

Review

Symmetry, Optical Properties and Thermodynamics of Neptunium(V) Complexes

Linfeng Rao * and Guoxin Tian

Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA; E-Mail: gtian@lbl.gov

* Author to whom correspondence should be addressed; E-Mail: lrao@lbl.gov.

Received: 25 November 2009; in revised form: 19 December 2009 / Accepted: 21 December 2009 / Published: 28 December 2009

Abstract: Recent results on the optical absorption and symmetry of the Np(V) complexes with dicarboxylate and diamide ligands are reviewed. The importance of recognizing the “silent” feature of centrosymmetric Np(V) species in analyzing the absorption spectra and calculating the thermodynamic constants of Np(V) complexes is emphasized.

Keywords: symmetry; optical absorption; thermodynamics; neptunium; complexation

1. Introduction

Neptunium, an element in the actinide series of the periodic table, has an electronic configuration of $[\text{Rn}]5f^67s^2$ (or $[\text{Rn}]5f^46d^17s^2$). The most stable oxidation state of neptunium in aqueous solutions is Np(V) with an electronic configuration of $[\text{Rn}]5f^2$. Np(V) exists in aqueous solutions as the hydrated NpO_2^+ cation and exhibits characteristic absorption bands in the near IR region. In particular, the hydrated NpO_2^+ cation has an intensive absorption band at 980 nm ($\epsilon = 395 \text{ M}^{-1}\text{cm}^{-1}$) that is widely used in the studies of the complexation of Np(V) with various ligands. On one hand, the intensity of the band is used for analytical purposes to determine the concentration of Np(V) in solution because it follows the Beer-Lambert behavior. On the other hand, the intensity and position of the band are sensitive to the coordination environment of NpO_2^+ and the shift of the band position is indicative of the formation of Np(V) complexes. Therefore, the stability of the complexes can be determined by analyzing the sets of spectra obtained in spectrophotometric titrations [1-4].

As an f^2 electronic system, the absorption bands of Np(V) in the near IR region all originate from f - f transitions and they are electric-dipole forbidden by Laporte's rule [5,6]. As a result, the intensities of

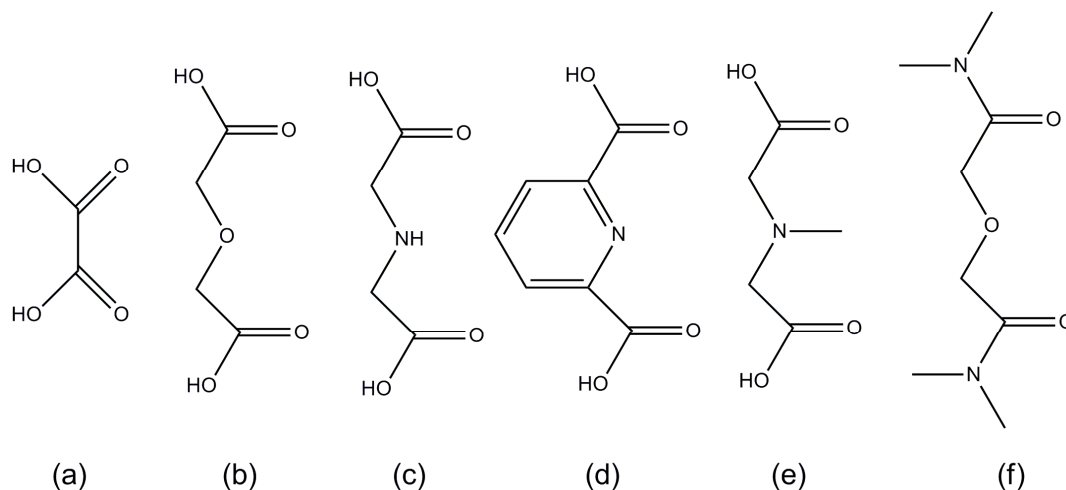
the absorption bands of Np(V) are closely related to the symmetry of the Np(V) complexes, as discussed by the theoretical calculations by Matsika and Pitzer [5,6]. If the Np(V) complex is centrosymmetric and the neptunium atom is at the inversion center, the f-f transitions of Np(V) are forbidden and the near-IR absorption bands will be “silent”. Only if the arrangement of ligands around NpO_2^+ destroys the center of inversion, can the characteristic band near 980 nm be observed. This relationship between the absorption spectra and the symmetry has been extensively studied in aqueous solutions for a number of Np(V) complexes by Krot and co-workers [7-11] and discussed for the hydrolyzed $\text{NpO}_2(\text{OH})_x^{(x-1)-}$ species ($x = 2$ or 4) [12,13].

Due to the radiological hazards associated with the handling of transuranic elements and the limited availability of neptunium, the number of crystal structures of Np(V) complexes in the Cambridge Crystallographic Data Centre (CCDC) database is small, among which only a couple of structures possess a center of inversion with Np at the center (e.g., a Np(V) complex with triphenylphosphine oxide in crystal [14] and a bis(*N*-methyliminodiacetato) Np(V) complex, $\{\text{C}(\text{NH}_2)_3\}_3[\text{NpO}_2(\text{mida})_2]$ [15]). As a result, little effort was made to correlate the optical absorption property of Np(V) complexes in solution with the structures of the complexes in crystals. Until recently, there have been no studies that demonstrate the importance of understanding the relationship between optical properties and symmetry and recognizing the “silent” feature of centrosymmetric Np(V) species in thermodynamic measurements.

The recent development of the third-generation synchrotron radiation sources, such as the Advanced Light Source at Lawrence Berkeley National Laboratory (Berkeley, California, USA), has significantly benefited the studies of crystal structures of transuranic elements. With the bright and focused X-ray beam from the synchrotron radiation source, diffraction data of tiny crystals (tens of micrometers in dimensions) can be collected within an hour so that the radiological hazards are greatly reduced. A number of crystal structures of Np(V) complexes with an inversion center were identified [16,17,18], and the structural information has helped to interpret the optical absorption spectra and calculate the thermodynamic parameters of the complexation. In fact, recent studies have indicated that failure to recognize the “silent” feature of centrosymmetric Np(V) species could lead to the neglect of important Np(V) complexes and result in erroneous thermodynamic constants and incorrect speciation [17,18].

This paper reviews the results of recent studies on the thermodynamics, optical properties and structures of Np(V) complexes with a series of dicarboxylate and oxydiamide ligands (Figure 1), emphasizing the relationship between the symmetry and optical properties and its importance in the interpretation of absorption spectra and the determination of thermodynamic parameters.

Figure 1. Oxydiamide and dicarboxylic acid ligands. (a) oxalic acid (ox), (b) oxydiacetic acid (ODA), (c) iminodiacetic acid (IDA), (d) dipicolinic acid (DPA), (e) *N*-methyliminodiacetic acid (MIDA), (f) *N,N,N',N'*-tetramethyl-3-oxa-glutaramide (TMOGA).

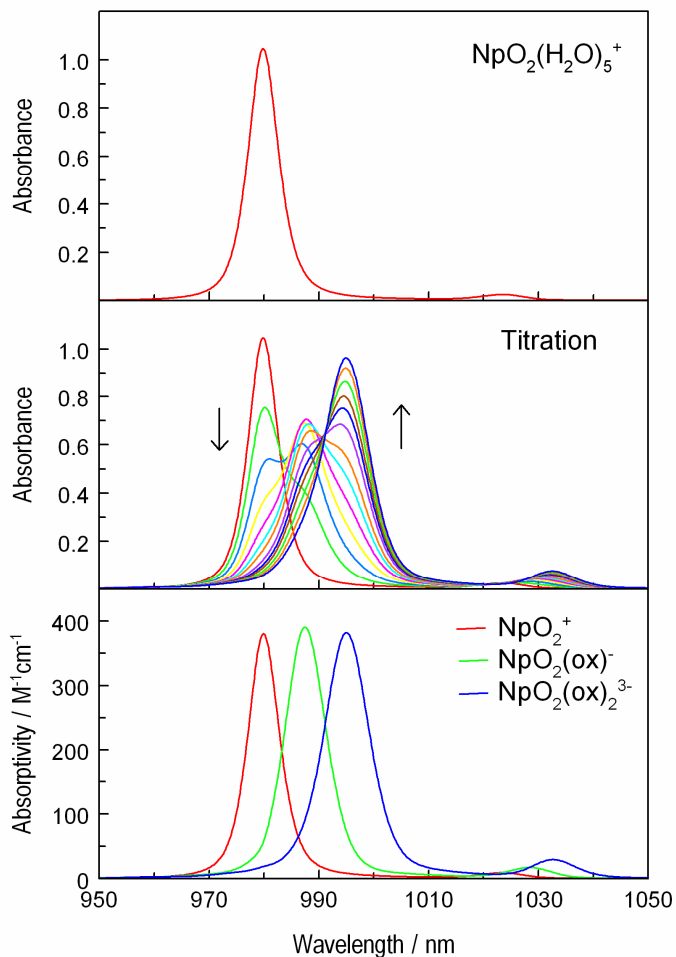


2. The Hydrated NpO_2^+ ion and the Np(V)/oxalate Complexes

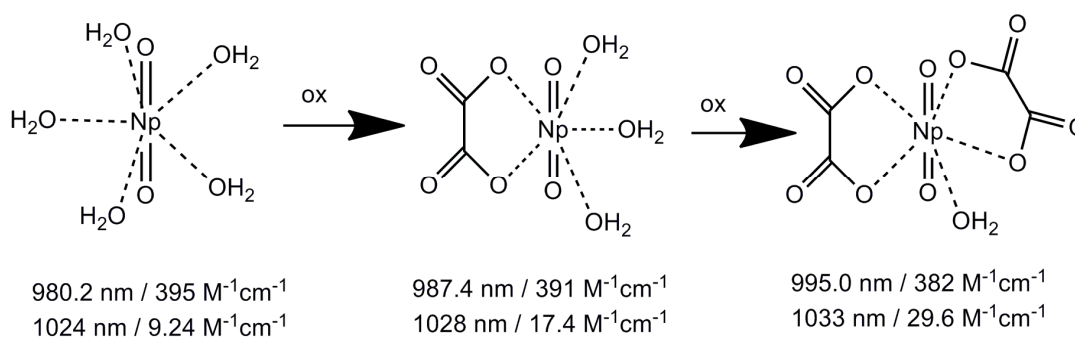
X-ray absorption studies have shown that the NpO_2^+ cation in aqueous solutions has five H_2O molecules in the equatorial plane [19,20], resulting in a structure without a center of inversion. As a result, the f-f transitions are allowed and the absorption bands at 980 and 1024 nm observed (Figure 2, top).

Oxalate could behave as a monodentate, bidentate, and/or bridging ligand coordinating to NpO_2^+ via its equatorial plane. A number of crystal structures of Np(V)/oxalate complexes have been identified, but none of the structures possesses a center of inversion [21–28]. In solution, neither the 1:1 nor 1:2 Np(V)/oxalate complex is centrosymmetric because the equatorial plane of NpO_2^+ contains one bidentate oxalate ligand and three water molecules in $\text{NpO}_2(\text{ox})(\text{H}_2\text{O})_3^-$, and two bidentate oxalate ligands and one water molecule in $\text{NpO}_2(\text{ox})_2(\text{H}_2\text{O})^{3-}$. Therefore, the f-f transitions in the 1:1 and 1:2 Np(V)/oxalate complexes should be allowed and absorption bands of the complexes in the near IR region should be observed. This has indeed been demonstrated by a spectrophotometric titration shown in Figure 2 (center figure). In the near-IR spectra, two well-defined isobestic points were observed, consistent with the formation of two successive complexes, $\text{NpO}_2(\text{ox})^-$ and $\text{NpO}_2(\text{ox})_2^{3-}$. Beside the absorption band at 980 nm for the free NpO_2^+ , two distinctive absorption bands at 987 and 995 nm were assigned to $\text{NpO}_2(\text{ox})^-$ and $\text{NpO}_2(\text{ox})_2^{3-}$, respectively [29]. The successive complexation of Np(V) with oxalate and the accompanying changes in symmetry and absorption spectra are illustrated by Scheme 1.

Figure 2. (top) Absorption spectra of free NpO_2^+ ($C_{\text{Np}}^0 = 2.7 \text{ mM}$); (center) spectrophotometric titration of the $\text{Np(V)}/\text{oxalate}$ system; (bottom) molar absorptivities for NpO_2^+ , $\text{NpO}_2(\text{ox})^-$ and $\text{NpO}_2(\text{ox})_2^{3-}$ complexes [29].



Scheme 1. Stepwise formation of Np(V) complexes with oxalate and the accompanying changes in symmetry and optical absorption properties (band position / molar absorptivity).



3. Np(V) Complexes with Four Structurally-related Tridentate Dicarboxylic Acids: Oxydiacetic Acid (ODA), Iminodiacetic Acid (IDA), Dipicolinic Acid (DPA), and *N*-Methyliminodiacetic Acid (MIDA)

Unlike oxalate, the four dicarboxylic acids (ODA, IDA, DPA and MIDA) are all capable of coordinating to NpO_2^+ in a tridentate mode. The equatorial plane of NpO_2^+ can accommodate two such ligands. Therefore, the 1:2 Np(V)/ligand complexes, $\text{NpO}_2(\text{L})_2^{3-}$ where L stands for the deprotonated ODA, IDA, DPA or MIDA, may or may not absorb in the near IR region, depending on the symmetry of the complexes. Spectrophotometric titrations of Np(V) with ODA, IDA and DPA are shown in Figure 3. The relationship between the optical absorption properties and the symmetry of the complexes is discussed below for each system.

3.1 The $\text{NpO}_2(\text{ODA})_2^{3-}$ Complex

Until recently, spectrophotometric titrations of Np(V)/ODA had suggested that Np(V) forms only the 1:1 complex with ODA [30, 31]. No evidence had been found for the formation of the 1:2 Np(V)/ODA complex in solution or solid. The absence of the 1:2 Np(V)/ODA complex is surprising since ODA is a relatively strong ligand and the equatorial plane of NpO_2^+ seems adequate to accommodate two ODA ligands. Therefore, it was logical to hypothesize that the 1:2 Np(V)/ODA complex may in fact exist, but has been “missed” because it may possess an inversion center so that the f-f transitions are not allowed and this species doesn’t have observable absorption bands in the near IR region. Indeed, the hypothesis was proved to be true by a recent spectroscopic and structural study [16].

As Figure 3a shows, in the beginning of the titration (Phase I), the intensities of the absorption bands at 980 and 1024 nm that belong to the free NpO_2^+ cation decreased when the concentration of ODA was increased, while new bands appeared at 989 and 1035 nm and their intensities increased, corresponding to the formation of a 1:1 $\text{NpO}_2(\text{ODA})^-$ complex. As the concentration of ODA was further increased (Phase II), the intensities at 989 and 1035 nm started to decrease but no new absorption peaks appeared at longer wavelengths. These changes in the spectra are different from those for the NpO_2^+ complexation with oxalate (Figure 2) where 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 spectra in Figure 3a is interpreted with the assumption that two complexes of NpO_2^+ with ODA form in solution successively but the second complex, $\text{NpO}_2(\text{ODA})_2^{3-}$, does not absorb in the region. Based on this assumption, the spectra were deconvoluted and the formation constants of $\text{NpO}_2(\text{ODA})^-$ and $\text{NpO}_2(\text{ODA})_2^{3-}$ were calculated [16]. Previous studies did not observe the formation of the 1:2 complexes because the concentrations of ODA were insufficient and, probably, because the non-absorbing nature of the $\text{NpO}_2(\text{ODA})_2^{3-}$ complex was not recognized.

The hypotheses that the $\text{NpO}_2(\text{ODA})_2^{3-}$ complex is centrosymmetric is further proved to be true by the crystal structure of $\text{Na}_3\text{NpO}_2(\text{ODA})_2 \cdot 2\text{H}_2\text{O}$ (Figure 4). In the structure, the Np atom is located at an inversion center. It is coordinated equatorially by three oxygens of each of the two coplanar ODA ligands. Dissolution of the $\text{Na}_3\text{NpO}_2(\text{ODA})_2 \cdot 2\text{H}_2\text{O}$ compound in aqueous solution generates Na^+ and

$\text{NpO}_2(\text{ODA})_2^{3-}$. It is very likely that the inversion center in the solid $\text{Na}_3\text{NpO}_2(\text{ODA})_2 \cdot 2\text{H}_2\text{O}$ is maintained in the $\text{NpO}_2(\text{ODA})_2^{3-}$ anion in solution. In fact, the latter could have higher symmetry than the $\text{NpO}_2(\text{ODA})_2^{3-}$ moiety in the solid, because of the absence of crystal lattice constraints in solution.

The results of this study [16] have validated the theoretical calculations of the probability of f-f transitions and, more significantly, have emphasized the importance of understanding the relationship between the spectroscopic features and symmetry. Failure to recognize the “silent” features of the f-f transitions of centrosymmetric species in absorption spectra could result in the “missing” of such species and lead to incorrect speciation.

Figure 3. Spectrophotometric titrations of NpO_2^+ complexation with dicarboxylic acids. Top figures – Phase I of the titrations; mid figures – Phase II of the titrations; bottom figures – molar absorptivities of Np(V) species. (3a) $\text{Np(V)}/\text{ODA}$: $C_{\text{Np}}^0 = 1.78 \text{ mM}$, $C_{\text{ODA}} = 0 - 0.5 \text{ M}$ [16]; (3b) $\text{Np(V)}/\text{IDA}$: $C_{\text{Np}}^0 = 0.68 \text{ mM}$, $C_{\text{IDA}} = 0 - 0.65 \text{ M}$ [29]; (3c) $\text{Np(V)}/\text{DPA}$: $C_{\text{Np}}^0 = 2.02 \text{ mM}$, $C_{\text{DPA}} = 0 - 0.01 \text{ M}$ [17].

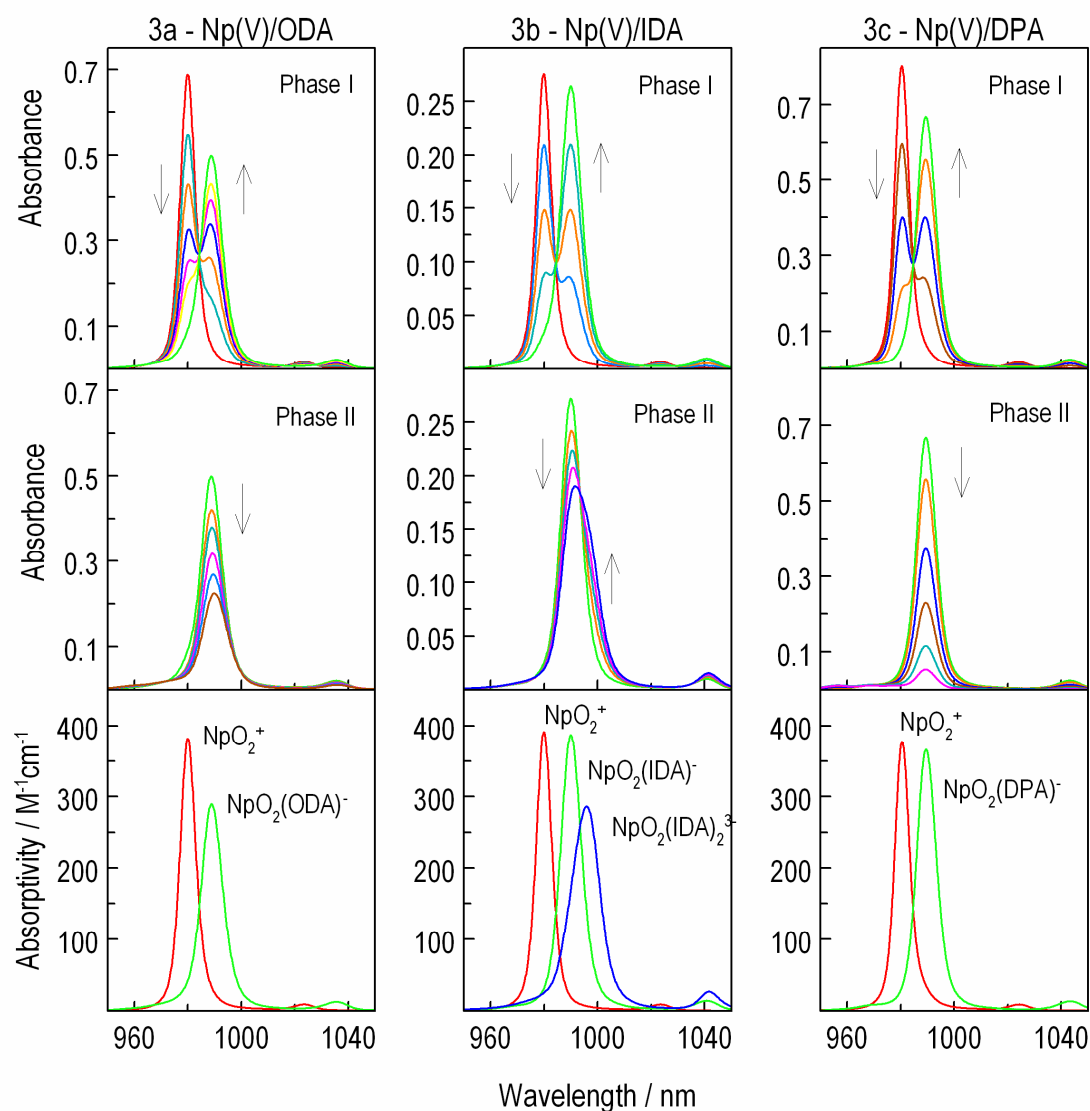
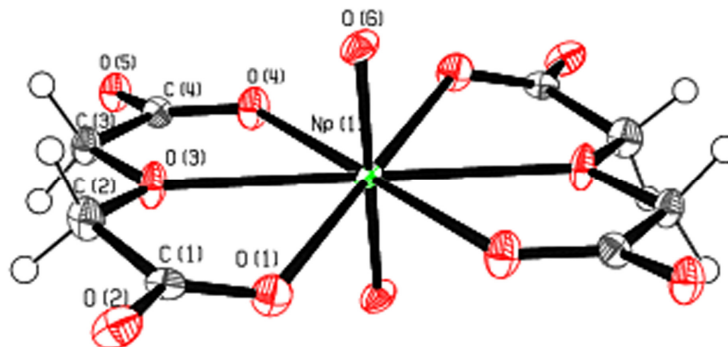


Figure 4. Single crystal structure of $\text{NpO}_2(\text{ODA})_2^{3-}$. The unit cell contains the $\text{NpO}_2(\text{ODA})_2^{3-}$ anion, three sodium cations and two water molecules. The sodium atoms and water molecules are not shown for clarity. Np – green, O – red, C – gray, H – white [16].



3.2 The $\text{NpO}_2(\text{IDA})_2^{3-}$ Complex

Structurally, IDA is a very close analog of ODA with the only difference in the central donor atom (–NH– vs. –O–, Figure 1). Both can coordinate to NpO_2^+ in a tridentate mode. However, the absorption spectra of Np(V)/IDA complexes are different from those of ODA. Figure 3b shows the spectrophotometric titrations of Np(V) with IDA [29]. As the concentration of IDA was increased (Phase I), a new band at 990 nm appeared, corresponding to the formation of the 1:1 complex, $\text{NpO}_2(\text{IDA})^-$. As the concentration of IDA was further increased (Phase II), the intensity at 990 nm decreased while a shoulder appeared and increased gradually at a longer wavelength (~ 996 nm), corresponding to the formation of the 1:2 complex, $\text{NpO}_2(\text{IDA})_2^{3-}$. The changes in the spectra of the Np(V)/IDA system (Figure 3b) are quite different from those of the Np(V)/ODA system where no new absorption bands appear as the $\text{NpO}_2(\text{ODA})_2^{3-}$ complex forms (Figure 3a), but similar to those of the Np(V)/oxalate system where the formation of $\text{NpO}_2(\text{ox})_2^{3-}$ is accompanied by a new absorption band at a longer wavelength (Figure 2).

The results of the spectrophotometric titrations imply that the $\text{NpO}_2(\text{IDA})_2^{3-}$ complex, unlike $\text{NpO}_2(\text{ODA})_2^{3-}$, is not centrosymmetric. In the absence of structural data for $\text{NpO}_2(\text{IDA})_2^{3-}$ in solid or solution, the difference in the symmetry between $\text{NpO}_2(\text{IDA})_2^{3-}$ and $\text{NpO}_2(\text{ODA})_2^{3-}$ was explained by assuming that $\text{NpO}_2(\text{IDA})_2^{3-}$ exists in *cis*- and *trans*- configurations, depending on the positions of the two imino-hydrogen atoms with respect to the equatorial plane of NpO_2^+ . The energy difference between the two configurations is expected to be small. The *cis*-isomer, with the imino-hydrogen atoms on the same side of the plane, is obviously not centrosymmetric and should absorb in the near IR region. The *trans*- isomer of $\text{NpO}_2(\text{IDA})_2^{3-}$ is centrosymmetric and does not absorb. The coexistence of the *cis*- and *trans*- isomers in solution results in an absorption band at 996 nm with low intensity [29].

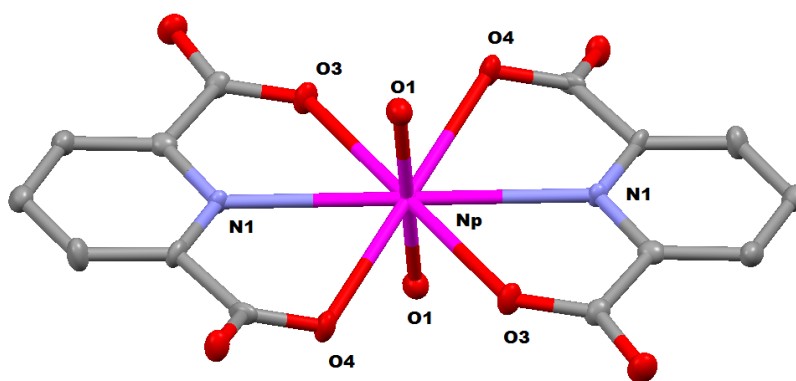
3.3 The $\text{NpO}_2(\text{DPA})_2^{3-}$ Complex

In the DPA molecule, the two carboxylate groups are bridged by a pyridine unit, forming a rigid and conjugated planar tridentate ligand (Figure 1). DPA coordinates to NpO_2^+ with the nitrogen and two oxygen atoms from the carboxylate groups in a similar tridentate manner as IDA. However, the

absence of the imino-hydrogen and the presence of a rigid and conjugated configuration in DPA eliminate the possibility of *cis*- or *trans*- isomerization and result in the formation of a centrosymmetric 1:2 Np(V)/DPA complex, $\text{NpO}_2(\text{DPA})_2^{3-}$. As Figure 5 shows, the sodium salt of $\text{NpO}_2(\text{DPA})_2^{3-}$ crystallized in a triclinic space group, $P\bar{1}$. In the unit cell, the Np atom is located at an inversion center at [0, 0, -1]. The axial $\text{O}=\text{Np}=\text{O}$ moiety is perfectly linear (180° angle) and symmetrical (two $\text{Np}=\text{O}$ bonds are equal in length, 1.825(6) Å). The $\text{O}=\text{Np}=\text{O}$ moiety is coordinated equatorially by two DPA ligands. Each DPA ligand is tridentate and coordinates to Np with the N atom of the pyridine and two O atoms of two different carboxylate groups. The symmetry of the $\text{NpO}_2(\text{DPA})_2^{3-}$ unit is very similar to that of $\text{NpO}_2(\text{ODA})_2^{3-}$ in $\text{Na}_3\text{NpO}_2(\text{ODA})_2(\text{H}_2\text{O})_2$ (Figure 4).

The absorption spectra of a spectrophotometric titration of Np(V) with DPA are shown in Figure 3c. The spectra changes during the titration are very similar to those of the titrations for Np(V)/ODA (Figure 3a), but different from those for Np(V)/oxalate (Figure 2) or Np(V)/IDA (Figure 3b). In Phase II of the titration ($C_{\text{DPA}}/C_{\text{Np}} > 1$), as the concentration of DPA was further increased, the intensities of the band at 990 nm (for the 1:1 Np(V)/DPA complex) gradually decreased, but no new absorption bands appeared. With sufficiently high concentration of DPA, the spectra could become flat and featureless. By including both 1:1 and 1:2 Np(V)/DPA complexes in the system, the absorption spectra were correctly deconvoluted and the stability constants of both $\text{NpO}_2(\text{DPA})^-$ and $\text{NpO}_2(\text{DPA})_2^{3-}$ were calculated. The stability constant of $\text{NpO}_2(\text{DPA})_2^{3-}$ is the first value available for this species, because this complex was neglected in previous studies due to the failure in recognizing its “silent” feature in the absorption spectra.

Figure 5. Structure of the $\text{NpO}_2(\text{DPA})_2^{3-}$ complex in the single crystal of $\text{Na}_3\text{NpO}_2(\text{DPA})_2(\text{H}_2\text{O})_6$. The H and Na atoms, and water molecules are not shown for clarity. Np – purple, O – red, C – grey, and N – blue [17].



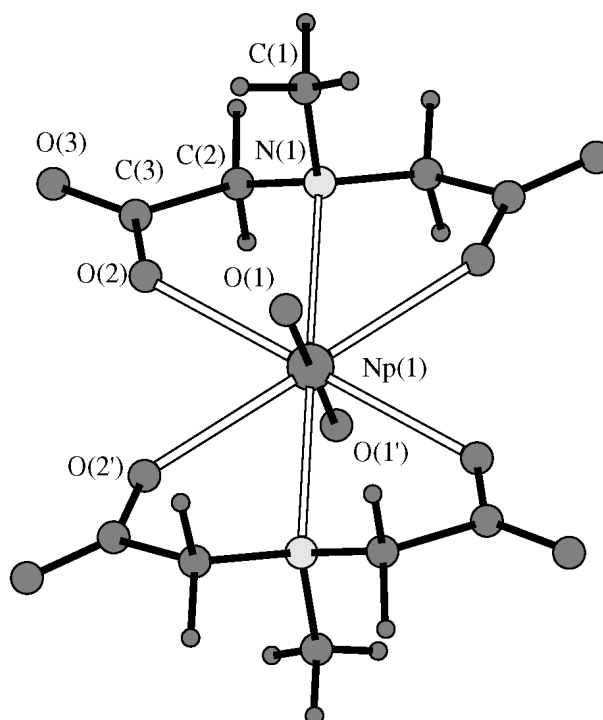
3.4 The $\text{NpO}_2(\text{MIDA})_2^{3-}$ Complex

MIDA differs from IDA in the substitution of the imino hydrogens with methyl groups (Figure 1). This change in structure has significant consequence in the symmetry of the 1:2 Np(V) complexes with the two ligands. As discussed in Section 3.2, the formation of a *cis*- isomer of $\text{NpO}_2(\text{IDA})_2^{3-}$ that is not centrosymmetric makes the f-f transition allowed and an absorption band observed at 996 nm for $\text{NpO}_2(\text{IDA})_2^{3-}$. In contrast, a *cis*- isomer of $\text{NpO}_2(\text{MIDA})_2^{3-}$ with the two methyl groups on the same side of the equatorial plane is less likely to form, because the steric hindrance in the *cis*-configuration

of $\text{NpO}_2(\text{MIDA})_2^{3-}$ could be large so that the energy of the *cis*- isomer is significantly higher than the *trans*- isomer. A crystal structure of $\text{NpO}_2(\text{MIDA})_2^{3-}$ (Figure 6) shows that the two methyl groups are *trans*- with respect to the equatorial plane of NpO_2^+ [15].

In a recent spectrophotometric study of the complexation of Np(V) with MIDA in the aqueous solution, spectra changes similar to those in the $\text{Np(V)}/\text{DPA}$ system were observed and interpreted with the successive formation of $\text{NpO}_2(\text{MIDA})^-$ and $\text{NpO}_2(\text{MIDA})_2^{3-}$, the latter not absorbing in the near-IR region because it is centrosymmetric [32].

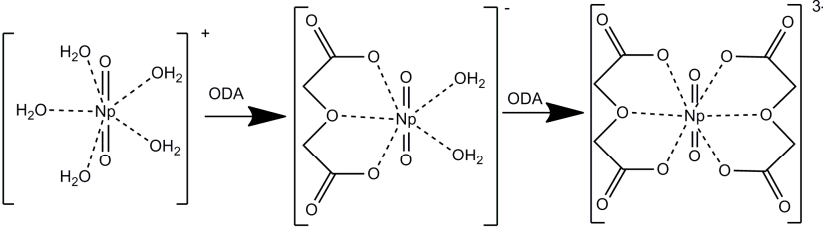
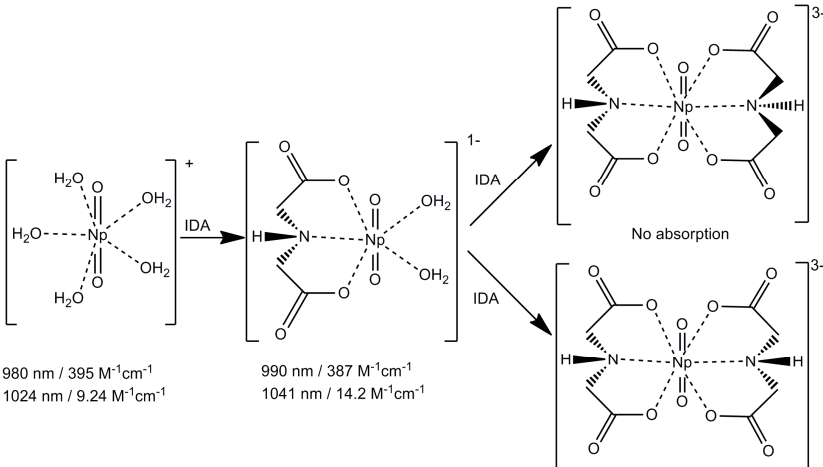
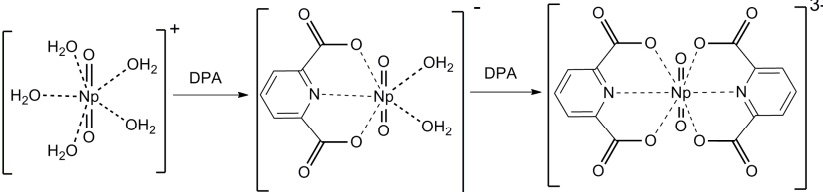
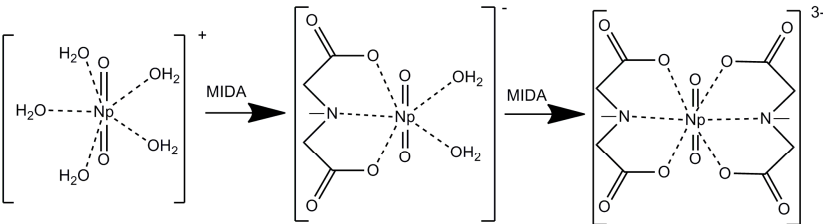
Figure 6. Single crystal structure of $\text{NpO}_2(\text{MIDA})_2^{3-}$ [15].



3.5 Comparison of Np(V) Complexes with ODA, IDA, DPA and MIDA

Schemes for the stepwise formation of Np(V) complexes with the four structurally-related tridentate dicarboxylates and the accompanying changes in symmetry and optical absorption properties are summarized in Table 1. The 1:1 Np(V) complexes all have two water molecules in the equatorial plane and none of the 1:1 complexes is centrosymmetric. Therefore, the 1:1 Np(V) complexes all exhibit intense absorption bands in the near IR region (at ~ 990 nm and $1035 - 1045$ nm). On the contrary, the 1:2 Np(V) complexes with ODA, DPA and MIDA are centrosymmetric and become “silent” in optical absorption in the near-IR region. In the case of the 1:2 $\text{Np(V)}/\text{IDA}$ complex, one of the isomers is “silent” and the other is “active” in optical absorption.

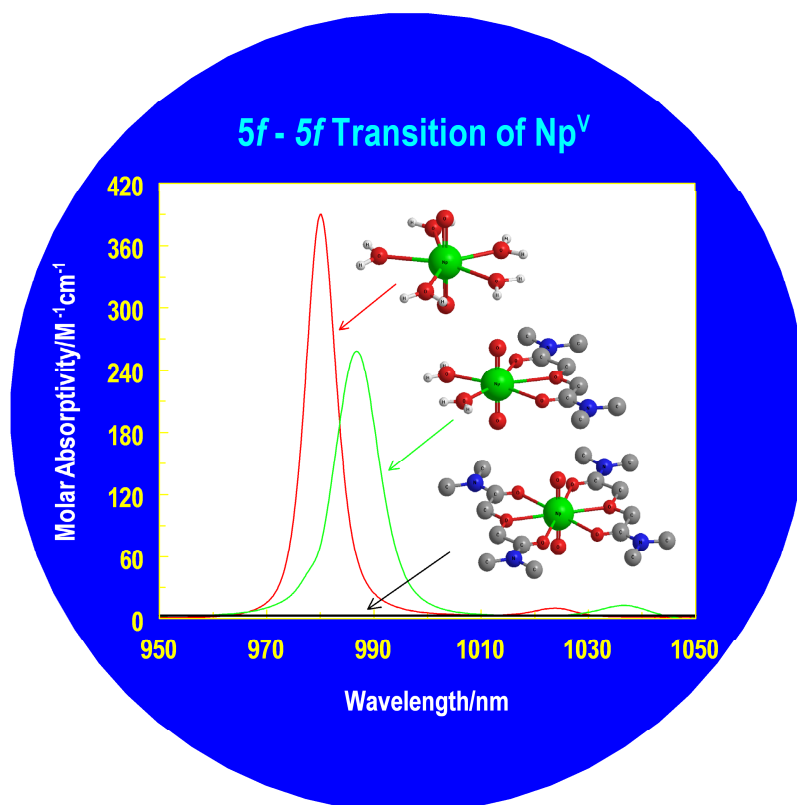
Table 1. Stepwise formation of Np(V) complexes and the accompanying changes in symmetry and optical absorption properties (band position / molar absorptivity).

Ligand	Stepwise formation of Np(V) complexes		
ODA [16]	<div><p>980.2 nm / 395 M⁻¹cm⁻¹ 1024 nm / 9.24 M⁻¹cm⁻¹</p><p>989.4 nm / 287 M⁻¹cm⁻¹ 1035 nm / 12.9 M⁻¹cm⁻¹</p><p>No absorption</p></div>		
IDA [29]	<div><p>980 nm / 395 M⁻¹cm⁻¹ 1024 nm / 9.24 M⁻¹cm⁻¹</p><p>990 nm / 387 M⁻¹cm⁻¹ 1041 nm / 14.2 M⁻¹cm⁻¹</p><p>No absorption</p><p>996 nm / 274 M⁻¹cm⁻¹ 1042 nm / 26.8 M⁻¹cm⁻¹</p></div>		
DPA [17]	<div><p>980.2 nm / 395 M⁻¹cm⁻¹ 1024 nm / 9.68 M⁻¹cm⁻¹</p><p>989.9 nm / 360 M⁻¹cm⁻¹ 1045 nm / 12.9 M⁻¹cm⁻¹</p><p>No absorption</p></div>		
MIDA [32]	<div><p>980.2 nm / 395 M⁻¹cm⁻¹ 1024 nm / 9.24 M⁻¹cm⁻¹</p><p>990 / 384 1039 nm / 14.4 M⁻¹cm⁻¹</p><p>No absorption</p></div>		

4. The $\text{NpO}_2(\text{TMOGA})_2^+$ Complex

TMOGA, one of the diamide analogs of ODA, is a neutral ligand and also coordinates to NpO_2^+ with three oxygen donor atoms. In a recent study of the complexation of Np(V) with TMOGA, spectrophotometric titrations show that the absorption spectra vary in a similar way to those in the titrations of the Np(V)/ODA and Np(V)/DPA systems [18]. As the concentration of TMOGA was increased, the intensities of the absorption band at 980 nm that belongs to the free NpO_2^+ cation decreased and new bands appeared at 987 nm, corresponding to the formation of a 1:1 Np(V)/TMOGA complex, $\text{NpO}_2(\text{TMOGA})^+$. As the concentration of TMOGA was further increased, the intensities at 987 nm decreased but no new absorption peaks appeared at longer wavelengths. Similar to the titrations of the Np(V)/ODA and Np(V)/DPA systems, the variation of spectra is interpreted with the assumption that two complexes of Np(V) with TMOGA formed in solution successively but the second complex, $\text{NpO}_2(\text{TMOGA})_2^+$, did not absorb in the wavelength region. X-ray crystallographic data of the perchlorate salt of the 1:2 complex, $\text{NpO}_2(\text{TMOGA})_2\text{ClO}_4$, confirmed that $\text{NpO}_2(\text{TMOGA})_2^+$ is highly symmetrical. The neptunium atom sits at the cross point of three mirror planes perpendicular to each other. The two TMOGA ligands are coplanar and are mirror images of each other. The O=Np=O moiety is perfectly linear and symmetrical [18]. The molar absorptivities and structures of NpO_2^+ , $\text{NpO}_2(\text{TMOGA})^+$ and $\text{NpO}_2(\text{TMOGA})_2^+$ are shown in Figure 7. Again, this study has demonstrated that it is very important to recognize the “silent” feature of centrosymmetric species in optical absorption, and failure to do so could result in erroneous thermodynamic data and speciation.

Figure 7. Molar absorptivities for NpO_2^+ (red), $\text{NpO}_2(\text{TMOGA})^+$ (green) and $\text{NpO}_2(\text{TMOGA})_2^+$ (black) complexes. The atoms: Np – green, O – red, N – blue, C – gray.



5. Conclusions

A number of crystal structures of Np(V) complexes with an inversion center were identified in recent studies of the complexation of Np(V) with a series of dicarboxylate and diamide ligands. It has been demonstrated that the optical absorption properties of the Np(V) complexes are governed by their symmetry. The structural information has helped to interpret the optical absorption spectra and calculate the thermodynamic parameters of the complexation. Failure to recognize the “silent” feature of centrosymmetric Np(V) species in the optical absorption could lead to the neglect of important Np(V) complexes and result in erroneous thermodynamic constants and incorrect speciation.

Acknowledgements

This research was supported by the Director, Office of Science, Office of Basic Energy Science of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH 11231 at Lawrence Berkeley National Laboratory (LBNL). The X-ray diffraction crystallographic data for $\text{NpO}_2(\text{TMOGA})_2\text{ClO}_4$, $\text{Na}_3\text{NpO}_2(\text{ODA})_2 \cdot 2\text{H}_2\text{O}(\text{s})$, and $\text{Na}_3\text{NpO}_2(\text{DPA})_2(\text{H}_2\text{O})_6(\text{s})$ are collected at the Advanced Light Source (ALS). ALS is operated by LBNL for U.S. DOE.

References and Notes

1. Ryan, J.L. Absorption spectra of actinide compounds. In *Lanthanides and Actinides*, Vol. 7, *Inorganic Chemistry Series One*; Bagnall, K. W., Ed.; Butterworths: London, 1972; pp. 323-367.
2. Sjoblom, R.; Hindman, J.C. Spectrophotometry of neptunium in perchloric acid solutions. *J. Am. Chem. Soc.* **1951**, *73*, 1744-1751.
3. Gruen, D.M.; Katz, J.J. Spectrophotometric study of Np(V) oxalate complexes. *J. Am. Chem. Soc.* **1953**, *75*, 3772-3776.
4. Cooper, J.; Reents, W.D.; Woods, M.; Sjoblom, R.; Sullivan, J.C. Kinetic study of the reduction of Np(VI) and Pu(VI) by iodide ion in aqueous perchlorate media. *Inorg. Chem.* **1977**, *16*, 1030-1032.
5. Matsika, S.; Pitzer, R.M. Electronic spectrum of the NpO_2^{2+} and NpO_2^+ ions. *J. Phys. Chem. A.* **2000**, *104*, 4064-4068.
6. Matsika, S.; Pitzer, R.M.; Reed, D.T. Intensities in the spectra of actinyl ions. *J. Phys. Chem. A.* **2000**, *104*, 11983-11992.
7. Krot, N.N.; Bessonov, A.A.; Perminov, V.P. Electron absorption-spectra of neptunium(V) solid compounds. *Dokl. Akad. Nauk SSSR* **1990**, *312*, 1402-1404.
8. Bessonov, A.A.; Afonas'eva, T.V.; Krot, N.N. Electronic absorption-spectra of solid actinide(V) compounds. 2. Neptunium(V) carboxylates. *Soviet Radiochemistry* **1990**, *32*, 453-457.
9. Bessonov, A.A.; Afonas'eva, T.V.; Krot, N.N. Electronic absorption-spectra of solid actinide compounds - neptunium(V) perchlorates, chlorides, and nitrates. *Soviet Radiochemistry* **1991**, *33*, 245-250.
10. Grigor'ev, M.S.; Baturin, N.A.; Bessonov, A.A.; Krot, N.N. Crystal-structure and electronic absorption-spectrum of neptunyl(V) perchlorate $\text{NpO}_2\text{ClO}_4 \cdot 4\text{H}_2\text{O}$. *Radiochemistry* **1995**, *37*, 12-14.

11. Garnov, A.Yu.; Krot, N.N.; Bessonov, A.A.; Perminov, V.P. Hydration and solvation numbers of actinide dioxo cations. *Radiochemistry* **1996**, *38*, 402-406.
12. Tananaev, G. Forms of Np(V) and Am(V) in basic aqueous-media. *Soviet Radiochemistry* **1990**, *32*, 476-479.
13. Rao, L.; Srinivasan, T.G.; Garnov, A.Yu.; Zanonato, P.; Di Bernardo, P.; Bismondo, A. Hydrolysis of neptunium(V) at variable temperatures (10 – 85°C). *Geochim. Cosmochim. Acta* **2004**, *68*, 4821-4830.
14. Charushnikova, I.A.; Krot, N.N.; Starikova, Z.A. Synthesis, crystal structure, and spectral characteristics of the Np(V) complex with triphenylphosphine oxide $[\text{NpO}_2(\text{PO}(\text{C}_6\text{H}_5)_3)_4]\text{ClO}_4$. *Radiochemistry* **2001**, *43*, 24-29.
15. Budantseva, N.A.; Andreev, G.B.; Fedoseev, A.M.; Antipin M.Yu. Crystal structure and absorption spectra of triguanidinium bis(*N*-methyliminodiacetato)dioxoneptunate(V) $\{\text{C}(\text{NH}_2)_3\}_3[\text{NpO}_2(\text{mida})_2]$. *Doklady Chemistry* **2002**, *384*, 159-162.
16. Tian, G.; Rao, L.; Oliver, A. Symmetry and optical spectra: a “silent” 1:2 Np(V)/oxydiacetate complex. *Chem. Commun.* **2007**, *40*, 4119-4121.
17. Tian, G.; Rao, L.; Teat, S.J. Thermodynamics, Optical properties and coordination modes of Np(V) with dipicolinic acid. *Inorg. Chem.* **2009**, *48*, 10158-10164.
18. Tian, G.; Xu, J.; Rao, L. Optical absorption and structure of a highly symmetrical neptunium^V diamide complex. *Angew. Chem. Int. Ed.* **2005**, *44*, 6200-6203.
19. Combes, J.-M.; Chisholm-Brause, C.J.; Brown, Jr., G.E.; Parks, G.A.; Conradson, S.D.; Eller, P.G.; Triay, I.R.; Hobart, D.E.; Meijer, A. EXAFS spectroscopic study of neptunium(V) sorption at the α -iron hydroxide oxide (α -FeOOH)/water interface. *Environ. Sci. Technol.* **1992**, *26*, 376-382.
20. Allen, P.G.; Bucher, J.J.; Shuh, D.K.; Edelstein, N.M.; Reich, T. Investigation of aquo and chloro complexes of UO_2^{2+} , NpO_2^+ , Np^{4+} , and Pu^{3+} by X-ray absorption fine structure spectroscopy. *Inorg. Chem.* **1997**, *36*, 4676-4683.
21. Mefod'eva, M.P.; Grigor'ev, M.S.; Afonas'eva, T.V.; Kryukov, E.B. New data on oxalate compounds of neptunium(VI). *Soviet Radiochemistry* **1981**, *23*, 565-570.
22. Tomilin, S.V.; Volkov, Yu.F.; Visyashcheva, G.I.; Kapshukov, I.I. Crystal-structure of the compound $\text{NaNpPO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$. *Soviet Radiochemistry* **1984**, *26*, 696-701.
23. Grigor'ev, M.S.; Baturin, N.A.; Regel', L.L.; Krot, N.N. Synthesis, crystallization and molecular-structure of crystal hydrates of the complex neptunium(v) oxalate $[\text{Co}(\text{NH}_3)_6][\text{NpO}_2(\text{C}_2\text{O}_4)_2] \cdot n\text{H}_2\text{O}$ ($n=3, 4$). *Soviet Radiochemistry* **1991**, *33*, 121-126.
24. Grigor'ev, M.S.; Bessonov, A.A.; Yanovsky, A.I.; Struchkov, Yu.T.; Krot, N.N. Crystal-structure of the complex neptunium(v) oxalate $(\text{NH}_4)\text{NpO}_2\text{C}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. *Soviet Radiochemistry* **1991**, *33*, 499-503.
25. Charushnikova, I.A.; Krot, N.N.; Katser, S.B. Electronic absorption spectra and structure of some neptunium(IV) oxalates. *Radiochemistry* **1998**, *40*, 558-564.
26. Grigor'ev, M.S.; Charushnikova, I.A.; Krot, N.N.; Yanovsky, A.I.; Struchkov, Yu.T. Crystal structure of neptunium(V) oxalate hexahydrate $\text{NpO}_2(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. *Zh. Neorg. Khim. (Russ.)* **1996**, *41*, 539-542.

27. Krot, N.N.; Bessonov, A.A.; Grigor'ev, M.S.; Charushnikova, I.A.; Makarenkov, V.I. Synthesis of new crystalline Pu(V) compounds from solutions: II. Double Pu(V) oxalates with $\text{Co}(\text{NH}_3)_6^{3+}$ ions in the outer sphere. *Radiochemistry* **2005**, *47*, 107-113.
28. Grigor'ev, M.S.; Charushnikova, I.A.; Krot, N.N.; Yanovsky, A.I.; Struchkov, Yu.T. Crystal structure of neptunium(V) oxalate hexahydrate $\text{NpO}_2(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. *Radiochemistry* **1997**, *39*, 420-423.
29. Tian, G.; Rao, L. Optical Absorption, Stability and Structure of NpO_2^+ Complexes with Dicarboxylic Acids. In *Actinides 2005 -- Basic Science, Applications and Technology*, Mater. Res. Soc. Symp. Proc. 893, Warrendale, PA, 2006; Sarrao, J.L., Schwartz, A.J., Antonio, M.R., Burns, P.C., Haire, R.G., Nitsche, H., Eds.; Paper # 0893-JJ05-17.
30. Rizkalla, E.N.; Nectoux, F.; Dabos-Seignon, S.; Pages, M. Complexation of neptunium(V) by polyaminocarboxylate ligands. *Radiochim. Acta* **1990**, *51*, 151-155.
31. Jensen, M.P.; Nash, K.L. Thermodynamics of dioxoneptunium(V) complexation by dicarboxylic acids. *Radiochim. Acta* **2001**, *89*, 557-564.
32. Tian, G.; Rao, L. Complexation of Np(V) with *N*-methyliminodiacetic acid in the aqueous solution. Unpublished data.

© 2010 by the authors; licensee Molecular Diversity Preservation International, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).