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Complexation of High-Valency Mid-Actinides by a Lipophilic Schiff Base Ligand: Synthesis, Structural Characterization, and Progress toward Selective Extraction

Christian G. Bustillos,[†,‡] Cory A. Hawkins,[§] Roy Copping,[‡,∥] Sean D. Reilly,[‡] Brian L. Scott,[‡] Iain May,[‡] and Mikael Nilsson*,[†,⊥]

[†]Department of Chemical and Biomolecular Engineering, University of California—Irvine, Irvine, California 92697-2580, United States

[‡]Science, Technology, and Engineering, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

[§]Department of Chemistry, Tennessee Technological University, Cookeville, Tennessee 38505, United States

[⊥]Department of Chemistry, University of California—Irvine, Irvine, California 92697, United States

Supporting Information

ABSTRACT: Separation of U, Np, and Pu from used nuclear fuel (UNF) would result in lower long-term radiotoxicity, alleviating constraints on the storage and handling of the material. The complexity of UNF requires several industrial-scale processes with multiple waste streams. A one-step solution to the group removal of the elements, U−Pu, is desirable. Here we present a possible solution to group actinide separation utilizing the unique dioxy conformation of An(V/VI) cations and demonstrate the ability of a tetradentate lipophilic Schiff base ligand (L) to yield isostructural complexes of the general formula $[(An^{VI}O_2)(L)(CH_3CN)]$ (where An = U, Np, or Pu). Extraction of An(VI) with the ligand follows the order U > Pu > Np, likely reflecting the decreased stability of the hexavalent actinide across the series. While the results indicate a promising path toward a one-step process, further improvement in the ligand stability and control of the redox chemistry is required.

The successful removal of long-lived radiotoxic elements from nuclear waste is instrumental in driving support toward a closed nuclear fuel cycle.[1] Constraints on the final waste repository stem from the radiotoxicity and heat load of long-lived actinides. Numerous separation processes for removal of these elements, U, Np, and Pu, have been developed and proposed, but the cost of implementing a series of large-scale processes has hindered their implementation.[2,3] In addition, traditional separation processes may provide purified Pu as a product, causing concern regarding the proliferation of sensitive nuclear material.[4] Further exploration of the coordination chemistry of the mid-actinide elements (U−Pu) can present the means to a one-step solution to the complete separation of these elements from high-level waste.[5,6] In this context, enhanced exploitation of actinide−ligand interactions under nonaqueous conditions is important for the development of biphasic organic−aqueous actinide separation systems, while group extraction of the mid-actinides can also yield enhanced proliferation resistance.[5−8] A feature ubiquitous to the mid-actinides (U, Np, and Pu) is the possession of a wide range of accessible oxidation states (+III, +IV, +V and +VI), with the linear dioxoactinyl cation moiety (AnO_2^{n+}) dominating the chemistry of the +V and +VI oxidation states.[9−11] A multitude of ligand systems have been employed as extractants for biphasic solvent extraction including, but not limited to, organophosphorous compounds,[12,13] crown ethers,[14] diglycolamides,[15−17] bipyridines,[18,19] and Schiff base ligands.[20−22] Specifically, multidentate Schiff base ligands provide a framework that can be easily functionalized, possess multiple coordination sites, and can accommodate the steric demands of the linear dioxo moiety. It has been demonstrated that Schiff base ligands can extract UO_2^{2+} in liquid−liquid extraction experiments,[21,22] as well as stabilize UO_2^{+}.[23−25] In this context, we have previously reported on an aqueous soluble Schiff base that selectively coordinates UO_2^{2+} and NpO_2^{+} in an aqueous phase, yielding separation from a range of trivalent f-element cations.[26,27] We report here synthetic, spectroscopic, crystallographic, and metal-ion-partitioning studies involving a tetradentate, lipophilic Schiff base, *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamine (*t*Bu-Salen; Figure 1), and the hexavalent mid-actinides (UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}).

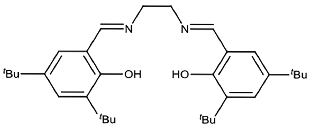

Figure 1. Structure of *t*Bu-Salen.

Crystals of the complexes formed between *t*Bu-Salen and UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} in CH_3CN were analyzed by single-crystal X-ray crystallography, revealing isostructural complexes (Figure 2 shows the *t*Bu-Salen-Pu complex as an example). While the UO_2^{2+} cation is stable under common conditions, hexavalent Np and Pu were prepared utilizing ozone as an oxidant prior to coordination of the Schiff base.[9,28] The linear

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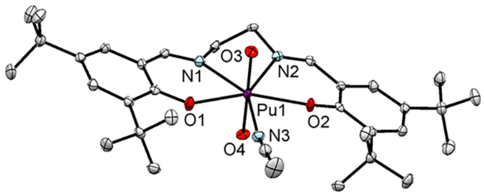

Figure 2. Structural representation of (PuO_2)(*t*Bu-Salen)(CH_3CN) with 50% probability ellipsoids. All H atoms have been removed for clarity. Color code: C, gray; N, blue; O, red; Pu, purple. Space group $P2_1/c$, $a = 16.5781(17)$ Å, $b = 7.7308(8)$ Å, $c = 27.058(3)$ Å, $\alpha = 90.00°$, $\beta = 93.0523(16)°$, $\gamma = 90.00°$, $V = 3462.89(60)$ Å^3.

dioxoactinyl moieties are coordinated by the two imine N atoms and two deprotonated phenolic O atoms of the ligand with a CH_3CN molecule at the fifth coordination position in a distorted pentagonal-bipyramidal geometry, a common geometric arrangement for seven-coordinate actinyl complexes.[29−31]

Selected bond distances and angles are listed in Table S1. The An−O_{yl} bond distances of the linear actinyl moiety are typical and in the range of other structurally characterized actinyl(VI) cations.[29,32,33] The bond distances and angles around the equatorial plane of U^{VI} and Np^{VI} are similar to those in other structurally characterized tetradentate Salen-actinyl(VI) structures.[34,35] An interesting trend is the apparent decrease in the An−O(phenolic) bond length upon going from the U^{VI} to Np^{VI} complex, followed by an increase in this bond length in the Pu^{VI} complex. While uncertainties in the bond lengths suggest that these differences may be minor, such a trend has been observed previously for isostructural U^{VI}, Np^{VI}, and Pu^{VI} complexes, specifically the An−Cl and An−O bond lengths observed in actinide(VI) chloride, dipicolinate, and proprionate complexes.[36−39] There would also appear to be a slight decrease in the average bond length between the central actinyl moiety and the imine N atoms upon going across the mid-actinide series. Again, it is important to consider the uncertainties associated with the data, especially for the Pu complex, and we caution against over interpretation.

A significant decrease is observed in the bond angle between the central actinyl moiety and two deprotonated phenolic O atoms (O1−An1−O2) upon moving across the mid-actinide series. In addition, there is an overall increase in the imine−actinyl−oxygen (O−An−N) bond angle across the U, Np, and Pu series. These trends in the bond angles suggest that the actinyl(VI) cation is located deeper in the N_2O_2 bonding site of the Schiff base as the U/Np/Pu isostructural series is traversed. The bond lengths between the actinide center and CH_3CN molecule occupying the fifth equatorial position are similar for the three complexes and longer than the An−O bond lengths of bound water molecules [2.447(9) Å[40]] and methanol molecules [2.4415(14) Å[35]] in other An^{VI} structures.

Overall, the solid-state structural data provided clear evidence for near-identical coordination environments for the three actinyl(VI) cations upon coordination with *t*Bu-Salen. Our working hypothesis was that similar complexation behavior would be observed in solution and, assuming redox stability, similar extraction behavior in a two-phase system.

Solution-state absorption spectra related to actinyl(VI) cation complexation by *t*Bu-Salen are presented in Figures 3 and S3. The absorption bands for the ligand are observed around 330 nm, arising from $\pi \rightarrow \pi^*$ transitions in the aromatic ring and azomethine,[41] with a lower-energy absorption band at 342 nm possibly attributed to $n \rightarrow \pi^*$ transitions in the azomethine group.[42] An appreciable amount of red shift is observed upon complexation of UO_2^{2+} by *t*Bu-Salen. Absorption bands that appear at 342, 420, and 500 nm most likely result from ligand−metal charge-transfer transitions, while the Laporte forbidden f−f transitions of the uranyl moiety itself is likely masked by these high-intensity bands.[43,44]

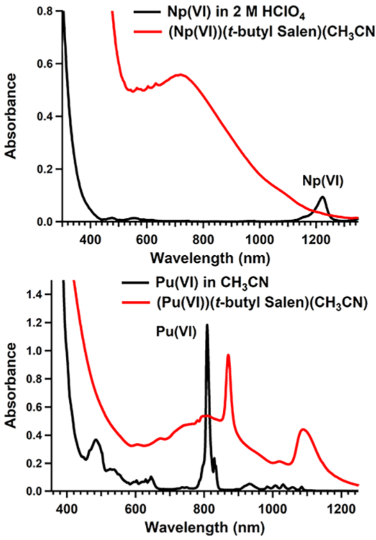

Figure 3. UV−vis−near-IR spectra of *t*Bu-Salen complexes formed with Np^{VI} (top) and Pu^{VI} (bottom).

In mineral acids, the absorption spectrum of NpO_2^{2+} is primarily characterized by a band at 1223 nm, attributed to an intra-5f transition, two bands at 460 and 560 nm, and a charge-transfer transition at higher energy (<400 nm).[45,46] Upon complexation by the ligand, the spectrum is characterized by an intense charge-transfer transition (200−1300 nm) with several bands in the 540−650 nm range. Characteristically, the aquo Np^{VI} band at 1223 nm will likely undergo a hypsochromic shift to 1120−1140 nm upon complexation.[47−49] This band may be obscured by the intense charge-transfer feature. In addition, a band at 1000 nm has been observed for the main f−f transition in Schiff-base-complexed Np^V.[31,27] Although it is possible that a transition at 1000 nm may be obscured by the charge-transfer band, a sharp band would likely be observed if there had been a significant reduction of Np^{VI} to Np^V. In contrast, we have shown that an aqueous soluble Schiff-base ligand will complex NpO_2^{2+} but rapidly reduce it to NpO_2^{+}.[27] Returning to the *t*Bu-Salen-Np^{VI} system in CH_3CN, we observe vibrational progression bands between 540 and 650 nm. Such transitions are observed in this region for other Np^{VI} complexes, e.g., $[NpO_2(CO_3)_3]^{4-}$[50] and NpO_2Cl_2 in THF.[51]

The major f−f transition ($^3H_{4g}$ to $^3\Pi_{2g}$) for the PuO_2^{2+} cation in 1 M $HClO_4$ is observed at 830 nm.[52] Low-energy transitions are also observed at 950 and 980 nm along with higher-energy transitions at 460, 520, and 622 nm. The absorption spectrum for PuO_2^{2+} in CH_3CN exhibits a transition at 805 nm with a slight shoulder at 830 nm and multiple transitions in the 400−650 and 900−1100 nm ranges. The absorption spectrum bears a strong resemblance to that of Pu^{VI} in 15.2 M HNO_3, which could be attributed to the use of nitric acid during the preparation of Pu^{VI}.[40] Upon the addition of *t*Bu-Salen to the Pu^{VI} solution, there is a decrease in absorption and a shift to 870 nm of the major near-IR transition. A shift to a longer wavelength by the principal f−f transition would imply coordination of the actinyl cation about the equatorial plane. The red shift is consistent with previously characterized Pu^{VI} structures,[30,53,54] including a plutonyl(VI) chloride complex (also analyzed in CH_3CN) showing a prominent band at 850 nm.[30]

Solvent-extraction experiments were carried out with the ligand (0.025 M) dissolved in a mixture of 7:3 1-octanol/toluene and contacted with an aqueous solution containing the actinyl cation U^{VI} and a non-actinyl lanthanide cation, Dy^{III}, for varying time periods (Figure S8). Distribution ratios revealed negligible extraction of Dy^{III} and increased U^{VI} extraction as a function of time, with the extraction of U^{VI} almost 5 times the order of magnitude of Dy^{III} at 120 min. Additional extraction studies were carried out where the 0.025 M ligand in 7:3 1-octanol/toluene was contacted with aqueous solutions of U^{VI}, Np^{VI}, or Pu^{VI}, each metal ion in separate experiments, for varying periods of time (Figure 4).

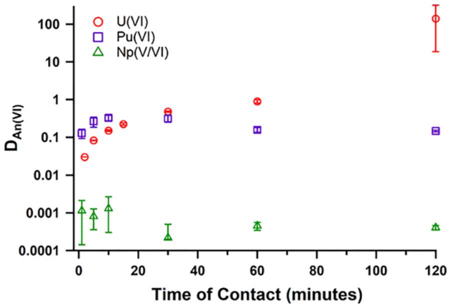

Figure 4. Distribution ratios as a function of time for U^{VI} (1×10^{-3} M), $Np^{V/VI}$ (1×10^{-4} M), and Pu^{VI} (1×10^{-7} M) at 0.1 M KNO_3 and pH_i = 3.00.

Care was taken to introduce Np and Pu into the extraction experiment in the hexavalent oxidation state (see the Supporting Information). As previously observed, the extraction of U^{VI} increases with increasing contact time, with a sharp increase in the distribution ratio at a contact time of 2 h. Pu extraction was marked by a significant decrease in the distribution ratios after 10 min. This behavior can be attributed to the partial reduction of Pu^{VI} to Pu^{V}, where the lower charge density of the pentavalent cation would decrease the extractability of Pu.[55] Perhaps more consequentially, the ligand would most likely not extract pentavalent actinides into an organic solvent because the extractable neutral complex could only be formed by the exchange of one of the phenolic H atoms, and this would be a much less stable complex. By extension to this argument, low D_{Np} values suggest that there is a significant reduction of Np^{VI} to Np^{V} because Np^{VI} should exhibit similar extraction behavior for U^{VI} and Pu^{VI}. Although *t*Bu-Salen stabilized Np^{VI} in a single solvent (CH_3CN), the same redox stability of the ligand−actinyl clearly may not be translated in a biphasic solvent system. The reduction of Np^{VI}, and to a lesser extent Pu^{VI}, could be attributed to hydrolysis of the ligand or, if Np^{V} is produced in the biphasic system, cation−cation interactions.[56] Hydrolysis, or partial hydrolysis, of the ligand results in the formation of ethylenediamine and/or a mono Schiff base with a free amine. Such amine-containing compounds could act as reductants and aqueous holdback reagents for both Np^{VI} and Pu^{VI}.

In summary, isostructural U^{VI}, Np^{VI}, and Pu^{VI} complexes with a tetradentate Schiff base (*t*Bu-Salen) ligand were synthesized and structurally characterized. In CH_3CN, the ligand was successful in complexing and stabilizing the VI+ oxidation state of Np and Pu. An additional promising feature was the selective extraction of U^{VI} in the presence of inextractable Dy^{III} in a solvent-extraction process containing organic-phase *t*Bu-Salen. However, although U^{VI} and, to a certain extent, Pu^{VI} were successfully extracted, no extraction of Np^{VI} was observed. This decrease in extraction can most likely be attributed to partial ligand decomposition and reduction of the transuranic cations to less extractable species. These results point to the importance of combining coordination and solvent extraction chemistry when developing new selective extractants for redox-sensitive actinide elements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02849.

> Experimental details for the preparation of actinyl(VI)-*tert*-butyl-Salen complexes, crystals, NMR, IR, and Raman spectroscopy, and solvent extraction (PDF)

Accession Codes

CCDC 1870518−1870520 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nilssonm@uci.edu. Phone: +1-949-824-2800. Fax: +1-949-824-2571.

ORCID

Mikael Nilsson: 0000-0003-1475-0331

Present Address

‖R.C.: Nuclear and Radiochemistry Group, Oak Ridge National Laboratory, Oak Ridge, TN 37830.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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