Understanding the Interactions of Seawater Ions with Amidoxime through X-Ray Crystallography

Fuel Cycle Research and Development

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ABSTRACT:

Insoluble polymer substrates functionalized with the amidoxime (R-C(NH$_2$)=NOH) functional group have been demonstrated as a technically feasible platform for extracting uranium from seawater,\textsuperscript{1} a potential source of extremely abundant uranium for use as nuclear fuel.\textsuperscript{2} While it is possible to isolate macroscopic amounts of uranium from the ocean with a positive energy return on investment using these materials, both the economic and energetic costs are many times greater than those of terrestrial uranium mining.\textsuperscript{3} Currently, the major contribution to this cost is the production of the sorbent itself, so being able to recycle the sorbent even a small number of times will have a huge impact on lowering the cost of their use. However, amidoxime resins show capacity fading when stripped by strong acids, presently limiting their recyclability.\textsuperscript{4} Both alternative extractants\textsuperscript{5} and alternative elution chemistries\textsuperscript{6} are under development with promising results but are yet at too early a stage to make predictions about their ultimate success. Given the potentially huge impact of a successful recycling process on the viability of seawater extraction of uranium, there is a strong need to pursue additional routes to elution chemistry.

During the course of this project, we studied the interactions of amidoxime-containing small molecules with the abundant metal ions in seawater, including Li, Na, K, Mg, Ca, Fe, Cu, and V, to understand the interactions of [UO$_2$]$^{2+}$ with amidoxime. By using small molecules with multiple adjacent functional groups, we crystallized the resulting metal complexes and used single crystal X-ray diffraction (SCXRD) as our primary tool for structural characterization. We also investigated the use of solutions of hydroxylammonium salts in weak acids as eluents for stripping and recycling amidoxime-based sorbents. The replacement of strong acids, which react with and destroy the amidoxime functional groups, with weak acids based on hydroxylammonium, a reagent that is actually used to make the amidoxime groups, is expected to avoid capacity loss on recycling and possibly even regenerate functionality that was lost due to exposure to the marine environment.
The overall goal of this project was to understand how metal ions from seawater bind to uranium-selective amidoxime functionalized sorbents by experimentally determining the structures of metal complexes with molecules simulating the possible binding sites and characterizing these binding sites spectroscopically to produce spectroscopic signatures which can be used to identify particular metal coordination modes on actual seawater sorbents. Based on this new understanding, we also aimed to develop a method for recovering the metals and recycling the sorbent by using hydroxylammonium salts as stripping agents which mimic the chemical character of the sorbent.

Objective 1: Crystallize and structurally characterize complexes of seawater ions with small molecule analogs of possible binding sites to develop experimentally validated models for potential adsorbed species.

Executive Summary

- A series of amidoxime ligands based on both rigid (aromatic/imidazole) and flexible (aliphatic chain) backbone were synthesized from their nitrile precursors. The synthesized ligands were characterized with spectroscopic methods and single crystal X-ray diffraction (SCXRD).
  - Among those, two new amidoxime ligands (2-amino-4,5-diamidoximylimidazole and 4-amidoximylimidazole) were crystallized and characterized by SCXRD.
- Amidoxime-based liquid salts, as a new crystallization media, were prepared from amidoxime ligands by reaction with acid or base.
  - Two new chloride salts of benzamidoxime and 4-amidoximylimidazole were obtained after reaction with HCl and characterized by SCXRD.
  - Four amidoximium chloride salts of 4,5-diamidoximylimidazole, 2-amino 4,5-diamidoximylimidazole, and 1,4-diamidoximylbenzene were obtained after the reaction with HCl. One amidoximium acetate salt of succinamidedioxime was obtained after the reaction with acetic acid. These amidoximium salts were characterized by SCXRD.
  - Two amidoximate salts of 1,3-diamidoximylbenzene and 1,3 bishydroxyiminisoinindoline were obtained after the reaction with tetrapropylammonium hydroxide ([N\textsubscript{3333}][OH]). One amidoximate salt of 1,4-diamidoximylbenzene was obtained with tetraethylammonium hydroxide ([N\textsubscript{2222}][OH]).
  - In amidoximium salts, the imine nitrogen is protonated during the reaction. However, the O-H group of amidoximes is deprotonated in amidoximate salts.
- The ability of synthesized amidoxime ligands to form complexes with seawater ions (vanadium, uranium, copper, sodium, potassium etc.) was investigated. New metal-amidoxime complexes (with uranyl, vanadium, and copper) were obtained and metal-ligand binding modes were investigated with SCXRD.
As compared to uranyl, a different binding mode of amidoxime ligand (4,5-diamidoximylimidazole) was observed in the copper complex. The ligand was coordinated to copper via the oxime nitrogen and the nitrogen atom from the imidazole ring, while uranyl coordinated through both the oxime groups (both nitrogen and oxygen atoms) to uranyl center.7

The 1,4-diamidoximylbenzene (1,4-DAOBz) ligand formed an outer sphere complex with no coordination to vanadium oxide cluster. A series of polymeric coordination (2D/3D) complexes with monodentate binding to the uranyl center via oxime oxygen atom was observed.

A complex of octahedral [V10O28]6− anions and 1,4-diamidoximylbenzene cation was obtained from the reaction of VOSO4·xH2O with 1,4-diamidoximylbenzene (1:1 molar ratio) in water. The crystals of the vanadium complex were characterized with SCXRD.

The vanadium cluster is sandwiched between the amidoxime ligand layers and also has 6 water molecules which were involved in noncovalent interactions stabilizing the structure.

A uranyl-amidoxime complex was obtained from the reaction of UO2(OAc)2·2H2O, 4-amidoximylimidazole, and 1-ethyl-3-methylimidazolium acetate [C2mim][OAc] at a 1:1:1 molar ratio. The crystals of the vanadium complex were characterized with SCXRD.

[C2mim][OAc] IL provides a solventless medium to coordinate the ligands with U via η2 coordination.

Three cyclic amidoxime ligands were synthesized from their cyano precursors by reacting them with hydroxylamine. These ligands were characterized using single crystal X-ray diffraction (SCXRD) and spectroscopic methods.

Details:
The world’s oceans are a potential source of uranium for nuclear power. Approximately 7.6 million tons of uranium have been identified on the earth’s land, whereas there are hundreds of times more uranium (approx. 4.5 billion tons) in sea water. Despite of presence of the massive amount of uranium in seawater, the selective extraction of uranium from high saline seawater that contains many other competing ions is still extremely challenging. Uranium extraction from seawater is a potential cleaner alternative to terrestrial mining that provides the long-term source of nuclear fuel that require its selective removal from many other seawater ions, a task accomplished by amidoxime-functionalized sorbents. To date, amidoxime continues to be the center of efforts to design higher capacity extractants and serves as the benchmark against which new extractants are compared.8 Various amidoxime based adsorbents such as nanoporous polymers, amidoximated Al series adsorbents, electrospun nanofibrous adsorbents, magnetic microspheres, and porous aromatic frameworks were developed to capture uranyl from seawater during the past few decades, however the binding selectivity of amidoxime to uranyl ion is still
not maturely explored that is crucial for adsorption in seawater environment. Even less is known about binding of ligands with multiple amidoxime groups (poly-amidoxime) in the structure. Poly-amidoxime-based polymers are the current state-of-the-art sorbent materials use for uranium extraction from seawater. Unfortunately, many reported transition metal amidoxime complexes are likely ineffective to provide a deeper understanding of the interactions of the metals with amidoxime extractants in seawater due to the presence of multiple functional groups that influence the binding. Knowing the importance of seawater-amidoxime chemistry, a series of amidoxime functionalized ligands were synthesized and their complexation reactions with seawater ions were investigated.

1. **Ligand synthesis**

![Scheme 1](image)

Scheme 1. Structures of a) 1,4-diamidoximylbenzene; b) 1,3-diamidoximylbenzene; c) 1,3-bishydroxyiminoisoindoline; d) benzamidoxime; e) (1E,3E,5E,7E)-pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone tetraoxime; f) 4,5-diamidoximylimidazole; g) 2-amino-4,5-diamidoximylimidazole; h) 4-amidoximylimidazole; i) glutaroimidedioxime; and j) succinamidedioxime.

The amidoxime ligands were synthesized from nitrile precursors by converting nitrile groups to amidoxime functionality using hydroxylamine according to the previously reported procedure. The synthesized amidoxime ligands are shown in Scheme 1. Simple amidoximes are well-known to bind uranyl in aqueous solution and, recent data suggest an $\eta^2$-binding mode in the polymer. In principle, the cyclic amidoximes ligands provides a tridentate binding site and is believed to play an important role in uranyl uptake by the adsorbent. It has also been shown in the literature.
that the cyclic amidoxime is more effective than the open-chain amidoxime ligand for complexing UO$_2^{2+}$ because the former can afford tridentate coordination.$^{11}$

The ligands were chosen to systematically study the effect of flexibility and basicity of amidoxime groups on complexation with seawater ions. Therefore, the ligands ‘a-h’ were synthesized from rigid nitrile precursors, while flexible aliphatic precursors were used for synthesis of ‘i’ and ‘j’ ligands. From the structure, the ligands ‘i’ and ‘j’ are expected to provide conformational flexibility for metal coordination, while spacing between the functional group in ligand “a-c” and “e” is fixed. Ligands ‘f-h’ are imidazolium-based ligands with the additional nitrogen atoms in the ring which introduces basicity to the backbone. The monodentate amidoximate ligands (d, h) were chosen as a benchmark for comparison to bidentate amidoximes.

a. Synthesis of 1,3-bishydroxyiminoisoindoline: 1,2-Dicyanobenzene was dissolved in methanol together with NH$_2$OH (Scheme 2). An aqueous solution of K$_2$CO$_3$ was added to the methanolic solution with stirring. The solution was refluxed overnight and monitored by TLC until no starting material remained. Cyclization of the neighbouring amidoximyl group at 1 and 2 positions on benzene ring occurred during the reaction. 1,3-bishydroxyiminoisoindoline ligand was obtained as a yellow crystalline precipitate which was washed with methanol and dried under vacuum. Single crystal X-ray Diffraction (SCXRD) was used to determine the unit cell parameters for the crystals that matched with the reported structure.$^{12}$

![Scheme 2: Synthesis route for 1,3-bishydroxyiminoisoindoline ligand (left) and the crystal structure of the ligand (right).](image)

b. Synthesis of glutarimidedioxime: Glutaronitrile and hydroxylamine (50% in H$_2$O) were dissolved in (1:1) ethanol:water solvent with stirring for 5 days, resulting in a white crystalline solid of glutarimidedioxime ligand (Scheme 3). Single crystals of the products were analyzed with SCXRD and the unit cell dimensions of the crystals matched with the reported structure.$^{13}$
Scheme 3: Synthesis route for glutarimidedioxime ligand (left) and the crystal structure of the ligand (right).

c. *Synthesis of 1E,3E,5E,7E-pyrrolo[3,4]isoindole-1,3,5,7(2H,6H)-tetraonetetraoxime:* 1,2,4,5-Tetracyanobenzene and NH₂OH·HCl were dissolved in methanol. An aqueous solution of K₂CO₃ was added in the methanolic solution (Scheme 4). The solution was refluxed overnight until everything dissolved. Upon cooling, the ligand precipitated in orange color from the reaction mixture and was filtered, washed with acetone, and dried under vacuum. The precipitate, insoluble in all the common solvents, was characterized by ATR FT-IR spectroscopy (Figure 1). The following peaks of FT-IR spectra were assigned 1344 cm⁻¹ (ν -NH); 1414 cm⁻¹ (ν C=N); 1651 cm⁻¹ (ν C=C) and 3155 cm⁻¹ (ν O-H) which indicate that condensation of cyano group to cyclic amidoxime group has occurred in course of reaction.

Figure 1: ATR FT-IR spectra of 1E,3E,5E,7E-pyrrolo[3,4]isoindole-1,3,5,7(2H,6H)-tetraonetetraoxime ligand.
Scheme 4: Synthesis route for 1E,3E,5E,7E-pyrrolo[3,4]isoindole-1,3,5,7(2H,6H)-tetraonetetraoxime ligand.

The synthesized ligands were used in the synthesis of amidoxime based salts or ILs and in the complexation reactions with seawater ions to investigate the possible binding modes. The complexation reaction of uranyl and vanadyl salts with these synthesized ligands was conducted to obtain new unique chelated complexes. The chelated complexes obtained after the complexation reactions were analyzed with SCXRD, PXRD, and other spectroscopic methods. The results of metal ion–ligands binding are described in details in the complexation reactions of the amidoxime ligands in conventional solvents section. While majority of the synthesized ligands is known in the literature, the ligands, g and h, are new. The crystal structures of the new ligands determined with SCXRD are shown in Figure 2.

Figure 2. ORTEP diagram of 2-amino-4,5-diamidoximylimidazole (ligand g), and 4-amidoximylimidazole (ligand h).

2. Ionic Liquid Synthesis of the amidoxime ligands

One of the challenges to form V or U crystals with amidoxime ligands is their tendency to form insoluble coordinating polymers, where the amidoxime ligands are linked to the metal center. Our group has developed techniques for growing metal complexes from low melting salts (ionic liquids, ILs) at high concentrations and converting ligands into IL forms. ILs have various advantages over traditional solvents for f-element separations including high radiolytic stabilities, low vapor pressures, and generally low flammability. Use of amidoxime ligands in a form of ILs
can help access new structures which are otherwise inaccessible when conventional solvents are used. Indeed, crystallization using conventional solvents is mostly influenced by the solvent media and rarely results in crystal formation making the understanding of metal-ligand coordination challenging. Contrarily, amidoxime ligands in the form of ILs could provide a unique solvent medium for metal complex formation. Thus, novel and previously unobserved metal-amidoxime binding modes that might provide insight on amidoxime selectivity can be found. Therefore, we have attempted synthesis of ILs from amidoxime ligands a-d, and f-h (Scheme 1). The synthesis was performed by reaction of amidoxime ligands with appropriate acid or base (Scheme 5).

\[
\text{Amidoxime Ligand} + \text{Acid/Base} \xrightarrow{N_2} \text{Salt Crystals or precipitate}
\]

**Scheme 5.** General schematics of ionic liquid synthesis from amidoxime ligands.

**Figure 3.** ORTEP diagram for chloride salts of 1,4-diamidoximylbenzene (a; top left), 4,5-diamidoximylimidazole (e; top right), 2-amino 4,5-diamidoximylimidazole (f; middle left), acetate salt of succinamidedioxime (c; middle right), benzamidoxime (d, bottom left), and 4-amidoximylimidazole (h, bottom right)
a. Amidoxinium Salts or ILs: To obtain the amidoxinium salts or ILs, acids such as hydrochloric acid (HCl), acetic acid (CH₃COOH), and tosylic acid were chosen due to their ability to protonate the amidoxime ligands. All the ligands mentioned in Scheme 6 were reacted with HCl and CH₃COOH, while ligands a-d were reacted with tosylic acid however, only few ligands were protonated (Figure 3). The imine nitrogen of the amidoxime group was protonated during the reaction with HCl and CH₃COOH. The crystals of chloride salts were obtained from the five ligands a, d, e, f, and h (Scheme 1), while the crystals of acetate salts were obtained using ligand c. SCXRD was used to solve the crystal structure for chloride and acetate salts (Figure 3). Only precipitates were obtained when tosylic acid was used.

Once we successfully obtained the cationic amidoxime-based liquid salts, we investigated the possibility to obtained anionic amidoximate ILs. For that, triethyl amine was used as the base to deprotonate the amidoxime ligand ‘a’ (Scheme 1). The product of the reaction was analyzed with powder X-ray diffraction (PXRD) and the collected spectrum is shown in Figure 4. As seen, ligand ‘a’ did not react with triethyl amine and PXRD data matches the data collected for the starting material (Figure 4) indicating that stronger base should be selected for this reaction.

![Figure 4](image_url). PXRD spectra of reactant (1,4-diamidoximyl benzene (1,4-DAOBz) (red) and the reaction mixture of 1,4-diamidoximylbenzene and trimethylamine (black).
b. Amidoximate Salts or ILs: To obtain the amidoximate salts or ILs, the bulky quaternary ammonium and phosphonium hydroxides such as tetraethylammonium hydroxide ([N₂₂₂₂][OH]), tetrapropylammonium hydroxide ([N₃₃₃₃][OH]), tetrabutylphosphonium hydroxide ([P₄₄₄₄][OH]), tributylmethylphosphonium hydroxide ([P₄₄₄₁][OH]), tetrabutylammonium hydroxide ([N₄₄₄₄][OH]), tributylmethylammonium hydroxide ([N₄₄₄₁][OH]), and trihexyltetradecylphosphonium hydroxide ([P₆₆₆₁₄][OH]) were chosen to deprotonate the hydroxyl group of the amidoxime group of the ligands (Scheme 1). The reaction of 1,4-diamidoximylbenzene with [N₂₂₂₂][OH] resulted in amidoximate salt [N₂₂₂₂][C₈H₈N₄O₂]·3H₂O (Figure 5). However, the reaction of 1,3-diamidoximyl benzene and 1,3-bishydroxyiminoisoindoline with [N₃₃₃₃][OH] produced amidoximate salts with quaternary base as [N₃₃₃₃][C₈H₉N₄O₂]·H₂O and [N₃₃₃₃][C₈H₅N₃O₂] (Figure 5), respectively.

![ORTEP diagram for [N₂₂₂₂][C₈H₈N₄O₂]·3H₂O (a; top left), [N₃₃₃₃][C₈H₉N₄O₂]·H₂O (g, top right), and [N₃₃₃₃][C₈H₅N₃O₂] (d; bottom).](image-url)
3. **Complexation reactions of the amidoxime ligands in conventional solvents**

The complexation reactions with metal salts of Na⁺, K⁺, Li⁺, Mg²⁺, Ca²⁺, Cu²⁺, V⁴⁺/⁵⁺, and UO₂²⁺ were conducted in different stoichiometric ratios (1:1, 1:2, 2:1, 4:1, 6:1, and 8:1) with some of the amidoxime ligands: a-c, and f-j (Scheme 1). The reactions of the ligands b, c, and g-j with metal-ions resulted in the formation of either precipitate or ligand crystals indexed using SCXRD. Ligand ‘a’ formed metal complexes with UO₂²⁺ and V⁵⁺; Ligand ‘f’ was successfully complexed with Cu²⁺ ion. First, we analyzed the copper complex obtained by reacting copper nitrate with 4,5-diamidoximylimidazole ligand in 1:1 stoichiometric ratio using SCXRD and PXRD. The products of the reaction were both green crystals and green precipitate (Scheme 6).

![Scheme 6](image.png)

**Scheme 6.** Synthetic scheme for the preparation of copper complex of 4,5-diamidoximylimidazole.

The ORTEP diagram of the crystal structure shows a square planar complex with chelate binding of the ligand to the copper center via the oxime nitrogen atom and the nitrogen atom from the imidazole ring (Figure 6a). The binding mode observed here is different than that observed for uranium and vanadium complexes with same ligand reported in literature. The PXRD was used to analyze the green precipitate obtained during reaction and the recorded pattern differs from the simulated indicating formation of other products (Figure 6b). To better understand the nature of precipitate, recrystallization from different solvents was performed. However, the crystals suitable for analysis were not obtained.

![Figure 6](image.png)

**Figure 6.** a) ORTEP diagram of copper:4,5-diamidoximylimidazole complex; b) PXRD spectra comparison of green precipitate (*black*) with the simulated pattern (*red*) of the single crystal structure.
Next, we investigated complex formation of ligand ‘a’ with V$_2$O$_5$ (Scheme 7). The reaction mixture was a pale-yellow color solution which on slow evaporation (two weeks) formed yellow crystals. The crystals were analyzed using SCXRD (Figure 7).

\[
\text{Scheme 7. Synthesis of vanadium oxide cluster with 1,4-diamidoxymylbenzene.}
\]

\[
\begin{align*}
\text{1,4-diamidoxymylbenzene} & \quad \text{V$_2$O$_5$ (H$_2$O)} \quad \text{filtered}\text{ kept for slow evaporation} \\
& \rightarrow [\text{C}_8\text{H}_{11}\text{N}_4\text{O}_2]_2[V(\text{H}_2\text{O})_6][\text{V}_{10}\text{O}_{28}]\cdot[(\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)]_\cdot 6\text{(H}_2\text{O})
\end{align*}
\]

\[
\text{Figure 7. ORTEP diagram of outer sphere complex of vanadium oxide cluster with 1,4-diamidoxymylbenzene.}
\]

The reaction of V$_2$O$_5$ with 1,4-DAOBz yielded single crystals of the compound containing octahedral [V(\text{H}_2\text{O})_6]^{4+} cations, [\text{V}_{10}\text{O}_{28}]^{6-} anions, and both neutral and protonated outer-sphere molecules of the ligand. Notably, V$^{4+}$ and V$^{5+}$, which have extremely high affinities for amidoxime, were able to crystallize alongside a neutral, non-coordinating amidoxime ligand. The crystal structure is stabilized by noncovalent N-H⋯O hydrogen bond interactions. Also, the vanadium cluster, sandwiched between the amidoxime layers, interacts with amidoxime via N-H⋯O hydrogen bond interactions. In the complex, amidoxime ligand acts as a counterion and as an outer sphere ligand which does not coordinate to vanadium. Furthermore, the complex has vanadium in mixed oxidation states of +4 and +5 and both neutral and cationic ligands are present.

Once we established that vanadium does not coordinate to 1,4-DAOBz, we studied its complex formation ability with uranyl salts (uranyl acetate, uranyl nitrate, and uranyl chloride) (Scheme 8). The complex formation resulted in three different crystal structures.
Scheme 8. Synthetic scheme for complexation of uranyl salts with 1,4-diamidoximylbenzene.

The ORTEP diagram of the complexes obtained with different uranyl salts are presented in Figure 8. In case of uranyl nitrate, the crystal structure shows a two dimensional polymeric sheet-like pattern where the ligand coordinates only through the oxime oxygen atom. The tetranuclear core extends in both directions giving rise to a 2D polymer (Figure 8a). The coordination environment around uranyl shows pentagonal bipyramidal geometry made up of amidoxime ligands, water, hydroxide ion bridges, and oxygen atoms. The same reaction with uranyl chloride resulted in a 3D polymer, where the ligand coordinates via the oxime oxygen atom, bridging the tetranuclear cores forming a 3D network (Figure 8b). The geometry around the uranyl core is also pentagonal bipyramidal with both neutral and anionic amidoxime ligands in the pentagonal plane. In case of uranyl acetate, a 2D polymeric sheet-like pattern was observed with the amidoxime ligand coordinates to uranyl through the oxime oxygen atom\(^\text{16}\) (Figure 8c). This complex can be visualized as a trinuclear uranyl core, which is attached to neighboring trinuclear cores by hydroxyl and acetate ion bridges forming a 1D polymer. The polymers are further stitched together by the amidoxime ligands to form 2D polymer. The trinuclear core has three uranyls which have two different coordination environments.

**Detailed comparison of 1,4-DAOBz Complexes with Vanadium and Uranium**

To better understand the difference between vanadium and uranium complexes with 1,4-DAOBz detailed structural comparison was performed. Amidoxime ligand forms outer sphere complex with vanadium pentoxide with no coordination observed to the vanadium centers. A rare coordination of the ligand in a monodentate fashion through the oxygen atom was observed for the uranyl complexes resulting in different polymeric complexes. Thus 1,4-diamidoximylbenzene depicts an interesting dual ionic nature, *i.e.*, cationic with vanadium and anionic with uranium.
The results on 1,4-diamidoximylbenzene- complex formation show that the ligand does not coordinate to vanadium even though amidoxime ligands have higher affinity for vanadium. The same ligand forms a variety of polymeric sheet like structures with monodentate coordination acting as bridging ligand with different uranyl salts. This monodentate coordination in the uranyl structures can be attributed to the para positioning of the amidoxime group on the benzene moiety, which helps it to bridge the uranyls giving rise to the polymeric nature of the complexes. The amidoxime groups at the one and four positions in a benzene ring cannot bind cooperatively to the same metal ion, yet are in resonance with each other, thereby showing that through purely
electronic effects, two amidoximes can disrupt their usual coordination which might have profound implications for metal selectivity.

The reaction of VOSO₄·xH₂O with 1,4-diamidoximylbenzene (1:1 molar ratio) in water as a solvent yielded single crystals of a vanadium complex (Scheme 9). The crystals were analysed with SCXRD that revealed the chemical formula [C₈H₁₂N₄O₂][V₁₀O₂₈]·6H₂O.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} \\
\text{OH} & \quad \text{+} \\
\text{N} & \quad \text{NH}_2 \\
\text{OH} & \quad \text{H}_2\text{O} \\
\end{align*}
\]

\[\text{VOSO}_4 \cdot \text{xH}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{R.T.} [\text{C}_8\text{H}_{12}\text{N}_4\text{O}_2][\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}\]

Scheme 9. Synthetic scheme for the preparation of vanadium complex of 1,4-diamidoximylbenzene.

![Scheme 9](image)

Figure 9. ORTEP diagram of vanadium complex [C₈H₁₂N₄O₂][V₁₀O₂₈]·6H₂O (left) and interaction environment around the vanadium cluster anion [V₁₀O₂₈]⁻ (right).

The ORTEP diagram of the crystal structure shows an octahedral [V₁₀O₂₈]⁻ anions balanced with three protonated outer-sphere molecules (as a cation) of the 1,4-diamidoximylbenzene ligand (Figure 9, left). In the crystals structure, the vanadium cluster anion [V₁₀O₂₈]⁻ sandwiches between the protonated 1,4-diamidoximylbenzene ligand layers (Figure 9, right). The water molecules and protonated 1,4-diamidoximylbenzene ligand are involved in noncovalent interactions, i.e. hydrogen bonding to stabilize the crystal structure. These results show that the oxidation of vanadium changes from +4 to +5 during the reaction. The crystal structure of the
complex demonstrates that the ligand doesn’t coordinate to vanadium even though amidoxime ligands have higher affinity for vanadium.

4. Complexation reactions in ionic liquids

The complementarity of ILs with respect to other solvent systems is particularly useful in metal ion coordination chemistry. Molecular solvents typically used in coordination chemistry usually dissociate ionic compounds by solvating the ions with strong interactions and therefore heavily influence the speciation. ILs allow cation-anion interactions to be controlled in a way not possible with molecular solvents, as they can readily dissolve or be mixed with other ionic compound without requiring any neutral molecules that would affect cation-anion interactions. ILs provide a unique solvent medium to force coordination with metal ions and find new binding modes. This alternative crystallization approaches may lead to growth of metal complexes that resist crystallization from conventional solvents.

1-ethyl-3-methylimidazolium acetate ([C$_{2}$mim][OAc]): Here, we have conducted the complexation reaction of seawater metal salts including Ca$^{2+}$, Cu$^{2+}$, V$^{4+/5+}$, and UO$_2^{2+}$ with amidoxime ligands (mentioned in Scheme 1) in different stoichiometric ratios 1:1, 1:2, 2:1, 1:3, and 3:1 in presence of the IL 1-ethyl-3-methylimidazolium acetate ([C$_{2}$mim][OAc]). In few cases, we obtained crystals and precipitates after the complexation reactions. The reaction of UO$_2$(OAc)$_2$·2H$_2$O, 4-amidoximylimidazole, and [C$_{2}$mim][OAc] at a 1:1:1 molar ratio produced the crystals of a uranyl complex of 4-amidoximylimidazole (Scheme 10). The central molecular formula for the complex is [C$_{2}$mim][UO$_2$(OAc)$_2$(4-AOIm)] where 4-AOIm is 4-amidoximylimidazole. The complex crystallizes in the orthorhombic space group Pbca with 8 molecules in the unit cell. The coordination number around uranium is eight with a distorted hexagonal bipyramidal geometry (Figure 10). The hexagonal plane around uranium consists of two acetate ions and $\eta^2$ coordination of the oxime group from the 4-amidoximylimidazolide ion while the axial atoms are occupied by the two oxygen atoms. The charge on the complex is counter balanced by 1-ethyl-3-methylimidazolium cation.

Scheme 10. Synthetic scheme for the preparation of uranyl complex of 4-amidoximylimidazole.
There are no intramolecular interactions present in the complex molecules, while N-H⋯O intermolecular interactions form complex dimers (Figure 11, left). These complex dimers are further crosslinked with other dimers through N-H⋯O and N-H⋯N interactions to form a cage type supramolecular network (Figure 11, right). Accessing such structures through IL synthesis may allow the anionic complexes themselves to be used as crystallization media to study their interactions with other metal ions. This study provides the following insights: (1) IL provides a solventless medium to coordinate the 4-AOIm ligand with uranyl via $\eta^2$ coordination; (2) Amidoxime ligand competing with acetate ligand in a pool of acetate medium; (3) [C$_2$mim][OAc] provides an ionic environment for amidoximes to coordinate with uranium.
Tetrabutylphosphonium hydroxide ([P$_{4444}$][OH]): The complexation reactions of vanadyl and uranyl salts has been also conducted with various oximes ligands in two certain ratios in the presence of [P$_{4444}$][OH] (Table 1). The reactions were carried out at 100 °C for 12 h.

Table 1: Complexation of vanadyl and uranyl salts with [P$_{4444}$][OH].

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>IL</th>
<th>B</th>
<th>C</th>
<th>Ratio (A:B:C)</th>
<th>Time and temp</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[P$_{4444}$][OH]</td>
<td>1,4-diamidoximyl benzene</td>
<td>VOSO$_4$</td>
<td>2:1:1</td>
<td>12 h @ 100 °C</td>
<td>Crystals</td>
</tr>
<tr>
<td>2</td>
<td>[P$_{4444}$][OH]</td>
<td>1,4-diamidoximyl benzene</td>
<td>VOSO$_4$</td>
<td>4:1:1</td>
<td>12 h @ 100 °C</td>
<td>Semi solid</td>
</tr>
<tr>
<td>3</td>
<td>[P$_{4444}$][OH]</td>
<td>1,4-diamidoximyl benzene</td>
<td>V$_2$O$_5$</td>
<td>2:1:1</td>
<td>12 h @ 100 °C</td>
<td>Crystals</td>
</tr>
<tr>
<td>4</td>
<td>[P$_{4444}$][OH]</td>
<td>1,4-diamidoximyl benzene</td>
<td>V$_2$O$_5$</td>
<td>4:1:1</td>
<td>12 h @ 100 °C</td>
<td>Crystals</td>
</tr>
<tr>
<td>5</td>
<td>[P$_{4444}$][OH]</td>
<td>Glutarimidodioxime</td>
<td>NH$_4$VO$_3$</td>
<td>2:1:1</td>
<td>12 h @ 100 °C</td>
<td>Semi solid</td>
</tr>
<tr>
<td>6</td>
<td>[P$_{4444}$][OH]</td>
<td>Glutarimidodioxime</td>
<td>NH$_4$VO$_3$</td>
<td>4:1:1</td>
<td>12 h @ 100 °C</td>
<td>Semi solid</td>
</tr>
<tr>
<td>7</td>
<td>[P$_{4444}$][OH]</td>
<td>1,4-diamidoximyl benzene</td>
<td>UO$_2$(NO$_3$)$_2$·6H$_2$O</td>
<td>2:1:1</td>
<td>12 h @ 100 °C</td>
<td>Crystals</td>
</tr>
<tr>
<td>8</td>
<td>[P$_{4444}$][OH]</td>
<td>1,4-diamidoximyl benzene</td>
<td>UO$_2$(NO$_3$)$_2$·6H$_2$O</td>
<td>4:1:1</td>
<td>12 h @ 100 °C</td>
<td>Semi solid</td>
</tr>
<tr>
<td>9</td>
<td>[P$_{4444}$][OH]</td>
<td>Glutarimidodioxime</td>
<td>UO$_2$(OAc)$_2$·2H$_2$O</td>
<td>2:1:1</td>
<td>12 h @ 100 °C</td>
<td>Crystals</td>
</tr>
<tr>
<td>10</td>
<td>[P$_{4444}$][OH]</td>
<td>Glutarimidodioxime</td>
<td>UO$_2$(OAc)$_2$·2H$_2$O</td>
<td>4:1:1</td>
<td>12 h @ 100 °C</td>
<td>Crystals</td>
</tr>
<tr>
<td>11</td>
<td>[P$_{4444}$][OH]</td>
<td>1,3-bis hydroxyiminoisoinolide</td>
<td>UO$_2$(SO$_4$)$_2$·3H$_2$O</td>
<td>2:1:1</td>
<td>12 h @ 100 °C</td>
<td>Semi solid</td>
</tr>
<tr>
<td>12</td>
<td>[P$_{4444}$][OH]</td>
<td>1,3-bis hydroxyiminoisoinolide</td>
<td>UO$_2$(SO$_4$)$_2$·3H$_2$O</td>
<td>4:1:1</td>
<td>12 h @ 100 °C</td>
<td>Crystals</td>
</tr>
</tbody>
</table>

A new crystal of a salt [P$_{4444}$]Br·1,4-Benzenedicarboxamide was obtained by reacting V$_2$O$_5$:1,4-diamidoximylbenzene in a 1:1 ratio of in the presence of 2 equivalent of [P$_{4444}$][OH] (Figure 12, Table 1 entry 3). The Br$^-$ is the impurity in the [P$_{4444}$][OH] solution, which is trapped in the crystal structure. In the asymmetric unit, two molecules of 1,4-Benzenedicarboxamide are present in the inversion center. The 1,4-Benzenedicarboxamide connects with the Br$^-$ through C-H···Br and N-H···Br hydrogen bonds. The [P$_{4444}$]$^+$ cation connects with Br through C-H···Br hydrogen bonds. The 1,4-Benzenedicarboxamide forms a linear chain through amide-amide dimer with N-H···O bond (Figure 2). This chain is sandwiched by [P$_{4444}$]$^+$ and Br$^-$.
also connected with neutral 1,4-Benzenedicarboxamide through weak C-H···N and C-H···O hydrogen bonds.

The 1,3-diamidoximylbenzene converted into 1,4-Benzenedicarboxamide due to the migration to electron deficient oxygen atom rearrangement reaction in the presence of aqueous the [P₄₄₄₄][OH] base to release amine nitrogen of 1,4-diamidoximylbenzene.

![Figure 12. ORTEP diagram of [P₄₄₄₄]Br·1,4-Benzenedicarboxamide salt.](image)

![Figure 13. Linear chain of 1,4-Benzenedicarboxamide formed through amide-amide dimer with N-H···O bond and sandwiched by [P₄₄₄₄]+ and Br-.](image)

A new crystal structure of uranium complex was obtained with cyclic amidoxime. The crystal was obtained by the reaction of 1,3-bishydroxyiminoisoindoline and uranyl sulphate in 1:1 ratio in the presence of [P₄₄₄₄][OH] at 4 times in excess (Figure 14, Table 1 entry 12). In the crystal structure, one 1,3-bishydroxyiminoisoindoline ligand coordinates with uranium via oxime oxygen
and another ligand shows chelate type binding mode to uranium (Figure 14). Two [P_{4444}] cations are also hanging in the crystal structure. The crystal quality was not good and therefore the refinement of the structure was really tough. The skeleton of the molecules breaks after certain refinement.

**Figure 14.** Structure fragment of uranium complex with cyclic 1,3-bishydroxyiminoisoindoline.

Trihexyltetradecylphosphonium hydroxide ([P_{66614}][OH]): Glutaroidimidedioxime and 1,3-bishydroxyiminoisoindoline were mixed with molten [P_{66614}][OH] in 1:2 ratio at 70 °C for 1 h. Further, the reaction mixtures were used for the complexation with vanadium and uranyl salts at 80 °C for 12 h (Table 2). The crystals were obtained upon cooling the reaction mixture at room temperature.

**Table 2: Complexation of vanadyl and uranyl salts with [P_{66614}][OH].**

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Ratio (A:B:C)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[P_{66614}][OH]</td>
<td>Glutaroidimidedioxime</td>
<td>VOSO₄</td>
<td>2:1:1</td>
<td>Liquid</td>
</tr>
<tr>
<td>2</td>
<td>[P_{66614}][OH]</td>
<td>Glutaroidimidedioxime</td>
<td>V₂O₅</td>
<td>2:1:1</td>
<td>Glutaroidimidedioxime crystal</td>
</tr>
<tr>
<td>3</td>
<td>[P_{66614}][OH]</td>
<td>1,3-bishydroxyiminoisoindoline</td>
<td>VOSO₄</td>
<td>2:1:1</td>
<td>Semi solid</td>
</tr>
<tr>
<td>4</td>
<td>[P_{66614}][OH]</td>
<td>1,3-bishydroxyiminoisoindoline</td>
<td>V₂O₅</td>
<td>2:1:1</td>
<td>Semi solid</td>
</tr>
<tr>
<td>5</td>
<td>[P_{66614}][OH]</td>
<td>Glutaroidimidedioxime</td>
<td>UO₂(NO₃)₂.6H₂O</td>
<td>2:1:1</td>
<td>Liquid</td>
</tr>
<tr>
<td>6</td>
<td>[P_{66614}][OH]</td>
<td>Glutaroidimidedioxime</td>
<td>UO₂(OAc)₂.6H₂O</td>
<td>2:1:1</td>
<td>Semi solid</td>
</tr>
<tr>
<td>7</td>
<td>[P_{66614}][OH]</td>
<td>1,3-bishydroxyiminoisoindoline</td>
<td>UO₂(NO₃)₂.6H₂O</td>
<td>2:1:1</td>
<td>Phthalimide Crystals</td>
</tr>
<tr>
<td>8</td>
<td>[P_{66614}][OH]</td>
<td>1,3-bishydroxyiminoisoindoline</td>
<td>UO₂(OAc)₂.6H₂O</td>
<td>2:1:1</td>
<td>Semi solid</td>
</tr>
</tbody>
</table>

Crystals of phthalimide were obtained by reacting 1,3-bishydroxyiminoisoindoline and uranyl nitrate in 1:1 ratio in the presence 2 equivalent of [P_{66614}][OH] (Table 2 entry 7). During the
reaction, hydrolysis of amidoxime ligand occurred due to the presence of aqueous $[\text{P}_{66614}]\text{[OH]}$ as a strong base which is called Beckmann reaction (Scheme 11).

![Reaction](image)  
**Scheme 11.** Beckmann rearrangement of 1,3-bishydroxyiminoisoindoline

Tetraethylammonium and tetrapropylammonium hydroxides ($[[\text{N}_{2222}]\text{[OH]}, [\text{N}_{3333}]\text{[OH]}]$): The ligands were mixed with $[\text{N}_{3333}]\text{[OH]}$ (40% solution in water) at 80 °C for one hour. Further, the reaction mixture were used for the complexation with vanadyl and uranyl salts at 60 °C for two days (Table 3).

<table>
<thead>
<tr>
<th>Exp no.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Ratio (A:B:C)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$[\text{N}_{2222}]\text{[OH]}$</td>
<td>1,4-diamidoximyl-benzene</td>
<td>$\text{UO}_2(\text{SO}_4)_2$. 3H$_2$O</td>
<td>2:1:1</td>
<td>Crystals of tetraethylammonium hydrogen carbonate</td>
</tr>
<tr>
<td>2</td>
<td>$[\text{N}_{3333}]\text{[OH]}$</td>
<td>Glutaroimide-dioxime</td>
<td>$\text{UO}_2(\text{SO}_4)_2$. 3H$_2$O</td>
<td>2:1:1</td>
<td>Semi solid</td>
</tr>
<tr>
<td>3</td>
<td>$[\text{N}_{3333}]\text{[OH]}$</td>
<td>1,4-diamidoximyl-benzene</td>
<td>$\text{UO}_2(\text{SO}_4)_2$. 3H$_2$O</td>
<td>2:1:1</td>
<td>Crystals of tetrapropylammonium bicarbonate</td>
</tr>
<tr>
<td>4</td>
<td>$[\text{N}_{3333}]\text{[OH]}$</td>
<td>1,3-diamidoximylbenzene</td>
<td>$\text{UO}_2(\text{SO}_4)_2$. 3H$_2$O</td>
<td>2:1:1</td>
<td>Crystals</td>
</tr>
<tr>
<td>5</td>
<td>$[\text{N}_{3333}]\text{[OH]}$</td>
<td>1,3-bishydroxyiminoisoindoline</td>
<td>$\text{UO}_2\text{Cl}_2$</td>
<td>4:2:1</td>
<td>Semi solid</td>
</tr>
<tr>
<td>6</td>
<td>$[\text{N}_{3333}]\text{[OH]}$</td>
<td>4,5-diamidoximylimidazole</td>
<td>$\text{UO}_2(\text{OAc})_2$. 6H$_2$O</td>
<td>2:1:1</td>
<td>Crystals of 4,5-diamidoximylimidazole</td>
</tr>
<tr>
<td>7</td>
<td>$[\text{N}_{3333}]\text{[OH]}$</td>
<td>1,4-diamidoximyl-benzene</td>
<td>$\text{UO}_2(\text{SO}_4)_2$. 3H$_2$O</td>
<td>4:2:1</td>
<td>Semi solid</td>
</tr>
<tr>
<td>8</td>
<td>$[\text{N}_{3333}]\text{[OH]}$</td>
<td>1,3-diamidoximylbenzene</td>
<td>$\text{UO}_2(\text{SO}_4)_2$. 3H$_2$O</td>
<td>2:1:1</td>
<td>Crystals</td>
</tr>
<tr>
<td>9</td>
<td>$[\text{N}_{3333}]\text{[OH]}$</td>
<td>1,3-bishydroxyiminoisoindoline</td>
<td>$\text{UO}_2\text{Cl}_2$</td>
<td>4:2:1</td>
<td>Semi solid</td>
</tr>
</tbody>
</table>

A new crystal of $[\text{N}_{2222}]\text{[HCO}_3]\cdot 3\text{H}_2\text{O}$ was obtained from the reaction of 1:1:2 ratio of $\text{UO}_2(\text{SO}_4)_2$. 1,4-diamidoximylbenzene:$[\text{N}_{2222}]\text{[OH]}$ at 80 °C for 12 h (Figure 15, Table 3 entry 1). The assigned space group is $P2_1/n$ containing five molecules in the asymmetric unit which could be an example of high Z’ structure. The hydrogen carbonate anion was trapped from the atmosphere in the crystal structure. The water molecules are arranged in a rare “six-membered ring” (Hexagon shape) by connecting through O-H···O hydrogen bonds. The cations and anions
are arranged in layered structures. The hydrogen carbonate and water molecules are connected in the same layer through O-H···O hydrogen bonds.

**Figure 15.** ORTEP diagram of [N$_{2222}$][HCO$_3$]·3H$_2$O salt (left) and the arrangement of water molecules in a rare “six-membered ring” (Hexagon shape) by connecting through O-H···O hydrogen bonds (right).

A new salt of [N$_{3333}$][1,4-diamidoximylbenzene]·H$_2$CO$_3$ obtained from the reaction of 1:1:2 ratio of UO$_2$(SO$_4$)$_2$:1,4-diamidoximylbenzene:[N$_{3333}$][OH] at 80 °C for 12 h (**Figure 16, Table 3 entry 4**). In the asymmetric unit, one [N$_{3333}$]$^+$ cation, half [1,4-diamidoimylbenzene]$^-$ anion and one disordered carbonic acid are present. The carbonic acid was trapped in the structure from the reaction of water and atmospheric carbon dioxide. The anion is alternately connected with carbonic acid through strong O-H···O hydrogen bond and formed one dimensional chains. Further, these chains are connected with cations and through weak C-H···O hydrogen bond.

**Figure 16.** ORTEP diagram of [N$_{3333}$][1,4-diamidoximylbenzene]·H$_2$CO$_3$ salt

A new complex crystal structure holding three molecules of [N$_{3333}$]$^+$ cation and six molecules of bicarbonate as anion in the asymmetric unit ($Z'= 9$) was also obtained (**Figure 17, Table 3 entry 6**). The crystals were obtained from the reaction of 1:1:2 ratio of UO$_2$(SO$_4$)$_2$:1,3-diamidoximylbenzene:[N$_{3333}$][OH] at 80 °C for 12 h. The assigned space group is $P2_1/c$. This
structure is an example of rare high $Z'$ structure. Six molecules of carbonic acid arrange in three pairs and each pair share a common H atom. In the crystal structure, the anion and cation are arranged in separated layers that show the possibility of anion-anion and cation-cation attraction interactions (Figure 17).

![ORTEP diagram of [N3333]$^+$ with bicarbonate (left) and layer packing of anion and cation along c-axis (right).](image)

**Figure 17.** ORTEP diagram of [N3333]$^+$ with bicarbonate (left) and layer packing of anion and cation along c-axis (right).

The carbonic acid was trapped from the atmosphere. The cations are connected with carbonates through weak C-H···O hydrogen bond. The cations make 3-dimensional cage-type structure and traps the carbonates inside the cages (Figure 18).

![Three-dimensional cage-type structure along b-axis.](image)

**Figure 18.** Three-dimensional cage-type structure along b-axis.

Another interesting crystal structure, [N3333]$^2^+$(CO$_3$)$_2^-$·2H$_2$CO$_3$·5H$_2$O, contains 10 molecules in the asymmetric unit (Figure 19). The assigned space group is P2$_1$/c. Again, this structure is an
example of high $Z'$ structure ($Z' = 10$) similar to previous structure. Two molecules of carbonic acid (H$_2$CO$_3$) show positional disorder of the hydrogen atoms. This structure was obtained from the reaction of 1:1:2 ratio of UO$_2$(SO$_4$)$_2$:1,4-diamidoximylbenzene:[N$_{3333}$][OH] (Table 3 entry 4) at 80 °C for 12 h.

The carbonate and carbonic acids trapped inside the structure are from the atmosphere. The water molecules are arranged in a “six-membered ring” (in hexagon shape) connected through O-H···O hydrogen bonds (Figure 20, left). Four-membered ring formed by water molecules is well known but the six-membered ring is still rare. The cations and anions are arranged in layered structures (Figure 20, right). Carbonic acids and water molecules are connected with the anions in the same layer through O-H···O hydrogen bonds.
Other results:

a. *Readily preparation of crystalline N-donor actinide coordination complexes:* We have developed a unique strategy (Scheme 12) to readily prepare crystalline N-donor actinide coordination complexes from readily available hydrated actinide salts by first dehydrating them with an ionic liquid containing a common anion and then reacting the anhydrous complexes with N-heterocyclic ligands. The strategy takes advantage of ILs that provide redox-inert, anhydrous environments for compounds which cannot normally be dissolved in organic solvents.

\[
\text{Th(NO}_3\text{)}_4\cdot 4\text{H}_2\text{O} \quad \rightarrow \quad \begin{cases} [\text{C}_2\text{mim}]\text{[NO}_3\text{]} \\
\text{w/ or w/o Solvents} \\
\text{-H}_2\text{O} \\
\text{[C}_2\text{mim]}\text{[Th(NO}_3\text{)]}_2 \\
\text{N-donor} \\
\text{Ligands} \\
\text{Actinide N-donor} \\
\text{Coordinated} \\
\text{Complexes}
\end{cases}
\]

*Scheme 12.* A unique strategy to prepare crystalline N-donor actinide coordination complexes.

b. *Developed a quick and easy synthetic methodology to form lanthanide complexes with dialkylimidazolium acetate ILs.* 1-ethyl-3-methylimidazolium and 1,3-diethyl imidazolium acetate-lanthanides anhydrous monomers and dimers were synthesized (Scheme 13) and structurally characterized by SCXRD (Figure 21) and PXRD. The monomers are 10 coordinate isostructural and have similarity to uranyl structures if considered that one acetate is replacing one uranyl oxygen atom. All dimers whether C2C1 or C2C2 are isostructural and are 9 coordinate and we found that they are less stable than the monomers.

\[
\text{LnCl}_3\cdot 6\text{H}_2\text{O} \quad + \quad [\text{C}_2\text{C}_1\text{im}][\text{OAc}] \\
\text{1eq} \quad \text{5eq} \\
\text{neat} \quad \text{24h, 100°C} \\
[\text{C}_2\text{C}_1\text{im}][\text{Ln}_2(\text{OAc})_7] + [\text{C}_2\text{C}_1\text{im}][\text{Ln}_2(\text{OAc})_8]
\]

*Scheme 13.* Representative reaction of dialkylimidazolium acetates ILs and lanthanides.

\[
[\text{C}_2\text{C}_2\text{im}]_2[\text{La(OAc)}_5] \\
[\text{C}_2\text{C}_1\text{im}]_2[\text{Er}_2(\text{OAc})_8]
\]

*Figure 21.* ORTEP structures of 1-ethyl-3-methylimidazolium (right) and 1,3-diethyl imidazolium (left) acetate-lanthanides complexes.
Objective 2: Spectroscopically characterize these metal complexes in order to identify spectral features which can be used to identify the actual adsorbed species on metal-loaded sorbents.

Executive Summary

- FT-IR spectra were collected for the complexes synthesized above and IR spectra showed a pronounced shift of the uranyl U=O asymmetric stretch in the amidoxime-uranyl complexes as compared to uranyl salts.
- Complexation reactions of Fe^{2+} and Ni^{2+} metal ions were conducted with four amidoxime ligands in H_{2}O and CH_{3}OH at different stoichiometric ratios such as 1:1, 1:2, and 2:1. These complexation reactions resulted in precipitation.
- The products of complexation reaction of Fe/Ni amidoxime complexes were characterized by XAFS.

Details:

Spectroscopy is often used to understand the solution chemistry of metal complexes or sometime provides information beyond what can be measured by SCXRD. Attenuated total reflectance (ATR) FTIR spectroscopy is quick and readily available method to determine specific binding modes present in the metal-complexes. The technique is especially useful to characterize UO_{2}^{2+} complexes because they have strong, characteristic and environment sensitive absorption peaks which have low interference from other functional groups. The complete library of spectroscopic signature depicting different binding modes of UO_{2}^{2+} and other seawater metal-ions would provide insight on the selectivity of amidoxime groups in seawater environment. Therefore, we have been collecting FT-IR data for all obtained crystal structures. Here, the collected data is exemplified with spectrum collected for 1,4-DAOBz uranyl acetate complex and uranyl acetate salt. The data was collected using ATR-FTIR Alpha spectrometer in the wavelength range from 400-4000 cm\(^{-1}\). As shown on Figure 22, characteristic asymmetric stretch of uranyl (U=O) in uranyl acetate dihydrate is seen at 932 cm\(^{-1}\). While in the 1,4-DAOBz uranyl acetate complex the characteristic U=O stretch is redshifted to 908 cm\(^{-1}\) due to replacement of water molecules with anionic amidoximate ligands as stronger electron-donor.

**Figure 22.** FTIR spectra of uranyl acetate (red) with 1,4-DAOBz Uranyl acetate complex (black).
X-ray absorption fine structure (XAFS) spectroscopy has been used to identify specific metal species in metal-complex including [UO₂]²⁺ ions adsorbed onto surfaces, and are well suited to the characterization of metal-loaded sorbents.¹⁹ XAFS provides the information of geometry of coordination modes of the liquid or amorphous samples of metal complexes. The study with XAFS on amidoxime-metal complexes would help us in species identification on the seawater-loaded adsorbents. The technique, however, requires modeling the spectra, which is susceptible to misinterpretation particularly when contributions from multiple species are present. XAFS on well-characterized crystalline samples, on the other hand, is a straightforward technique which is offered as user service at several DOE national lab synchrotron beam lines.

The initial XAFS data (Figure 23) unfortunately was not of good quality and publishable. Truncating the energy and k-space plots resulted in data loss. The truncated data in R-space might be fittable, but will be real challenging to get any real information from and a crystal model will likely need to be imposed on the data. We could not get more beamline access for further characterization. For publication purposes, we will continue to discuss potential publishable measurements to be done at one of the synchrotron beamline DOE lab.

![Figure 23. Initial XAFS results.](image)

We have also conducted complexation reactions of Fe⁺² and Ni⁺² salts with amidoxime ligands (Scheme 14) in H₂O and CH₃OH at different stoichiometric ratios such as 1:1, 1:2, and 2:1. All these complexation reactions formed precipitates. The XAFS study of these complexes was unfortunately unsuccessful.
Scheme 14: Types of ligands chosen for complexation reaction with Fe$^{+2}$ and Ni$^{+2}$.

**Objective 3:** Use hydroxylammonium based stripping agents to remove metals from loaded amidoxime sorbents and determine if elution is correlated with the affinity of the metal ion for hydroxylamine.

**Executive summary**

- Stripping sorbent performance was tested by measuring uranium removal and sorbent capacity on re-use using traditional hydrochloric acid (HCl), acetic acid (HOAc) and novel hydroxylammonium acetate [NH$_3$OH][OAc] as stripping agents.
  - The effect of variation of the hydroxylammonium [NH$_3$OH] counter-ion on stripping performance was examined.
  - Synthetic sorbents loaded with metals from seawater (obtained from Pacific Northwest National Laboratory (PNNL)) were stripped with solutions of HCl, HOAc, or [NH$_3$OH][OAc].
  - Stripped sorbents were re-exposed to enriched simulated seawater solutions (10 ppm U) to test capacity loss on re-use.
  - Recovery of uranium through bio-mimetic mineralization using shrimp shell was tested as a chemically-nonintensive back extraction.
- Using the optimized conditions from the previous study, another buffer solution of [NH$_3$OH][OAc]/phosphoric acid was investigated to study the absorption of uranium in the presence/absence of shrimp shells, however, no absorption was observed throughout the study.

**Details:**

1. **Uranium stripping using hydroxylammonium acetate:**

   The loss of sorbent capacity during multiple U-extracting cycles is a major challenge in sorbent efficiency that ultimately increases the cost of extraction. The co-adsorbed vanadium and other metal ions that prone to resist stripping even by strong acids are the cause for capacity loss in large. We identified hydroxylammonium acetate ([NH$_3$OH][OAc]) as a possible weakly acidic stripping agent which might promote the removal of U and V by taking advantage of their high affinity for oximes. [NH$_3$OH][OAc]/aqueous acetic acid (AcOH) solution was shown to effectively strip
uranium from synthetic amidoxime resins without capacity loss (in enriched simulated seawater) and remove vanadium (Figure 24). The acetic acid in the system was also found to play an important role which is still not known. These findings were published in *Ind. Eng. Chem. Res.*

Figure 24. Results on metal striping by \([\text{NH}_3\text{OH}][\text{OAc}]\) with and without acetic acid.

2. **Uranium stripping using hydroxylammonium acetate, ([NH₃OH][OAc]) in phosphoric acid:**

A new method or material with the ability to reuse the sorbent without pretreatment and with negligible loss combined with a chemically non-intensive method for uranium recovery could be considered as a sustainable technology for uranium extraction from seawater. Our group have developed a new stripping and recovery process to harvest the uranium recovered from seawater with amidoxime-functionalized polyethylene fiber sorbents as well as allow us to reuse the sorbent without loss of capacity without any recondition before reuse. By using phosphoric acid, we expected to decrease the stripping time needed to remove all metal ions from the sorbent due to higher acidity of phosphoric acid.

We investigated the stripping chemistry for uranium with hydroxylammonium acetate with and without phosphoric acid followed by our previous work. The motivation behind this experiment was to decrease the stripping time required to remove the metal ions from the sorbent in the presence of higher acidity of phosphoric acid as compare to acetic acid. A 100 mL stock solution of phosphoric acid in water was made by adding 26 wt% P₂O₅ in deionized water. This solution was used to make a 0.4 M solution of hydroxylammonium acetate (HA) solution. Both the phosphoric acid stock solution and 0.4 M HA solution were spiked with \(^{233}\text{U}\) tracer. A 3ml solution of both stock phosphoric acid solution and 0.4 M HA solution were removed in the aliquots containing 100 mg of shrimp shells (size < 125 microns). The aliquots were equilibrated by shaking. Then the \(^{233}\text{U}\) activity was recorded as a function of time and the results of the CPM counts are shown in Table 4.
Table 4: $^{233}$U activity as a function of time.

<table>
<thead>
<tr>
<th>Counts</th>
<th>Stock Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time</td>
</tr>
<tr>
<td></td>
<td>Phosphoric Acid as control without shrimp shells</td>
</tr>
<tr>
<td></td>
<td>0 hours</td>
</tr>
<tr>
<td></td>
<td>241.3 (5.9)</td>
</tr>
<tr>
<td></td>
<td>223.6 (2.9)</td>
</tr>
<tr>
<td></td>
<td>Phosphoric Acid solution with shrimp shells</td>
</tr>
<tr>
<td></td>
<td>2 hours</td>
</tr>
<tr>
<td></td>
<td>237.4 (4.3)</td>
</tr>
<tr>
<td></td>
<td>217.6 (4.7)</td>
</tr>
<tr>
<td></td>
<td>24 hours</td>
</tr>
<tr>
<td></td>
<td>244.3 (8.8)</td>
</tr>
<tr>
<td></td>
<td>224.3 (5.3)</td>
</tr>
<tr>
<td></td>
<td>7 days</td>
</tr>
<tr>
<td></td>
<td>239.0 (13.5)</td>
</tr>
<tr>
<td></td>
<td>219.9 (4.4)</td>
</tr>
</tbody>
</table>

(Note: All the readings were done in triplicates)

The counts were nearly the same for phosphoric acid stock solution and the phosphoric acid solution with shrimp shells, even after 7 days within the errors of standard deviation (in parentheses). It indicates that the shrimp shells did not adsorb the uranyl ions under these conditions. Same phenomena were observed in the case of 0.4 M hydroxyl ammonium acetate solution in phosphoric acid for both with or without shrimp shells. The reason for this inactivity can be attributed to highly acidic nature of phosphoric acid as compared to acetic acid which was used as eluting solution previously.

Products
1. Publications
2. Presentations
   - J. Zhang, Y. Patil, and R. D. Rogers, “In Search of Ionic Liquids for the Extraction of Hg (II) and Cd (II),” Presented by J. Zhang before the Gordon Research Conference on Ionic


References


17 Manuscript in preparation under the title “New Insight of coordination and extraction of uranium with amidoxime ligands in room temperature ionic liquids: [C2mim][OAc] IL as a case study”.

