (3 M KCl) was replaced with 1 M NaCl to avoid the clogging of the electrode junction due to the low solubility of KClO$_4$ and reduce the electrode junction potential.

In a potentiometric titration, the hydrogen ion concentration was related to the measured electromotive force (*EMF*, in millivolts) according to equations (1) and (2), in acidic and basic regions, respectively.

$$E = E^0 + RT/F \ln[H^+] + \gamma_H[H^+] \qquad (1)$$

$$E = E^0 + RT/F \ln(Q_w/[OH^-]) + \gamma_{OH}[OH^-] \qquad (2)$$

where E is the electromotive force, R is the gas constant, T is the temperature in Kelvin, and F is the Faraday constant. $Q_w = [H^+][OH^-]$. The last terms, $\gamma_H[H^+]$ in eq.(1) and $\gamma_{OH}[OH^-]$ in eq.(2), are the electrode junction potentials for the hydrogen ion or the hydroxide ion, assumed to be proportional to the concentration of the hydrogen or hydroxide ions. E^o, γ_H, and γ_{OH} are the electrode parameters that need to be determined in a "calibration" titration prior to each complexation titration. The calibration titration was conducted with standard HCl and NaOH solutions to determine the electrode parameters that allowed the calculation of hydrogen ion concentrations from the electrode potential in the subsequent titration.

Complexation of Th(IV) with glutaroimide-dioxime was studied by multiple potentiometric titrations with solutions of different concentrations of Th(IV) (C_{Th} as the total [Th(IV)]), ligand (C_L for the total ligand concentration including H_4L^+, H_3L(aq), H_2L^-, and HL^{2-}), and acidity (C_H for the total concentration of dissociable protons). Usually, 15 mL of Th(IV)/H$_3$L solutions were titrated with 0.1 M NaOH. About 50 data points were collected for each titration. The stability constants of the Th(IV)/glutaroimide-dioxime complexes were calculated using the nonlinear regression program Hyperquad 2008.[12]

2.3 Synthesis of crystals of glutaroimide-dioxime complexes with Np(IV) and Th(IV)

2.3.1 Complex I: [Np(H$_2$L)$_2$·Cl$_2$]

An aqueous solution of pyridine (0.15 mL, 20 % pyr v:v) was added to solid glutaroimide-dioxime (8.4 μmol). An aliquot of the stock solution of Np(V) chloride (20 μL, 4.2 μmol) was added and the resulting homogeneous solution was warmed to 40 °C for 15 min. The solution

was allowed to cool to room temperature. Slow evaporation over the course of 2 days resulted in growth of small yellow plates.

2.3.2 Complex II: [Np(H₂L)₃][ClO₄]

An aliquot of NpO_2ClO_4 solution (30 μL, 0.167 M Np(V)) was added to 3.0 mL aqueous solution of glutaroimide-dioxime (10 mM) that was neutralized with one equivalent of NaOH. After two weeks of slow evaporation in a ventilation hood, small yellow crystals formed in the solution.

2.3.3 Complex III: [Th(H₂L)₃][NO₃]

$[Th(H_2L)_3][NO_3]$ was synthesized by dissolving $Th(NO_3)_4 \cdot 4H_2O$ (59 mg, 0.107 mmol) in water (5 mL) followed by adding the ligand (H_3L, 46 mg, 0.32 mmol) with stirring until the ligand fully dissolved. Aliquots of 1 M NaOH (0.32 mL, 0.32 mmol) were added dropwise and the solution became cloudy. Then, 1 M HNO_3 solution (approx. 0.05 mL, 0.05 mmol) was added dropwise until the solution became clear again. The pH of the solution was measured to be 4 - 5. The solution was allowed to evaporate to near dryness, during which small colorless crystals formed.

2.4 X-ray crystallography

Representative crystals of the neptunium complexes (**I** and **II**) and the thorium complex (**III**) were mounted onto 10-micron MiTiGen Dual-Thickness loops. The mounted neptunium samples were then epoxy sealed inside clear, rigid plastic tubes to prevent sample loss during the data collections. X-ray diffraction data were collected on a Bruker diffractometer equipped with a PHOTON100 CMOS detector at the Small Molecule Crystallography Beamline 11.3.1 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) using a

silicon-monochromated beam of 16 keV (0.7749 Å) synchrotron radiation. Intensity data were collected using the Bruker APEX3 software package.[13] Integrations of the intensity data, cell refinement, and data reduction were performed by using the Bruker SAINT software package.[14] Absorption corrections were made using SADABS (for **II**) and TWINABS (for **I** and **III**).[15] The structures were solved by direct methods using SHELXT and refined against F^2 using SHELXL-2014.[16,17] Details of the crystallographic data for complexes **I** and **II** are provided in **Table 1**. Details regarding the structure of complex **III** can be found in the Supporting Information. CCDC 1828263, 1828264, and 1828265 contain the supplementary crystallographic information for complexes **I**, **II**, and **III**, respectively. These files can be accessed free-of-charge at The Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/). Figures of the structures in this report were generated using Mercury.[18]

Table 1 Crystallographic data and refinement information for complexes **I** and **II**.

	Complex I	**Complex II**
Empirical formula	C20 H29 Cl3 N8 Np O5	C15 H30 Cl N9 Np O11
Formula weight (g/mol)	804.86	834.94
Temperature (K)	150(2)	293(2)
Wavelength (Å)	0.7749	0.7749
Crystal system	Monoclinic	Monoclinic
Space group	C2/m	C2/c
Unit cell dimensions (Å)	$a = 13.9653(6)$ $b = 22.2882(9)$ $c = 10.1167(4)$ $\alpha = 90°$ $\beta = 118.238(2)°$ $\gamma = 90°$	$a = 25.765(20)$ $b = 10.221(7)$ $c = 11.280(8)$ $\alpha = 90°$ $\beta = 108.573(6)°$ $\gamma = 90°$
Volume (Å^3)	2774.2(2)	2816(4)
Z	4	4
Density (calculated) (Mg/m^3)	1.927	1.970
Absorption coefficient (mm^{-1})	3.556	3.864
$F(000)$	1556	1628
Crystal size (mm^3)	0.015 x 0.010 x 0.005	0.060 x 0.050 x 0.040
Theta range for data collection	2.491 to 36.606°	2.355 to 33.502°
Index ranges	$-21 <= h <= 18$ $0 <= k <= 34$ $0 <= l <= 15$	$-36 <= h <= 36$ $-14 <= k <= 14$ $-16 <= l <= 15$

| Reflections collected	38739	17710
Independent reflections	5375 [R(int) = 0.0463]	4259 [R(int) = 0.0219]
Completeness to theta = 27.706°	99.7 %	100%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.982 and 0.678	0.7466 and 0.6078
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5375 / 130 / 222	4259 / 43 / 233
Goodness-of-fit on F^2	1.100	1.123
Final R indices [$I >$ 2sigma(I)]	$R1$ = 0.0308 $wR2$ = 0.0735	$R1$ = 0.0193 $wR2$ = 0.0543
R indices (all data)	$R1$ = 0.0380 $wR2$ = 0.0758	$R1$ = 0.0198 $wR2$ = 0.0550
Largest diff. peak and hole (e.Å^{-3})	2.560 and -1.154	1.730 and -1.636

2.5 ^{1}H NMR

^{1}H NMR spectra of three aqueous solutions, one containing only glutaroimide-dioxime and two containing Th(IV) and glutaroimide-dioxime, were acquired on a Bruker AV-500 instrument (500 MHz) using a WATERGATE solvent suppression pulse sequence. Spectra were referenced to an external standard of C_6D_6. To prepare the Th(IV)/glutaroimide-dioxime solutions, glutaroimide-dioxime (1.2 mg) was suspended in 1 mL H_2O, and appropriate amounts of a stock solution of $ThCl_4$ (137 mM) was added slowly with stirring until the ligand completely dissolved. The L/Th ratios in the two solutions were 2:1 and 4:1, respectively. The pH of the 4:1 (L/Th) solution was about at 5 after mixing. NaOH was added to the 2:1 (L/Th) solution to bring the pH to 5.

3. Results and Discussion

3.1 Binding strength of glutaroimide-dioxime with Th(IV)

Figure 2 shows three titration curves for solutions with different ratios of C_L/C_{Th}. Based on the previous studies on the complexation of glutaroimide-dioxime with Fe^{3+},[6] UO_2^{2+},[1] NpO_2^+,[2] Ca^{2+}/Mg^{2+},[3] and V^{5+},[4] the ligand could form a variety of complexes with metal ions, including the protonated complexes MH_jL_k in acidic solutions and the mixed hydroxyl complexes, $M(OH)_jL_k$, in basic solutions. Various models with different combination of complexes were tested and the best fit was obtained by using the model including one 1:1, one 1:2, and four 1:3 Th/L complexes. The fitting (calculated vs. experimental values of $-\log[H^+]$) is shown in Figure 3, together with the distribution of Th(IV) species in the titrations. In the fitting, the protonation constants of glutaroimide-dioxime from a previous study[3] were used. The calculated stability constants of the Th(IV)-H_3L complexes are summarized in Table 2.
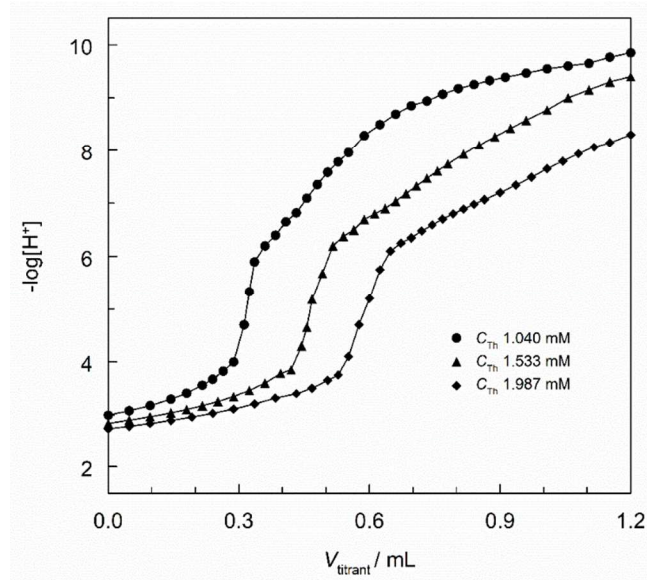
Figure 2 Potentiometric titrations of Th(IV)/glutaroimide-dioxime. $I = 1.0$ M $NaClO_4$, $t = (25.0 \pm 0.1)°C$. $V° = 15.0$ mL, $C_L° = 6.77$ mM, $C_H° = 20.3$ mM, $C_{Th}° = 1.040 – 1.987$ mM; Titrant: 0.1004 M NaOH.
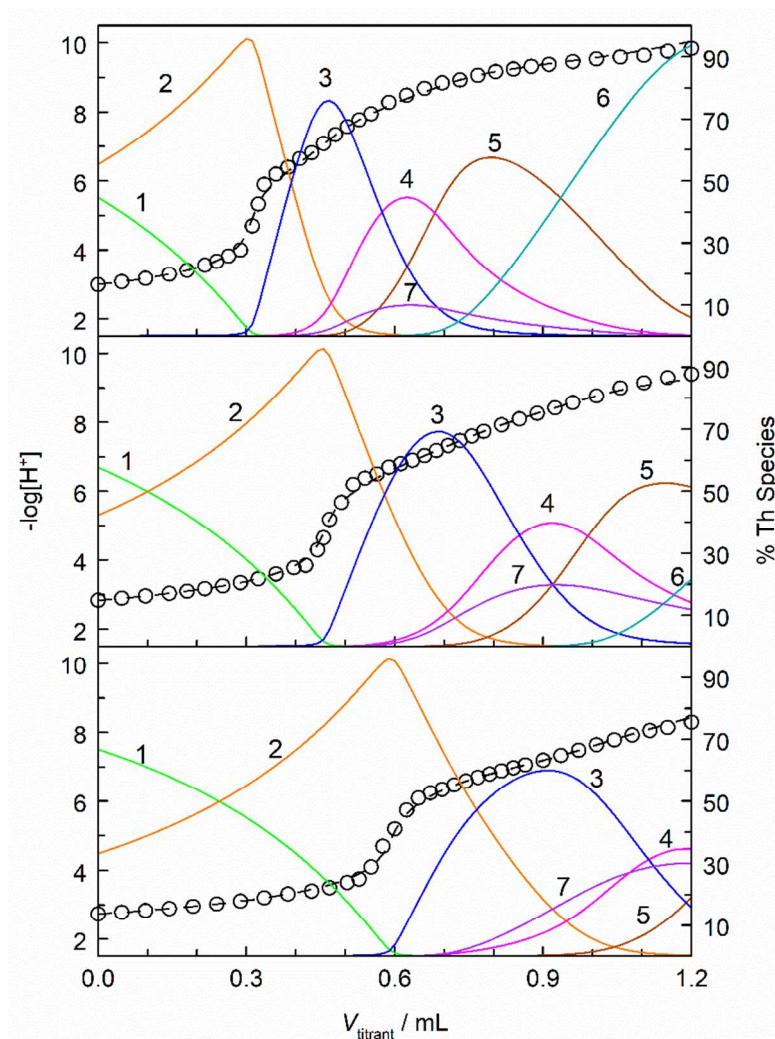
Figure 3 Fitting of potentiometric titration data for Th(IV)/glutaroimide-dioxime. $I = 1.0$ M NaClO$_4$, $t = (25.0 \pm 0.1)$°C. $V^o = 15.0$ mL; $C_L^o = 6.77$ mM; $C_H^o = 20.3$ mM; $C_{Th}^o = 1.040$ mM (top), 1.533 mM (middle), 1.987 mM (bottom); Titrant: 0.1004 M NaOH. Symbols: (○) experimental $-\log$ [H$^+$]; (dashed lines) fitted $-\log$ [H$^+$]; (solid lines) speciation of Th(IV), 1 – Th(H$_2$L)$^{3+}$, 2 – Th(H$_2$L)$_2^{2+}$, 3 – Th(H$_2$L)$_3^+$, 4 – Th(H$_2$L)$_2$(HL)$^+$, 5 – Th(H$_2$L)(HL)$_2^-$, 6 – Th(HL)$_3$(OH)$^{3-}$, 7 – Th(OH)$_4^-$.

Table 2 Equilibrium constants (log$K$) of the complexation of glutaroimide-dioxime (H$_3$L) with Th(IV) at 25°C, in comparison with Fe(III),[6] U(VI),[1] and Np(V).[2] $I = 1.0$ M NaClO$_4$ for Th(IV), 0.5 M NaCl for Fe^{3+}, U(VI), and Np(V).

Reactions[a]	Log K[b]			
	Th^{4+}	Fe^{3+}	UO_2^{2+}	NpO_2^+
$M^{j+} + H^+ + HL^{2-} = M(H_2L)^{j-1}$	25.9 ± 1.2	25.66 ± 1.09	22.7 ± 1.3	17.8 ± 0.1
$M^{j+} + 2\,H^+ + 2\,HL^{2-} = M(H_2L)_2^{j-2}$	48.1 ± 1.5	49.71 ± 1.08	43.0 ± 1.1	33.0 ± 0.2
$M^{j+} + 3\,H^+ + 3\,HL^{2-} = M(H_2L)_3^{j-3}$	66.9 ± 2.1	/	/	/
$M^{j+} + 2\,H^+ + 3\,HL^{2-} = M(H_2L)_2(HL)^{j-4}$	58.8 ± 2.0	/	/	/
$M^{j+} + H^+ + 3\,HL^{2-} = M(H_2L)(HL)_2^{j-5}$	50.1 ± 1.7	/	/	/
$M^{j+} + H_2O + 3\,HL^{2-} = M(OH)(HL)_3^{j-7} + H^+$	31.2 ± 1.4	/	/	/

[a]It should be noted that, because the neutral ligand is denoted as H_3L in this paper, not as H_2L in previous publications,[1,2,6] the notations for the Fe(III), U(VI), and Np(V) complexes differ from those in previous publications.
[b]Complexes of Fe(III) and U(VI) that have stoichiometry differing from those of Th(IV) complexes are not included for comparison.

Table 2 compares equilibrium constants of complex species of Fe^{3+}, UO_2^{2+}, and NpO_2^+ that have similar stoichiometry to that of Th(IV). For the 1:1 complex ($M(H_2L)^{j-1}$) and 1:2 complex ($M(H_2L)_2^{j-2}$), the binding strength of glutaroimide-dioxime with the metal ions follows the order: $Th^{4+} \sim Fe^{3+} > UO_2^{2+} \gg NpO_2^+$. This order roughly agrees with the trend in the charge density (ratio of electric charge over the ionic radius), implying that the interactions between glutaroimide-dioxime (with O and N donor atoms) and these cations are predominantly electrostatic in nature. A noticeable difference between the Th(IV) and other metal systems is that, a number of 1:3 metal/ligand complexes with varying degree of protonation were observed for the Th(IV)/glutaroimide dioxime system, but only up to 1:2 metal/ligand complexes were observed for the Fe(III), U(VI), and Np(V) systems. Because the glutaroimide dioxime ligand is known to be tridentate,[1,6] the linear configuration of UO_2^{2+} and NpO_2^+ only allows the ligand to approach the metal center via its equatorial plane so that the maximum ligand number in the U(VI) and Np(V) complexes is two. In the case of Fe^{3+}, its small ionic radius (0.55 Å for low spin Fe^{3+})[19] makes it impossible to accommodate three tridentate ligand molecules such as glutaroimide-dioxime. As for the much larger Th^{4+} cation (> 1.05 Å for coordination number

9),[20] complexes with coordination numbers of 8 and 9 are common. As shown in the crystal structure of $[Th(H_2L)_3][NO_3]$ discussed in the Supplementary Information, Th^{4+} indeed accommodates three glutaroimide-dioxime ligands with the coordination number of 9. In addition, ^{1}H NMR data of the Th(IV)/glutaroimide-dioxime solutions indicate that the equivalencies of the methylene protons of the ligand remain unchanged in the Th(IV)/glutaroimide-dioxime complexes, in agreement with the tridentate binding mode suggested by the thermodynamic data and confirmed by the crystallographic data. The NMR data and crystallographic data for Th(IV) complexes with glutaroimide-dioxime are presented in the Supplementary Information (Figure S1, Table S1, Figure S3).

3.2 Structures of glutaroimide-dioxime complexes with tetravalent Np(IV) and Th(IV)

Crystal structures of two Np(IV) complexes are shown in Figure 4. It is notable that the two Np(IV) complexes were obtained by using Np(V) solutions as the starting materials. It is our hypothesis that the Np(IV)/glutaroimide-dioxime complexes (**I** and **II**) formed and crystallized in aqueous solutions through a coupled complexation/reduction mechanism. Details of the structural aspects of tetravalent Np(IV) complexes and the mechanism of the formation of Np(IV) complexes from Np(V) are discussed below. Details of the structural aspects of a Th(IV)/glutaroimide-dioxime complex (Complex **III**) are provided in Supporting Information.
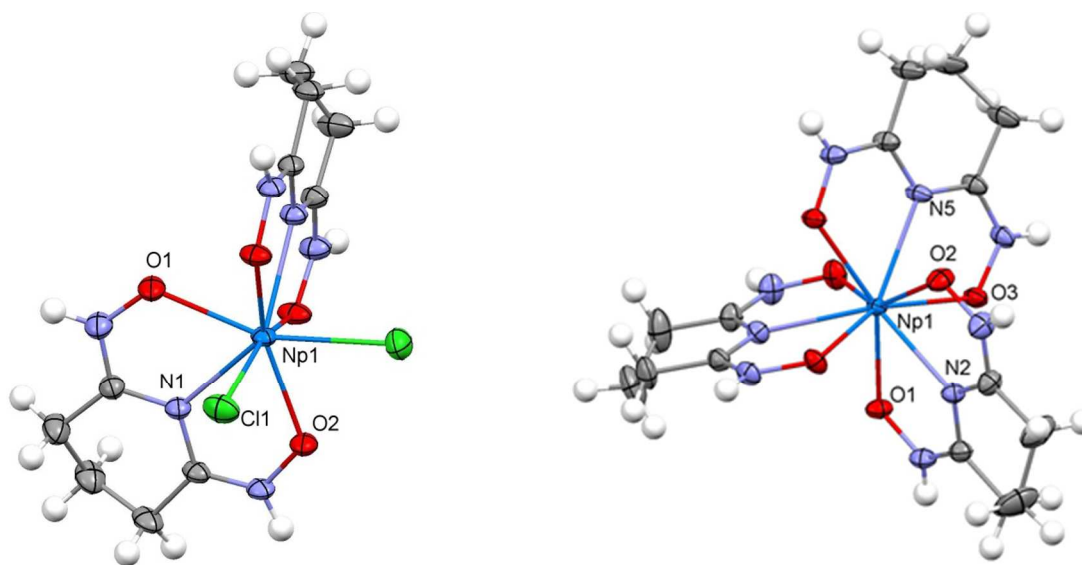
Figure 4. X-ray crystal structures of glutaroimide-dioxime complexes with Np(IV). (Left) Complex **I**, [Np(H$_2$L)$_2$·Cl$_2$]; (right) complex **II**, [Np(H$_2$L)$_3$][ClO$_4$]. Thermal ellipsoids are set to 50% probability. Outer sphere ions and solvent molecules have been excluded for clarity.

3.2.1 Structure I: [Np(H$_2$L)$_2$·Cl$_2$]

The neptunium(IV) bis(glutaroimide-dioxime) dichloride complex **I** was found to crystallize from its pyridine-water reaction solution in the monoclinic space group *C2/m*, with the neptunium center lying along a crystallographic two-fold axis. Each of the two glutaroimide-dioxime ligands is bound quite symmetrically to the metal center, with nearly identical Np-O distances of 2.355(2) Å and 2.350(2) Å. Of the three nitrogen atoms in the glutaroimide-dioxime ligand, only the central N atom is deprotonated and bound to the metal center (Np-N = 2.454(3) Å). Similar to the coordination of glutaroimide-dioxime to UO$_2$$^{2+}$ discussed in a previous paper,[1] two unusual and remarkable features are observed in the structure of the complex **I**: (1) the protons of both oxime groups (-CH=N-O**H**) relocate from the oxygen atom to the nitrogen atom, resulting in the tautomerization of the flanking oxime groups to a Zwitterionic form (the N-bound hydrogens in question were identified as distinct peaks in the X-ray crystal structure and were refined without idealization or restraint); (2) the middle imide group (-CH-**N**H-CH-) is

deprotonated, resulting in a -1 charged H_2A^- ligand that coordinates to Np in a tridentate mode (*via* the two oxime oxygen atoms and the imide nitrogen atom). With such configuration, the electron density on the H_2A^- ligand is delocalized on –O-N-C-N-C-N-O-, forming a conjugated system that coordinates to Np strongly. In fact, the bond length of the N-O bond of the oxime group is 1.42 Å in the H_3A molecule, but 1.36/1.37 Å in complex **I**. The significant shortening of the N-O bond upon complexation with Np supports the above arguments for a conjugated ligand system with delocalization of electron density on –O-N-C-N-C-N-O-.

Additionally, complex **I** was found to co-crystallize with an equivalent of chloride ion in the outer sphere, along with multiple equivalents of pyridine. The pyridine molecules in question are disordered over three positions, with the final refinement setting the total occupancy to two pyridine molecules per molecule of complex **I**. One of the pyridine nitrogens is in close contact (ca. 2.84 Å) to one of the deprotonated binding O atoms of the glutaroimide-dioxime ligand. We found this to be clear evidence of an H-bonding interaction, in which case the pyridine must be protonated in order to act as the donor. The presence of this pyridinium (Py-H) then allows for the charge of the free chloride ion to be accounted for, which resolves any ambiguity as to the oxidation state of neptunium in complex **I**, which we conclude is a neutral Np(IV) complex.

3.2.2 Structure II: [Np(H₂L)₃][ClO₄]

The crystal structure of the tris(glutaroimide-dioxime) complex **II** is much more straightforward. Complex **II** crystallizes from its aqueous reaction solution in the monoclinic space group *C2/c*. The Np center, as well as one of the glutaroimide-dioxime ligands, lies along a crystallographic 2-fold axis. In the structure of **II**, it is apparent that the ligands are in the same tautomerized, monoanionic form as they are in **I**, making the $Np(H_2L)_3^+$ unit overall cationic. The 9-coordinate geometry around the Np center resembles a distorted tri-capped trigonal prism. The Np-O

distances in **II**, of 2.405(2) Å, 2.409(2) Å, and 2.389(2) Å, are slightly extended from those observed in **I**, perhaps due to the higher coordination number at the metal. Likewise, the Np-N distances from the central, anionic nitrogens of the ligands are also slightly extended by similar amounts (Np-N = 2.497(3) Å and 2.479(3) Å). The positive charge of **II** is balanced by a perchlorate ion that could be satisfactorily modeled to lie on a single site.

In summary, the glutaroimide-dioxime ligand coordinates to the tetravalent actinide (Np(IV)) in the monoanionic, tautomerized tridentate form where extensive delocalization of the negative charge on the ligand occurs as a result of the relocation of the protons of the oxime groups and the deprotonation of the middle imide group.

3.3 Formation of Np(IV)/glutaroimide-dioxime complexes from Np(V) via a complexation-assisted reduction mechanism

The observations that complexes of Np(IV) with glutaroimide-dioxime (complexes **I** and **II**) were obtained from initial Np(V) are interesting and worth further discussion. Based on the information on the redox potentials of Np(V)/Np(IV) couple[21] and glutaroimide-dioxime[22] and the equilibrium constants of glutaroimide-dioxime complexes with Np(V)[2] and Np(IV) that can be estimated from the equilibrium constants for glutaroimide-dioxime complexes with Th(IV) in Table 2, we postulate that a complexation-assisted reduction mechanism is responsible for the formation of Np(IV)/glutaroimide-dioxime complexes from Np(V) in solutions containing glutaroimide-dioxime.

The standard potential for the reduction of Np(V) (as NpO_2^+) to Np(IV) (as Np^{4+}) in acidic solutions, reaction 3, is known to be +0.739 V *vs*. NHE.[21] Although there are only limited data on the redox potentials of oximies and glutaroimide-dioxime in particular, a recent cyclic

voltammetric measurement[22] suggested that the reduction potential involving the deprotonated glutaroimide-dioxime ligand is about +0.64 V *vs*. SCE, equivalent to +0.84 V *vs*. NHE. This value is similar to that found by electrochemical methods for hydroxamic acids such as formohydroxamic acid (FHA) and acetahydroxamic acid (AHA) (+0.62 V *vs*. SCE, equivalent to +0.82 V *vs*. NHE).[23] Based on these values, the glutaroimide-dioxime ligand could not reduce Np(V) to Np(IV) in acidic solutions (in other words, Np(V) could not oxidize glutaroimide-dioxime) if NpO_2^+ were not complexed and remained as a free ion.

$$NpO_2^+ + 4H^+ + e^- = Np^{4+} + 2H_2O \qquad\qquad (3)$$

However, the reduction potential for the Np(V)/Np(IV) couple is expected to shift significantly because NpO_2^+ and Np^{4+} forms complexes with glutaroimide-dioxime and the stability constants of NpO_2^+ and Np^{4+} complexes are expected to differ significantly. If we consider only the 1:1 M/L complex, the stability constant ($\log\beta$) of $NpO_2(H_2L)$ was determined to be 17.8 (Table 2) in a previous study.[2] The stability constants of Np^{4+}/glutaroimide-dioxime complexes are not available, but can be estimated from those of Th^{4+}/glutaroimide-dioxime complexes in Table 2 of this study. As discussed in a previous section (Section 3.1), the complexation of glutaroimide-dioxime with the studied metal ions is dominantly electrostatic, thus the stability constants of the complexes are correlated to the charge density of metal ions. Therefore, the stability constants of Np^{4+}/glutaroimide-dioxime complexes are expected to be higher than those of corresponding Th^{4+}/glutaroimide-dioxime complexes due to the difference in ionic radii (1.048 Å for Th^{4+} and 0.980 Å for Np^{4+}).[20] From the data for $Th(H_2L)^{3+}$ in Table 2 ($\log\beta = 25.9$), we estimate that the value of $\log\beta$ is about 27.7 for $Np(H_2L)^{3+}$, about 10 orders of magnitude higher than that of $NpO_2(H_2L)$. This means that the redox potential of the $NpO_2(H_2L)/Np(H_2L)^{3+}$ couple (shown in reaction 4) would be upward shifted by about +0.6 V. If

the 1:2 M/L complex is considered, the upward shift in reduction potential would be even larger. As a result, in the presence of glutaroimide-dioxime, Np(V) becomes a much stronger oxidant (with an estimated reduction potential of $+1.339$ V $vs.$ NHE), is capable of oxidizing glutaroimide-dioxime, and itself is reduced to Np(IV).

$$NpO_2(H_2L) + 4H^+ + e^- = Np(H_2L)^{3+} + 2H_2O \qquad (4)$$
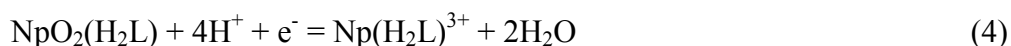
The shift of reduction potential due to complexation was also reported in other systems. For example, cyclic voltammetric measurements indicate that the reduction potential of the Pu(IV)/Pu(III) couple was shifted from $+0.733$ V $vs.$ SCE in the absence of AHA downward to $+0.581$ V $vs.$ SCE in the presence of AHA,[26] corresponding to a difference of $\Delta(\log\beta) = \log\beta_{Pu(IV)/AHA} - \log\beta_{Pu(III)/AHA} \approx 2.5$.

Although the delocalized electron density on the glutaroimide-dioxime ligand helps promote substitution of the oxido bonds, as previously discussed for the complexation of vanadium,[4,8] a kinetic barrier exists for the complexation-assisted reduction of $NpO_2(H_2L)$ to $Np(H_2L)^{3+}$ because the Np=O bonds in $NpO_2(H_2L)$ still needs to be replaced. This is consistent with the observation in a previous study that no reduction of Np(V) was identified in the presence of glutaroimide-dioxime in the first few hours when the absorption data were collected.[2] Also, in the preparation of the crystal of complex **II** with Np(V) as the initial material, absorption bands characterized as those for Np(IV) did not appear in the spectra of the solution until 1-2 days later and Np(V) complexes remained the major neptunium species in the mother liquor seven weeks after the mixing of Np(V) and glutaroimide-dioxime (Figure S2 in Supplementary Information), confirming that the reduction of Np(V) to Np(IV) is slow in the presence of glutaroimide-dioxime.

No efforts were made to identify the oxidation products of glutaroimide-dioxime in this work. However, data in the literature indicate that oximes (R_2C=NOH) could be oxidized to nitro compounds (R_2C-NO_2).[25,26] Oxidation of amidoximes ($RC(NH_2)NOH$) was also observed in the complex with molybdenum where the Mo(VI) center was reduced to Mo(II) while the aromatic amidoxime gave the corresponding nitroso complex in the presence of excess NH_2OH. The formation of the nitroso complexes was assumed to proceed via preliminary hydrolysis of the amidoxime, giving NH_2OH as one of the products.[27]

4. Conclusions

In an attempt to prepare non-oxido Np(V) complexes with glutaroimide-dioxime, Np(V) was observed to be reduced to Np(IV) and, instead, complexes of Np(IV)/glutaroimide-dioxime were obtained and the structures of a 1:2 and a 1:3 (Np(IV)/L) complexes were identified by single-crystal X-ray diffractometry. The formation of Np(IV)/glutaroimide-dioxime complexes from Np(V) was interpreted by a complexation-assisted reduction mechanism.

Thermodynamic equilibrium constants for the complexation of glutaroimide-dioxime with Th(IV) were determined. These data confirm that the interactions of glutaroimide-dioxime with the studied metal ions are predominantly electrostatic in nature and that the binding strength follows the order in charge density of the metal ions. Data for the Th(IV)/glutaroimide-dioxime complexes help to interpret the effect of complexation on the reduction potential of the Np(V)/Np(IV) couple and rationalize the complexation-assisted reduction mechanism.

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TOC Graphics

Glutaroimide-dioxime forms strong complexes with Np(IV) and Th(IV) in aqueous solution and in crystal. The formation of Np(IV) complexes from initial Np(V) is interpreted by a complexation-assisted reduction mechanism.