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Thermodynamic Studies to Support Extraction of Uranium from Seawater

Fuel Cycle Research & Development

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Development
Linfeng Rao
Lawrence Berkeley National Laboratory
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APPENDIX E

FCT DOCUMENT COVER SHEET ¹

Name/Title of Deliverable/Milestone/Revision No. Thermodynamic Studies to Support Efficient Extraction of Uranium from Seawater

Work Package Title and Number Fuel Resources – LBNL FT-16LB03020102

Work Package WBS Number 1.02.03.02.01

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SUMMARY

This milestone report summarizes the data obtained in FY16 on the major task of quantifying the binding strength of amidoxime-related ligands. Thermodynamic studies of the interaction between U(VI) and amidoxime ligand HL^{III} were studied to quantify the binding ability of U(VI) with amidoxime-related ligands and help to select grafting/reaction conditions so that higher yield of preferred amidoxime-related ligands is obtained.

Besides the thermodynamic task, structural studies on vanadium complexation with amidoxime ligand were conducted to help understand the extremely strong sorption of vanadium on poly(amidoxime) sorbents. Data processing and summarization of the vanadium system are in progress and will be included in the next milestone report.

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1. INTRODUCTION

To improve the extraction efficiency and reduce the extraction cost, fundamental understanding of the coordination chemistry of the extraction process is necessary. Therefore, thermodynamic and structural studies need to be conducted to determine the stability constants of the complexes of uranium with a series of amidoxime-type ligands and understand the coordination modes. In FY16, one major task was undertaken, to conduct thermodynamic studies of the interaction between U (VI) and Amidoxime ligand HL^{III}. Besides, structural studies of vanadium/glutaroimide-dioxime complex were performed. This report presents the data on the major task in FY16.

2. RESULTS

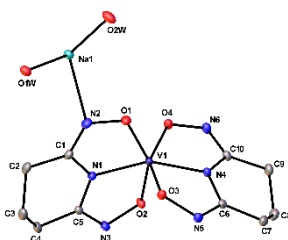
2.1 A rare non-oxido vanadium(V)-glutaroimide-dioxime complex forming in and crystallized from aqueous solution

Structural studies on vanadium complexation with amidoxime ligand were conducted to help understand the extremely strong sorption of vanadium on poly(amidoxime) sorbents. An unusual “bare” V⁵⁺ complex with glutaroimide-dioxime was synthesized from aqueous solution. Multinuclear NMR, ESI-MS and EPR studies were performed to characterization the structure of the complex in solution. Data processing and summarization of the vanadium system are in progress and will be included in the next milestone report.

2.1.1 Crystal structure of Na[V(L)₂].2H₂O(cr).

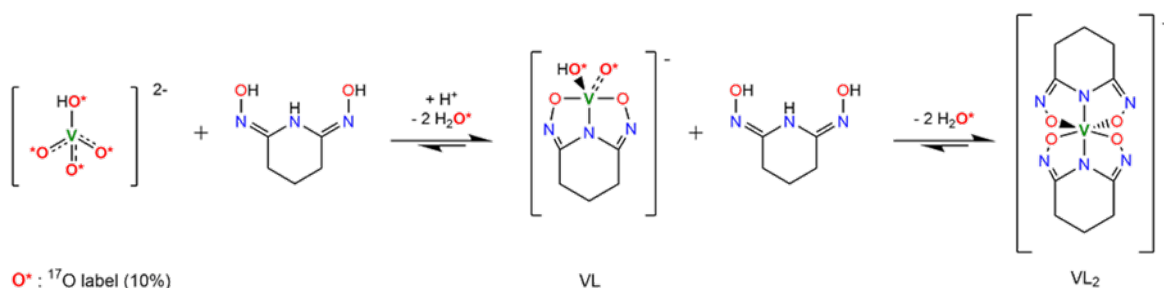
The asymmetric unit of Na[V(L)₂].2H₂O(cr) consists of a “bare” V⁵⁺ center bound to two fully deprotonated glutaroimide-dioxime ligands (L³⁻), through one nitrogen and two oxygen atoms of each ligand, along with a sodium ion and two water molecules (Figure 1). The binding of the ligands around the vanadium center results in a highly distorted octahedral coordination environment in the triclinic space group P-1 with unit cell parameters $a = 7.9375(3) \text{ \AA}$, $b = 8.7365(4) \text{ \AA}$, $c = 12.1972(5) \text{ \AA}$, $\alpha = 102.684(2)^\circ$, $\beta = 107.187(2)^\circ$, $\gamma = 103.796(2)^\circ$. The bond lengths for the V-N bonds are 1.9557(8) and 1.9551(8) \AA while those for the V-O bonds are 1.8667(8), 1.8741(7), 1.9039(6), and 1.9024(8) \AA . The extended crystal structure can be considered as successive VL₂⁻ complexes bridged by sodium atoms via N(2) and N(5) to form a one dimensional chain. The chains are then linked via bridging water molecules (O(1W)) between the sodium atoms to form a ribbon. The ribbons are connected by hydrogen bonding interactions between the water molecules and the ligands for O(1W)-O(3)*, O(1W)-N(3)*, O(2W)-O(2)*, and O(2W)-N(6)*, where the superscript * denotes symmetry related positions.

The V-O bond distances in Na[V(L)₂].2H₂O(cr) are within the range of V-O bond distances reported for other non-oxido V⁵⁺ compounds obtained from non-aqueous solutions (1.8 - 2.0 \AA), and much longer than those of the V=O double bonds (~ 1.6 \AA).



1.1.1 ^{51}V and ^{17}O NMR.

The successful synthesis of $\text{Na}[\text{V}(\text{L})_2] \cdot 2\text{H}_2\text{O}$ shows that, using an oxido vanadate species as the starting material, a non-oxido V(V) complex with glutaroimide-dioxime can be synthesized and crystallized from aqueous solution. In other words, the glutaroimide-dioxime ligand can displace the oxido $\text{V}=\text{O}$ bonds in vanadate and form a “bare” V^{5+} complex. In addition, the crystallization of a 1:1 $\text{Na}[\text{VO}_2(\text{HL})]$ complex suggests that an intermediate 1:1 complex, in which the oxido $\text{V}=\text{O}$ bonds in vanadate are only partially displaced by glutaroimide-dioxime, may also exist in aqueous solution. To verify the structure of the unusual non-oxido V^{5+} complex and demonstrate the stepwise displacement of the oxido $\text{V}=\text{O}$ bonds in aqueous solutions, we hypothesized a reaction scheme (Scheme 1) and designed concurrent $^{51}\text{V}/^{17}\text{O}/^1\text{H}/^{13}\text{C}$ NMR experiments, coupled with ESI-MS, in ^{17}O -enriched H_2O to test the hypothesis. The 1:1 intermediate complex hypothesized in Scheme 1, $[\text{V}(\text{O})(\text{OH})\text{L}]^-$, has the same stoichiometry as $[\text{VO}_2(\text{HL})]^-$, but differs in the location of one proton.



Scheme 1. Hypothesized reaction scheme for the formation of non-oxido V^{5+} /glutaroimide-dioxime complex using enriched H_2^{17}O .

As shown in Scheme 1, starting with ^{17}O labeled vanadate in solution, the vanadate signal should show V-O coupling in both ^{17}O and ^{51}V NMR spectra. If the complexation reaction proceeds to the 1:2 complex as Scheme 1 suggests, no ^{17}O NMR signal(s) should be observed at the end when the $[\text{V}(\text{L})_2]^-$ complex is the only vanadium species present. At this point, all of the $\text{V}=\text{O}$ bonds of the starting vanadate would be displaced by the donor atoms of glutaroimide-dioxime and there would be no ^{17}O atoms in the $[\text{V}(\text{L})_2]^-$ complex. Concurrently, the ^{51}V NMR signal for the vanadate (with V-O coupling) should disappear and a new ^{51}V NMR signal for the $[\text{V}(\text{L})_2]^-$ complex with no V-O coupling would appear.

The $^{51}\text{V}/^{17}\text{O}$ NMR spectra of a series of solutions with $[\text{L}]/[\text{V}]$ ratios ranging from 0 to 3 are shown in Figure 2. Additionally, the ^{51}V NMR spectrum of a D_2O solution of $\text{Na}[\text{V}(\text{L})_2] \cdot 2\text{H}_2\text{O}(\text{cr})$ was collected to help confirm the assignment of the vanadium signal and is also shown in Figure 2 (spectrum e). As Figure 2 shows, the ^{51}V NMR spectrum of the initial solution (a) in the absence of glutaroimide-dioxime shows the peaks for the vanadates (VO_4^{3-} and HVO_4^{2-}) at $\delta = -537, -561$ ppm. The vanadate peak (\diamond) has broad shoulders indicating the spin-spin coupling with ^{17}O (see the inset for spectrum a in Figure 2). Concurrently, the ^{17}O NMR spectrum of the initial solution (a) shows a broad peak at ~ 560 ppm for the vanadate species (\diamond), with an apparent linewidth of 5250 Hz due to coupling with the spin-7/2 ^{51}V nucleus. These $^{17}\text{O}/^{51}\text{V}$ spin-spin coupling features agree with those reported for ^{17}O -labelled NaVO_3 in the literature.

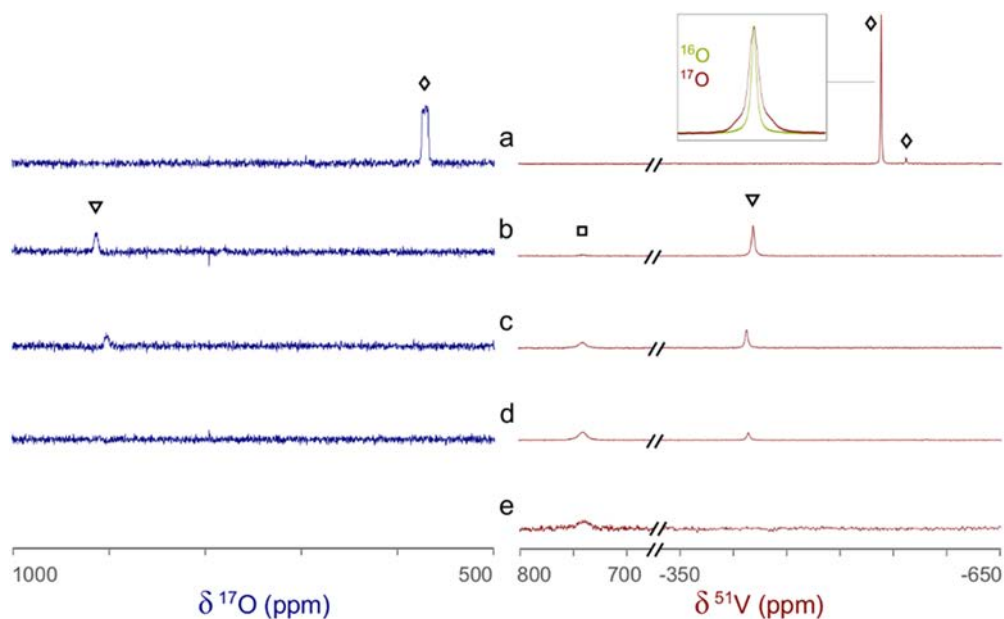


Figure 2. Concurrent $^{51}\text{V}/^{17}\text{O}$ NMR spectra demonstrating the formation of V(V)/glutaroimide-dioxime complexes in H_2^{17}O via the displacement of oxido V=O bonds. Solution labels: (a) vanadate only, no L; (b) 1:1 [L]/[V]; (c) 2:1 [L]/[V]; (d) 3:1 [L]/[V]; (e) D_2O solution of $\text{Na}[\text{V}(\text{L})_2]\cdot 2\text{H}_2\text{O}(\text{cr})$. Peak assignments: (\diamond) $\text{VO}_4^{3-}/\text{HVO}_4^{2-}$; (∇) 1:1 V/L complex, $[\text{V}(\text{O})(\text{OH})\text{L}]^-$; (\square) 1:2 V/L complex, $[\text{VL}_2]^-$. The inset on the ^{51}V spectrum a is an overlay of the ^{51}V peak in ^{17}O -enriched water and natural water showing the $^{17}\text{O}/^{51}\text{V}$ coupling.

As different equivalents (1, 2, and 3) of glutaroimide-dioxime were added to the vanadate solution, both the ^{51}V and ^{17}O signals for vanadates (\diamond) disappeared. In addition, a new ^{51}V signal in the ^{51}V spectra began to appear at $\delta = -410$ ppm (∇) and achieved maximum intensity at $[\text{L}]/[\text{V}] = 1$ (^{51}V spectrum b), diminished as $[\text{L}]/[\text{V}]$ was increased to 2 (^{51}V spectrum c), and nearly disappeared as $[\text{L}]/[\text{V}]$ was further increased to 3 (^{51}V spectrum d). Concurrently, a new peak appeared in the ^{17}O spectra around $\delta = 905$ ppm (∇) and achieved maximum intensity at $[\text{L}]/[\text{V}] = 1$ (^{17}O spectrum b), diminished at $[\text{L}]/[\text{V}] = 2$ (^{17}O spectrum c), and completely disappeared at $[\text{L}]/[\text{V}] = 3$ (^{17}O spectrum d).

Based on the changes in the peak intensities with the increase of $[\text{L}]/[\text{V}]$ and the occurrence of the maximum intensity at $[\text{L}]/[\text{V}] = 1$, it is reasonable to assign these peaks (∇) to a 1:1 intermediate complex, such as $[\text{V}(\text{O})(\text{OH})\text{L}]^-$, that is hypothesized in Scheme 1. The observation of the ^{17}O signal for the intermediate 1:1 V/L complex (∇) suggests that, in this complex, the glutaroimide-dioxime ligand only partially displaces the oxido V=O bond(s) from the initial ^{17}O -labelled vanadate, which is consistent with Scheme 1 and the crystal structure of the 1:1 complex, $\text{Na}[\text{VO}_2(\text{HL})]$ (Figure 3). The ^{17}O chemical shifts for the 1:1 V/L complex at $[\text{L}]/[\text{V}] = 1$ (^{17}O spectrum b) and 2 (^{17}O spectrum c) were noted to be slightly different. The difference probably results from different degrees of protonation in the $[\text{V}(\text{O})(\text{OH})\text{L}]^-$ species due to slight differences in pH between the two solutions (pH 7.5 and 8.5 for $[\text{L}]/[\text{V}] = 1$ and 2, respectively).

Accompanying the appearance and disappearance of the peaks (∇) for the 1:1 V/L complex, a new and extremely shifted ^{51}V peak at $\delta = 740$ ppm (\square) appears at $[\text{L}]/[\text{V}] = 1$ (^{51}V spectrum b), intensifies at $[\text{L}]/[\text{V}] = 2$ (^{51}V spectrum c), and achieves maximum intensity at $[\text{L}]/[\text{V}] > 2$ (^{51}V spectrum d). The chemical shift is identical to that of the ^{51}V peak in spectrum e for the solution

of $\text{Na}[\text{V}(\text{L})_2] \cdot 2\text{H}_2\text{O}$, implying that this peak (□), can be assigned to the 1:2 complex (□) should not be assigned to the 1:1 complex. The ^{51}V peak for the 1:2 complex (spectra d and e, show $^{17}\text{O}/^{51}\text{V}$ spin-spin coupling features because the ligands in the 1:2 complex completely displace the oxido $\text{V}=\text{O}$ bonds of the initial ^{17}O -labelled vanadate. However, the large linewidth of the ^{51}V signal resulting from the low symmetry of the complex precludes the verification of the absence or presence of the coupling features for the ^{51}V NMR signal of the 1:2 ($\delta = 740$ ppm) or 1:1 complex ($\delta = -410$ ppm). However, the absence of NMR signals on the ^{17}O spectrum d clearly indicates that the 1:2 complex does not contain oxido $\text{V}=\text{O}$ bonds and is a “bare” V^{5+} complex.

The intensity of the ^{51}V NMR signal for the final complex at $[\text{L}]/[\text{V}] > 2$ remained unchanged beyond 12 days, which suggests that vanadium remained in the $\text{V}(\text{V})$ oxidation state in the solution at neutral to slightly alkaline pH. If reduction of $\text{V}(\text{V})$ to the paramagnetic $\text{V}(\text{IV})$ species were to occur, it would diminish and eventually “wash-out” the ^{51}V NMR signal. Further reduction to $\text{V}(\text{III})$ is very unlikely: $\text{V}(\text{III})$ is generally much less stable in aqueous solutions, and no signals were observed in the lower ^{51}V chemical shift range of below $\delta = -1000$ ppm.

To summarize, concurrent $^{51}\text{V}/^{17}\text{O}$ NMR experiments have unprecedentedly demonstrated that the displacement of oxido $\text{V}=\text{O}$ bonds in vanadates by glutarimide-dioxime leads to the formation of a non-oxido V^{5+} complex in aqueous solution. The ^{51}V chemical shift of the complex is identical to that of the solution of $\text{Na}[\text{V}(\text{L})_2] \cdot 2\text{H}_2\text{O}(\text{cr})$, suggesting that the complex in solution is probably $[\text{V}(\text{L})_2]^-$. ESI-MS data described below provide further verification of the stoichiometry.

1.1.2 ESI-MS.

The negative mode ESI-MS spectra for two aqueous solutions (^{17}O -enriched H_2O : 10% ^{17}O ; 25% ^{18}O ; balance ^{16}O) with $[\text{L}]/[\text{V}] = 1$ and 2 are shown in Figure 3. Both spectra were obtained by diluting the solutions with ethanol/natural water (90/10 volume ratio) and directly spraying in the instrument. The spectrum of the solution with $[\text{L}]/[\text{V}] = 1$ (upper spectrum) shows two peaks at $m/z = 223.8$ and 251.8 , respectively. The peak at 223.8 corresponds to the intermediate 1:1 $[\text{V}(\text{O})(\text{OH})\text{L}]^-$ complex (calculated mass = 224.0) hypothesized in Scheme 1 while the peak at $m/z = 251.8$ corresponds to a 1:1 $[\text{V}(\text{O})(\text{OCH}_2\text{CH}_3)\text{L}]^-$ complex (calculated mass = 252.0). Evidently, ethoxide ($\text{OCH}_2\text{CH}_3^-$) from the electrospray solvent substituted the hydroxide (OH^-) of the $[\text{V}(\text{O})(\text{OH})\text{L}]^-$ complex during the dilution and/or electrospray process. The solution with $[\text{L}]/[\text{V}] = 2$ (lower spectrum) shows a single peak with $m/z = 330.8$ corresponding to $[\text{V}(\text{L})_2]^-$ (calculated mass of 331.0), confirming the formation of the 1:2 V/L complex.

According to the manufacturer's specifications, the 10% ^{17}O -enriched water also contains at least 25% ^{18}O . Consequently, the initial vanadate (Scheme 1) was actually labeled with ^{17}O as well as ^{18}O with the latter in a much higher yield. Therefore, unnatural isotopic patterns, particularly an $(m + 2)$ peak corresponding to an isotopologue containing one ^{18}O , should be observed if the vanadium complex still contains an oxido $\text{V}=\text{O}$ bond from the vanadate and, more importantly, the $(m + 2)$ peak should be absent if all oxido $\text{V}=\text{O}$ bonds of the vanadate are displaced by the glutarimide-dioxime ligand.

Notably, the base peak at $m/z = 330.8$ does not show the unnatural $(m + 2)$ isotopic pattern that could indicate the presence of one ^{18}O atom (or two ^{17}O atoms with a much lower probability) in the 1:2 complex (Figure 3, lower spectrum). This is because all of the oxido $\text{V}=\text{O}$ bonds of the initial $^{17,18}\text{O}$ -labelled vanadate are displaced by the ligands to form the non-oxido 1:2 $\text{V}(\text{V})$ /glutarimide-dioxime complex in solution. The presence of a small $(m + 1)$ peak at $m/z = 331.8$ is in accord with the natural $^{13}\text{C}/^{15}\text{N}$ abundances.

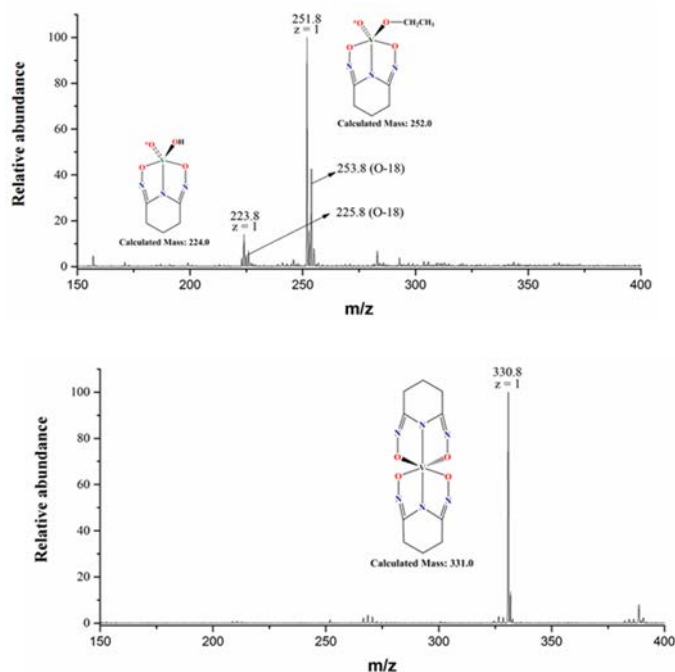


Figure 3. Negative mode ESI-MS spectra of V(V)/glutaroimide-dioxime complexes in $^{17,18}\text{O}$ -enriched H_2O (10% ^{17}O ; $\geq 25\%$ ^{18}O , balance ^{16}O), diluted and sprayed in (90/10) ethanol/water. (Upper) $[\text{L}]/[\text{V}] = 1$; (lower) $[\text{L}]/[\text{V}] = 2$. The $(m + 2)$ peaks in the upper spectrum indicate one ^{18}O atom and retention of an oxido $\text{V}=\text{O}$ bond in the 1:1 complex; the lower spectrum confirms elimination of all $\text{V}=\text{O}$ bonds in the 1:2 complex.

In contrast, the two base peaks for the 1:1 complexes ($[\text{V}(\text{O})(\text{OH})\text{L}]^-$ and $[\text{V}(\text{O})(\text{OCH}_2\text{CH}_3)\text{L}]^-$) show unnatural $(m + 2)$ peaks at 225.8 and 253.8, respectively, corresponding to the presence of one ^{18}O atom (or two ^{17}O atoms with a much low probability) in the complex. The presence of the $(m + 2)$ peak indicates incomplete displacement of the oxido $\text{V}=\text{O}$ bonds of the initial $^{17,18}\text{O}$ -labelled vanadate in the intermediate 1:1 complex, in agreement with Scheme 1. It should be remarked that, for the 1:1 complexes, the intensities of the $(m + 1)$ peaks include the contributions from the natural $^{13}\text{C}/^{15}\text{N}$ abundances, and the additional contribution from the isotopologue containing one ^{17}O atom.

To summarize, the ESI-MS data have validated the hypothesized reaction scheme (Scheme 1) and confirmed the formation of the 1:2 non-oxido V^{5+} /glutaroimide-dioxime complex, $[\text{V}(\text{L})_2]^-$, in aqueous solution via the displacement of the oxido $\text{V}=\text{O}$ bonds. The presence of an intermediate 1:1 complex that still contains oxido $\text{V}=\text{O}$ bonds, $[\text{V}(\text{O})(\text{OH})\text{L}]^-$, in solution has also been confirmed.

1.1.3 EPR.

EPR spectra of powdered crystals were recorded at 300 K and 4 K. At 4 K, only a weak signal with $g = 2.00$ and no hyperfine coupling was observed, which is due to the presence of organic radicals. This signal is frequently observed due to the high sensitivity of EPR spectroscopy. The lack of hyperfine coupling and the fact that the g value is quite different from that typical for V(IV), 1.95, strongly suggest that only V(V) is present at low temperature. Unlike the low temperature spectrum, the spectrum recorded at 300 K displays evidence for hyperfine coupling

typical of V(IV). However, the 300 K spectrum is still very weak, which indicates that V(IV) is only a minor component at this temperature. Overall, the EPR spectra are consistent with a V(V) ground state and indicate the potential presence of a low lying charge transfer state that could be populated at high temperatures.

3. CONCLUSION

A rare, non-oxido V(V) complex with glutarimide-dioxime (H_3L), $Na[V(L)_2] \cdot 2H_2O(cr)$, was crystallized from aqueous solution and characterized via x-ray diffraction. The complex was found to contain two fully deprotonated L^{3-} ligands bound to the bare V^{5+} cation via two oxime oxygens and the imide nitrogen. An intermediate complex, $Na[VO_2(HL)](cr)$, was also isolated and found to contain the typical VO_2^+ moiety present in many V(V) complexes.

Further characterizations using ^{51}V , ^{17}O , 1H , and ^{13}C NMR spectroscopy unprecedentedly demonstrated the stepwise displacement of the oxido oxygens to form the bare V(V)-glutarimide-dioxime complex. ESI-MS studies of V(V)-glutarimide-dioxime solutions allowed the identification the intermediate 1:1 M:L complex as well as the bare $V(L)_2$ complex at $m/z = 330.8$.

Structural insights into the much higher sorption of V(V) to amidoxime-based sorbents relative to U(VI) and Fe(III) were gained by comparing the structural parameters of the V(V)-glutarimide-dioxime complex with the analogous U(VI)- and Fe(III)-glutarimide-dioxime complexes. For these complexes, the degree of protonation of the ligand was found to decrease from U(VI) to V(V). In conjunction with the substantially shorter bond lengths observed for the V(V) complex relative to the other complexes, this implies stronger bonding in the V(V) complex and higher thermodynamic stability. In fact, the trend in binding strengths parallels the observed trend in sorption of these cations to poly(amidoxime) sorbents in marine tests.

4. PUBLICATIONS IN FY16

1. C. J. Leggett, B. F. Parker, S. J. Teat, Z. Zhang, P. D. Dau, W. W. Lukens, S. M. Peterson, A. J. P. Cardenas, M. G. Warner, J. K. Gibson, J. Arnold, L. Rao, Structural and Spectroscopic Studies of a Rare Non-Oxido V(V) Complex Crystallized from Aqueous Solution, *Chemical Science*, 2016, 7, 2775 – 2786. DOI: 10.1039/C5SC03958D.
2. S. Ansari, Y. Yang, Z. Zhang, K. Gagnon, S. J. Teat, S. Luo, L. Rao, Complexation of Lanthanides with Glutarimide-dioxime: Binding Strength and Coordination Modes, *Inorg. Chem.*, 2016, 55, 1315 -1323. DOI: 10.1021/acs.inorgchem.5b02653.
3. F. Endrizzi, C. J. Leggett, L. Rao, Scientific Basis for Efficient Extraction of Uranium from Seawater, I: Understanding the Chemical Speciation of Uranium under Seawater Conditions, *I&EC Research*, 2016, 55 (15), 4249-4256. DOI: 10.1021/acs.iecr.5b03679.
4. C. J. Leggett, F. Endrizzi, L. Rao, Scientific Basis for Efficient Extraction of Uranium from Seawater, II: Fundamental Thermodynamic and Structural Studies. *I&EC Research*, 2016, 55 (15), 4257-4263. DOI:10.1021/acs.iecr.5b03688

5. X. Sun, P. Zanonato, P. Di Bernardo, Z. Zhang, L. Rao, Sorption of Uranium and Other Metal Ions on Amine-Functionalized Silica Materials, *Separation Science and Technology*, 2015, 50, 2769–2775. DOI: 10.1080/01496395.2015.1085403.

5. ACKNOWLEDGMENTS

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