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Water-soluble Schiff base-actinyl complexes and their effect on the solvent extraction of f-elements

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Journal

Dalton Transactions, 45(39)

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Publication Date

2016-09-07

Data Availability

The data associated with this publication are available upon request.

Peer reviewed

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Paper**Water-soluble Schiff base-actinyl ion complexes and their effect on the solvent extraction of *f*-elements**Cory A. Hawkins,^{*a,b} Christian G. Bustillos,^{a,c} Iain May,^c Roy Copping,^{c,d} and Mikael Nilsson^a*Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX*

5 DOI: 10.1039/b000000x

Conventional solvent extraction of selected *f*-element cations by *bis*(2-ethylhexyl)phosphoric acid (HDEHP) yields increased extraction from aqueous to organic solution along the series Np(V) < Cm(III) < Eu(III) < U(VI), with distribution ratios all within two orders of magnitude. However, in the presence of the water-soluble tetradentate Schiff base (*N,N'*-bis(5-sulfonatosalicylidene)-ethylenediamine or H₂salenSO₃), selective complexation of the two actinyl cations (Np(V) and U(VI)) resulted in an extraction order of Np(V) < U(VI) << Eu(III) < Cm(III). The extraction of neither Cm(III) or Eu(III) by HDEHP are significantly impacted by the presence of the aqueous phase Schiff base. Despite observed hydrolytic decomposition of H₂salenSO₃ in aqueous solutions, the calculated high conditional stability constant ($\beta_{11} = 26$) for the complex [UO₂(salenSO₃)]²⁻ demonstrates its capacity for aqueous hold-back of U(VI). UV-visible-NIR spectroscopy of solutions prepared with a Np(VI) stock and H₂salenSO₃ suggest that reduction of Np(VI) to Np(V) by the ligand was rapid, resulting in a pentavalent Np complex that was substantially retained in the aqueous phase. Results from ¹H NMR of aqueous solutions of H₂salenSO₃ with U(VI) and La(III), Eu(III), and Lu(III) provides additional evidence that the ligand readily chelates U(VI), but has only weak interactions with trivalent lanthanide ions.

20

Introduction

Used nuclear fuel (UNF) and high-level radioactive waste (HLW) present significant waste management challenges, with permanent geological repositories being the leading candidate for safe long term disposal. In this context a recent US Department of Energy (DOE) report highlighted the need for continued research on advanced fuel cycles in the context of future energy demands, while concomitantly supporting non-proliferation and waste management objectives.¹ The development of novel actinide/lanthanide chemical separation processes will likely remain a fruitful area of scientific discovery in the context of the development of such fuel cycles as the separation of these two groups of elements pose a significant challenge.

There has been extensive research into the application of organophosphorus reagents for complexation and extraction of actinides and lanthanides.² The development of the TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorus Reagent Extraction from Aqueous Complexes) based processes is most relevant to the research we report here. In a typical process trivalent lanthanide cations are selectively extracted into an organic phase containing HDEHP (bis(2-ethylhexyl)phosphoric acid, with trivalent actinides being held back in the aqueous phase through selective complexation by aminopolyacetic acids.³⁻⁵

Taking inspiration from the TALSPEAK process, we have investigated an alternative approach to extraction selectivity among the *f*-elements that takes advantage of the higher valence states unique to several early actinide elements. U, Np, Pu, and Am have access to pentavalent and hexavalent states where they exist as linear dioxo-cations in aqueous solution (*i.e.*, actinyl ions).^{6,7} The unique geometric constraints imposed by the actinyl oxygens is absent from the trivalent lanthanide and trivalent actinide cations, the dominant oxidation state for the majority of the *f*-elements. Our proposed goal was to design a solvent extraction system in which one phase contains a ligand selective for trivalent *f*-elements and the other phase contains a ligand selective for actinyl(VI/V) cations, thus facilitating significant changes to conventional *f*-element separation chemistry.

For actinyl cation complexation we sought to exploit selective coordination by Schiff base ligands. Considering their flexible chemistry, ease of synthesis, and known complexation of hexavalent uranium, Schiff bases have received considerable attention. Proposed application of this coordination chemistry have included catalysis, host-guest chemistry, and utilization in chemical sensors.⁸⁻¹⁰ The ability of multidentate Schiff base ligands to accommodate the steric demands of the linear dioxo UO_2^{2+} moiety has, not surprisingly, led to interest in their application as organic phase extractants for this cation.¹¹⁻¹⁴ Numerous studies have reported that Schiff base chelation can stabilize pentavalent uranium,¹⁵⁻¹⁸ while additional publications have described coordination compounds with Np(V/VI) .^{19,20} In light of these reports, we have been investigating water-soluble salen-derived ligands for the selective complexation and separation of An(V/VI) -cations from other *f*-elements. Preliminary results related to Eu(III) and U(VI) extraction by *bis*(2-ethylhexyl)phosphoric acid (HDEHP) suggest that a significant increase in Ln(III)/An(VI) selectivity could be achieved by addition of a water-soluble Schiff base that preferentially binds to U(VI) under appropriate conditions.²¹ The chemistry of the extraction of U(VI) and Eu(III) by HDEHP in toluene is well known, both being readily extractable from mildly acidic aqueous solution.²² In our previous work we showed that the introduction of a water soluble Schiff base ($\text{N,N}'$ -*bis*(5-sulfonatosalicylidene)-ethylenediamine - $\text{H}_2\text{salenSO}_3$) to the aqueous phase led to a reversal in the extraction order of U(VI) and Eu(III) .²¹

In this paper, we report an extended study into the chemistry of disodium $\text{H}_2\text{salenSO}_3$, in the context of actinyl coordination and solvent extraction chemistry. Firstly, our previous report indicated that this Schiff base ligand will at least partially decompose in aqueous solution and we have thus investigated the extent of hydrolytic decomposition in order to quantify the stability of the U(VI) complex with this complexant.²¹ Finally, the chemical equilibrium basis for the trends observed in metal ion extraction were studied by various spectroscopic techniques.

Experimental

Caution! Work with the radioactive materials described here should be conducted only in appropriate radiological laboratories while following all necessary controls and regulations.

Materials

All chemicals used in these procedures were ACS certified reagent grade or higher and used without further purification, unless noted

otherwise.

Aqueous solutions were prepared using deionized water obtained with a resistivity of at least $18 \text{ M}\Omega \text{ cm}^{-1}$, using a MilliQ laboratory purification system (Millipore, Bedford, MA), and degassed by sparging with nitrogen gas. For the solution spectroscopy and solvent extraction experiments a $\text{UO}_2(\text{NO}_3)_2$ working stock solution was prepared from a commercial ICP standard solution of depleted (0.2% ^{235}U) uranyl nitrate (1000 ppm, Inorganic Ventures, Christiansburg, VA, USA) or from a depleted $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt (IBI Labs, Inc. Florida, USA) by diluting with deionized or acidified water and adjusting the pH to 4.0 dropwise with a 1 M KOH solution. Ammonium acetate buffer was prepared by combining 0.5 M acetic acid with 0.5 M ammonium acetate in a ratio that resulted in a final pH of 5.5. Further dilutions of this buffer were made using deionized water to obtain the desired strength.

Potassium nitrate was used as the inert-background electrolyte to maintain a constant ionic strength (0.1 M) of solutions. The europium nitrate stock solution was prepared by dissolving the oxide (Michigan Metals & Manufacturing, Inc., West Bloomfield, MI, 99.99%) in concentrated nitric acid and evaporated to dryness in several cycles to ensure complete conversion to the nitrate salt. The final residue was reconstituted to 0.1 M with 1 mM HNO_3 and the concentrations were verified by ion-exchange titration. A $^{152/154}\text{Eu}$ radiotracer was prepared by irradiating this 0.1 M Eu solution at the UC Irvine TRIGA reactor for ten hours at a flux of $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. The ^{237}Np and ^{244}Cm working solutions were prepared by evaporating radiotracer stock solutions in 3 M HNO_3 to dryness and reconstituting in the same volume with 0.1 M KNO_3 in 1 mM HNO_3 . Their concentrations were estimated by liquid scintillation counting (LSC) assuming 100% efficiency for the alpha events. HDEHP bis(2-ethylhexyl)phosphoric acid, 95%, ACROS Organics, Geel, Belgium) was purified using the Cu(II) complexation method.²³ The ^{237}Np and ^{244}Cm stock solutions were not purified prior to use. Upon receipt of the ^{244}Cm radiotracer, the in-growth of ^{240}Pu was not detected by alpha spectroscopy and in-growth since then is expected to be insignificant. On the other hand, the effect of the presence of ^{233}Pa in the ^{237}Np stock was mitigated by allowing the measured samples to reach secular equilibrium and the total count rates were used to calculate distribution ratios, as described by Fig. S1 in the supplemental information. The steady state of the total activity compensated for the presence of ^{233}Pa and the long half-life of the ^{233}U progenitor can be reasonably assumed to have no contribution to the alpha count rate. The synthesis of 5-sulfonato-salicylaldehyde (sodium salt) and N,N' -bis(5-sulfonatosalicylidene)-ethylenediamine ($\text{H}_2\text{salenSO}_3$), Fig. 1 were adapted from previously published procedures.^{24,25}

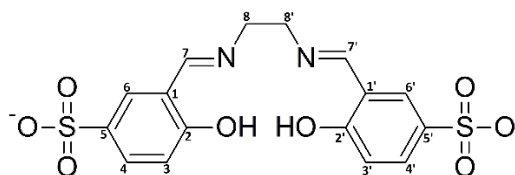


Fig. 1 Structure of N,N' -bis(5-sulfonatosalicylidene)-ethylenediamine ($\text{H}_2\text{salenSO}_3$), synthesized as the disodium salt. The carbon atoms are labelled according to mirror plane symmetry.

Extractions experiments

Extraction studies were conducted using an aqueous phase with and without 0.01 M $\text{H}_2\text{salenSO}_3$ (formal concentration) in 0.1 M KNO_3 with 0.01 M acetic acid (equilibrium $\text{pC}_\text{H} = 5.3$). Spiking of the aqueous phase with U(VI) and Eu(III) followed a previous procedure,²¹ except the $^{152/154}\text{Eu}$ tracer was added without U(VI) present. Preparation of the ^{237}Np and ^{244}Cm tracer solutions was undertaken by evaporating 0.2 mL of stock solutions

containing 0.003 M ^{237}Np and 1×10^{-7} M ^{244}Cm in 4 M HNO_3 to dryness, and then reconstituting with 1.5 mL of 0.001 M HNO_3 in 0.1 M KNO_3 . The resulting working solutions were 4×10^{-4} M Np and 1×10^{-8} M Cm . Finally, 0.1 mL of the working solution was added to 4.9 mL of the aqueous phase with and without the Schiff base. The initial aqueous phase concentrations of UO_2^{2+} , ^{237}Np , $^{152/154}\text{Eu}$, and ^{244}Cm were 1.0×10^{-4} M, 8×10^{-6} M, 5×10^{-5} M (radiotracer + carrier), and 2×10^{-10} M, respectively. Each metal ion was examined in a separate experiment by continuous mixing of the aqueous phase with pre-equilibrated 0.01 M HDEHP in toluene organic phase (1:1 v/v) to generate an emulsion. See the supplemental information[†] for details about the analysis of metal ion phase transfer.

Potentiometry

10 Solution electromotive forces were measured using a semi-micro refillable electrode (Beckman-Coulter, Indianapolis, IN), filled with saturated KCl and calibrated by standard buffer solutions (Fisher Scientific - pH 4, 7, and 10). Where indicated, electrode readings were converted to pC_H (negative logarithm of the formal hydrogen ion concentration) by determining the standard potential and Nernstian slope of the electrode at the ionic strength of interest. The linear conversion was evaluated by titration of a standardized acid with a standardized base.

15 ^1H NMR Spectroscopy

Proton NMR spectra were recorded using a Bruker GN500 (^1H , 500 MHz) spectrometer, equipped with a BBO probe and employed pulse gradient sequences for water solvent suppression.²⁶ Due to the prevalence of water in most of these samples, the exchangeable protons were not observable. The spectral width was maintained at 16 ppm centred at 4.9 ppm, unless otherwise noted.

20 NMR samples were prepared in a manner that resembles the conditions of the aqueous phase in the extraction systems. Samples for Schiff base ^1H NMR titration by U(VI) were prepared by dissolving a known weight of the ligand disodium salt in solutions of $\text{UO}_2(\text{NO}_3)_2$ (0 to 20 mM) with 0.1 M KNO_3 at pH 4 (adjusted using 0.1 M acetic acid to mitigate metal ion hydrolysis). The weight of the ligand and the total solution volume were held constant such that the formal concentration of the ligand was 0.01 M. To 900 μL aliquots of these samples, 100 μL D_2O (99.98%, Cambridge Isotope Labs, Tewksbury, MA, USA) was added and the resultant solutions were allowed to equilibrate for at least one hour prior to acquiring the spectra. Solutions for NMR spectroscopy of the Schiff base in the presence of lanthanide ions were prepared by combining 250 μL of 0.02 M $\text{H}_2\text{salenSO}_3$ (pH = 5.5 to mitigate metal ion hydrolysis,) with 500 μL 0.2 M KNO_3 , an appropriate volume of a 0.1 or 0.01 M $\text{Ln}(\text{NO}_3)_3$ stock, and 100 μL D_2O . Finally, the solutions were brought to volume with DI water such that the final formal concentration of the Schiff base was 5 mM and the range of Eu(III) concentrations were from 0 M to 5 mM. The final pH of solutions was measured by potentiometry.

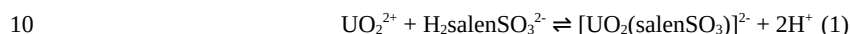
Spectrophotometric titration of U(VI) by $\text{H}_2\text{salenSO}_3$

The deep red colour associated with complexation of U(VI) by Schiff base ligands provides a characteristic ligand-to-metal charge transfer (LMCT) absorbance, which was used to estimate complex stability through variation of ligand concentration at constant pH. Batch titration solutions of $\text{H}_2\text{salenSO}_3$ (0.1 mM to 4.0 mM) with 0.75 mM $\text{UO}_2(\text{NO}_3)_3$ in 0.05 M ammonium acetate buffer pH 5.5 (to avoid pH excursions) with KNO_3 as the inert background electrolyte to maintain ionic strength at 0.1 M, were prepared and mixed periodically for five minutes before adding the $\text{UO}_2(\text{NO}_3)_3$ stock solution. This mixing time was found to be more than adequate to ensure equilibration, as the hydrolysis and complexation reactions occur in a matter of seconds to a few minutes.

Absorption spectra were collected in the wavelength range 350-650 nm on an Olis-upgraded Cary 14 UV-vis-NIR dual-beam spectrophotometer using 1.0 cm path length quartz cells. The instrument was equipped with a circulating water bath thermostatic system to control the temperature of the solutions in both the sample and reference cells, which were maintained at $25.0 \pm 0.1^\circ\text{C}$. The baseline spectrum was collected using 0.1 M ammonium acetate buffer pH 5.5 in both the sample and reference cells.

Aqueous U(VI)-Schiff Base Complex Stability Constant by UV-visible Spectrophotometry

The stability constant for the 1:1 U(VI) complex with $\text{H}_2\text{salenSO}_3$ was calculated by nonlinear least-squares regression using the HypSpec program²⁷ and based on the overall equilibrium involving the U(VI) ion and protonated ligand in the formation of a single 1:1 complex according to the reaction in Eqn. 1.



All relevant equilibria for these calculations are provided in the supplementary data.[†]

Neptunium speciation studies by visible-NIR spectroscopy

Acidic aqueous ²³⁷Np stock solutions were used to prepare samples for vis-nIR spectroscopy. Spectroscopic analysis was performed in specially adapted 1 cm path length cells using a Cary 6000i spectrophotometer, with more detailed experimental procedures reported previously.²⁸ Aqueous Np solutions were prepared using deionized water obtained with a resistivity of at least $18 \text{ M}\Omega \text{ cm}^{-1}$, using a Barnstead Nanopure Infinity ultrapure H₂O generator.

Results and Discussion

Extraction studies of uranium, curium, and europium

20 The distribution ratios for the partitioning of uranium, neptunium, europium, and curium between 0.01 M acetate in 0.1 M KNO_3 pH 5.5 without $\text{H}_2\text{salenSO}_3$ and a 0.1 M solution of HDEHP in toluene (30 min contact time) are displayed in Fig. 2 as the filled data points. For comparison, Table 1 provides the D_M and calculated separation factors for all the timepoints. The oxidation states for U, Eu and Cm will be well defined in this system, with U(VI), Eu(III) and Cm(III) by far the most stable species. As neptunium redox chemistry is more complex a
25 complimentary spectroscopic study was undertaken to determine the redox chemistry, see subsequent discussion.

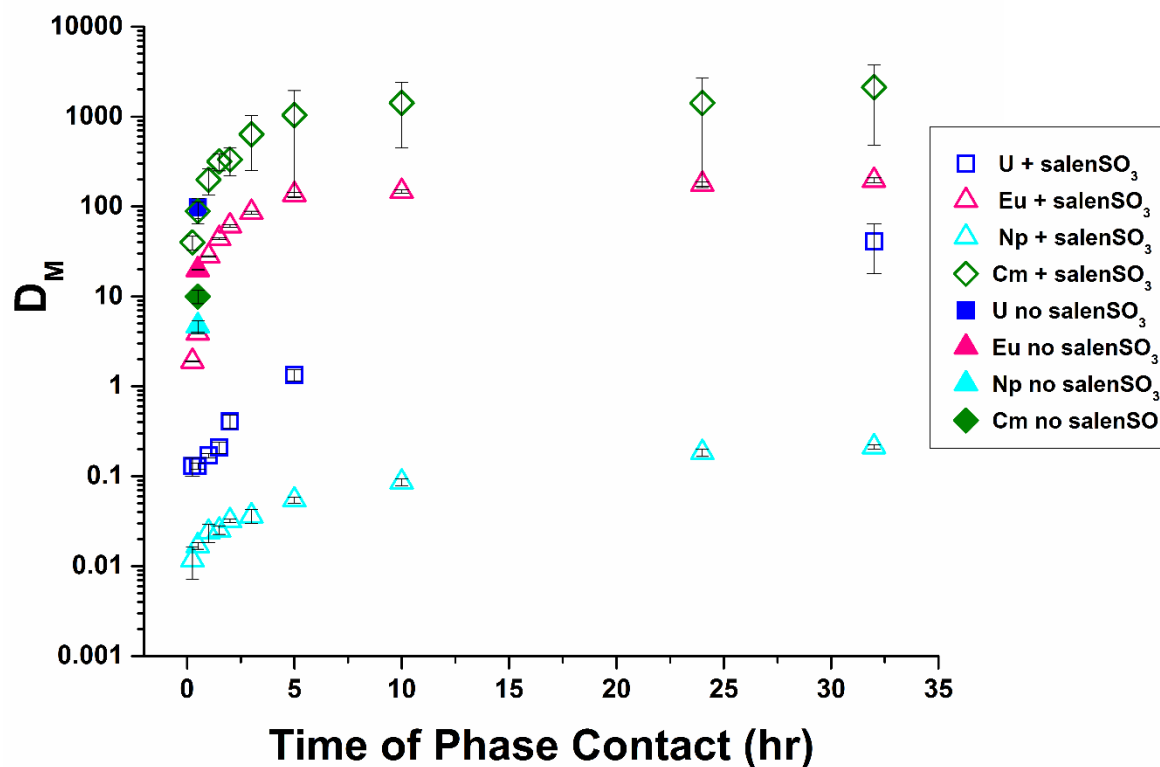


Fig. 2 Distribution ratio as a function of time of phase contact for extraction of metal cations: (U(VI), 10^{-4} M; Np(V/VI), 10^{-5} M; Cm(III), 10^{-10} M; and Eu(III), 10^{-5} M) from 0.01 M (formal concentration) $\text{H}_2\text{salenSO}_3$ in 0.1 M $\text{KNO}_3/0.01$ M acetic acid at equilibrium pC_H of 5.3 by 0.01 M HDEHP in toluene. Error bars consist of uncertainties calculated from the combination of 5 counting statistics and triplicate analysis at the 95% confidence interval.

Table 1. Summary of extraction results: metal ion distribution ratios (D_M) and calculated separation factors.

Timepoint (hours)	D_U	D_{Np}	D_{Eu}	D_{Cm}	$\frac{D_{Eu}}{D_U}$	$\frac{D_{Cm}}{D_U}$	$\frac{D_U}{D_{Np}}$	$\frac{D_{Eu}}{D_{Np}}$	$\frac{D_{Cm}}{D_{Np}}$
0.25	0.13	0.043012	1.9	40	15	308	311	44160	9303300
0.5	0.13	0.059017	3.9	89	30	685	28	66230	15085200
1	0.17	0.067024	28	199	165	1171	37	4181200	29708300
1.5	0.21	0.072025	44	318	210	1514	38	6111800	44171300
2	0.41	0.083032	61	334	149	815	513	7351900	40241000
3		0.083036	86	640				10362400	77001800
5	1.34	0.108055	136	1040	101	775	1224	12592500	96301900
10		0.142086	147	1420				10351700	100001600
24		0.24184	177	1420				738960	59108000
32	41	0.31213	195	2100	5	51	132192	629920	68009900

0.5, No H₂salenSO₃	98	4.7	19.9	10	0.2	0.1	21	4	2
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In the absence of the Schiff base, U extraction is greatest followed by Eu, Cm, and Np, an extraction order which is in accordance with separation factors calculated from previously published extraction constants in similar systems.^{29,30} Furthermore, an extraction order of $\text{UO}_2^{2+} > \text{Cm}^{3+} > \text{NpO}_2^+$ is in good agreement with the conventional strength of ligand:actinide coordination as described by Choppin and co-workers, assuming pentavalent Np predominates and in the absence of significant aqueous complexation.³¹⁻³³ In the presence of 0.01 M (formal concentration) of H₂salenSO₃ at 30 minutes of phase contact, there is an almost three orders of magnitude decrease in D_U and two orders of magnitude decline in D_{Np} . At the same contact time, distribution ratios for Eu(III) and Cm(III) do not fall below one. Assuming that both U and Np adopt dioxo-cationic states, these differences can be attributed to a known steric effect introduced by the formation of aqueous complexes between the actinyl ions and the Schiff base. The next sections explore the redox and extraction behaviour of Np in this system.

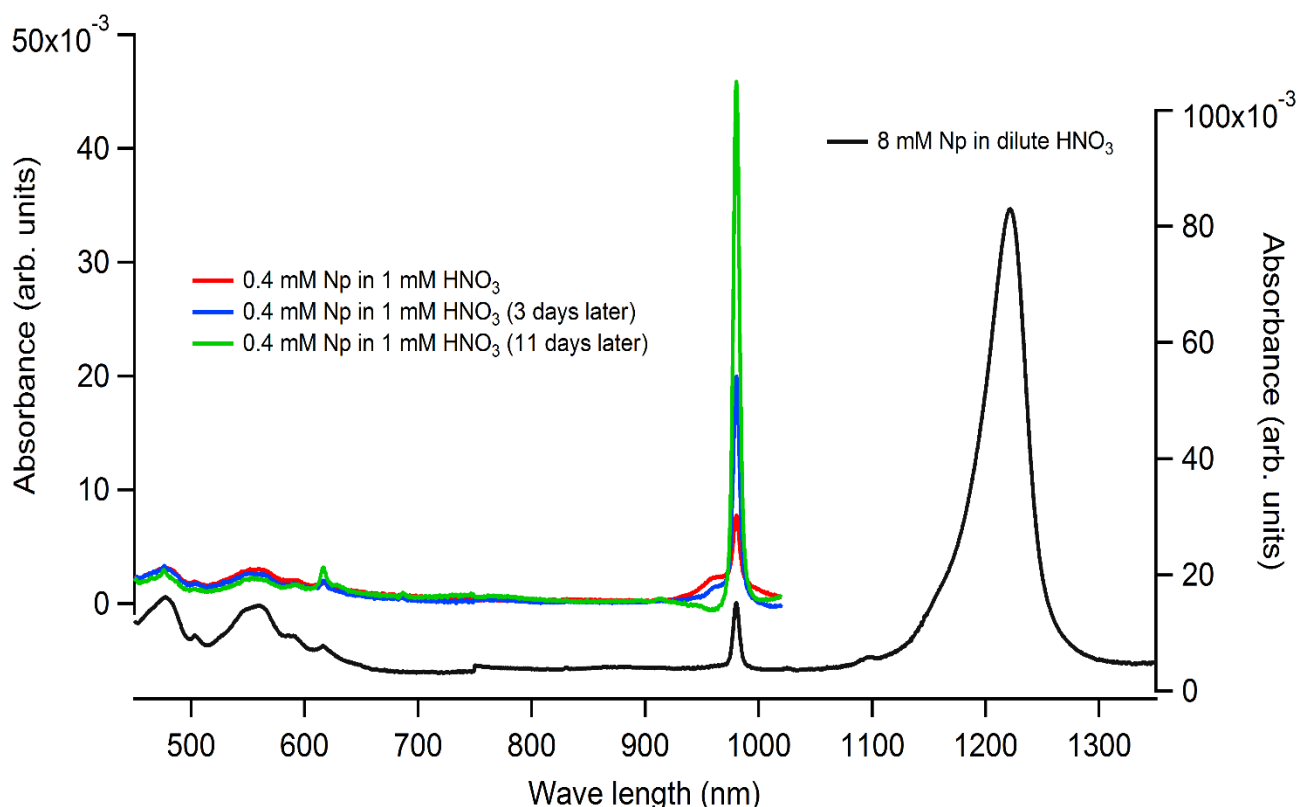
Extraction of Eu(III) in the presence of the Schiff base decreases by a factor of only five and exceeds that without the Schiff base at one hour of mixing, suggesting that Eu(III) is not appreciably complexed by aqueous ligands under these conditions. Curium(III), on the other hand, exhibits a nine-fold enhancement in the presence of H₂salenSO₃ at 30 minutes of phase contact and reaches peak distribution ratios ten-fold higher than Eu(III) in approximately the same timeframe. A nine-fold higher Cm extraction in the presence of H₂salenSO₃ suggests that weak aqueous complexes may promote faster phase transfer. Beyond three hours, however, the uncertainties in D_{Cm} are too large to draw any conclusions about the equilibrium values.

With respect to the Eu(III) and Cm(III) systems, the uranyl(VI) systems remain in non-equilibrium even at 32 hours of phase contact, with increase in distribution coefficient as a function of time. The increasing trend in all distribution ratios in the presence of H₂salenSO₃ is due to phase transfer kinetics, where the rates are expected to be slow. Clearly, the Schiff base forms complexes with U that compete with extraction by the organic phase. As a result of the selective retention of U(VI), separation factors for Eu/U range from 15 to 200 in a 0.25 to 1.5 hour window. For reasons that are not evident, Cm(III) extraction is much greater than that of Eu, leading to separation factors for Cm/U that range from 300 to 1500.

In our previous study, where the aqueous phases were spiked with a combination of the Eu(III) radiotracer and U(VI) (total metal ion concentration of 0.15 mM), the extraction of Eu(III) was less than observed here ($D_{Eu} \leq 2$, even up to 12 h contact time).²¹ Considering that the present data were acquired in the absence of U(VI), the difference in these results indicate that there was competition between the metal ions for complexation/extraction by HDEHP in the previous study, where the formal HDEHP concentration was 50-fold greater than the combined Eu(III) and U(VI) concentrations. We postulate that the activity of the extracting form of the ligand (*i.e.*, DEHP·HDEHP dimer)³⁴ at the organic-aqueous interface may be significantly reduced at this relatively high pH.³⁵ Neptunium speciation in the aqueous phase by visible-NIR spectroscopy

As the extractability of neptunium varies widely with oxidation state,^{36,37} the extraction behaviour of Np is best addressed in the context of its redox chemistry in solution. To examine the oxidation states of Np under conditions similar to the extraction studies, optical spectroscopic studies of solutions resembling the aqueous phase were undertaken. Reproduction of the working solution used to prepare the extraction aqueous phase involved combining 52 μL of a 0.15 M Np stock solution with 1 mL 4 M HNO₃ and evaporating to dryness. The colour

steadily changed from pale blue, to yellow, to brown. To the brown residue, 1 mL of 0.001 M HNO₃ was added, yielding an 8 mM pink solution, a colour consistent with the presence of Np(VI). 50 μL of this 8 mM Np solution was diluted with 0.95 mL of 0.001 M HNO₃ to make a 0.4 mM Np solution in dilute nitric acid. The electronic spectra of this solution acquired at the time of preparation and after 3 days and 11 days after are provided in Fig. 3.



5

Fig. 3 UV/vis/nIR spectra of 0.4 mM Np working solution in 0.001 M HNO₃ as a function of time, (left axis), with the original 8 mM stock solution also shown (right axis)

The band centered around 1220 nm in the spectrum from the more concentrated (8 mM Np) solution is consistent with the presence of Np(VI).³⁸⁻⁴⁰ In this solution the Np(V) fraction is estimated to have been ca. 3% of the total Np content, with ca. 97% Np(VI). Once the 0.4 mM Np working solution was prepared, the most intense Np(VI) band at 1220 nm was obscured by absorption transitions of water, and therefore estimations of the Np oxidation state species concentrations were less reliable. Nonetheless, the band associated with the Laporte forbidden electric-dipole transition of Np(V) at 980 nm clearly increases over time, indicating slow reduction of Np(VI) to Np(V) in the 0.4 mM solution.³⁸⁻⁴⁰ No features suggesting the presence of Np(IV) are observed. Because a fresh stock was prepared that day, these spectra provide good evidence that the working stock used for the extraction studies consisted of a mixture of Np(VI) and Np(V) at the time the extraction aqueous phase was spiked.

Near-infrared spectra of a 1:1 solution of H₂salenSO₃ and Np(V) at pH 2.73, 9.05, and 10.0, in Fig. S2,[†] indicate that formation of the Np(V) complex is favoured at higher pH, which is consistent with the expected protonation constants of the di-Schiff base. To assess the effect of H₂salenSO₃ on the speciation of Np in the aqueous phase of the extraction study, the working stock of 0.4 mM Np, at the time predominantly Np(VI), was diluted to 0.16 mM Np in an 8 mM H₂salenSO₃ solution and the spectra were collected over the same 11-day period previously used to study Np redox chemistry in the absence of complexant. The initial and three-day spectra, along with a reference

spectrum of a 1:1 combination of Np(V) and the Schiff base, are shown in Fig. 4. The band at 980 nm in the working solution (Fig. 3) is characteristic of the presence of Np(V). Here, the red-shift of the peak centred at 1001 nm is consistent with the same transition for a Np(V)-Schiff base complex.³⁸⁻⁴⁰ Although the total Np concentration in this solution is 20-times greater than that of the aqueous phase used in the extraction studies, these data support our hypothesis that Np(VI) was rapidly reduced to Np(V) by the ligand.

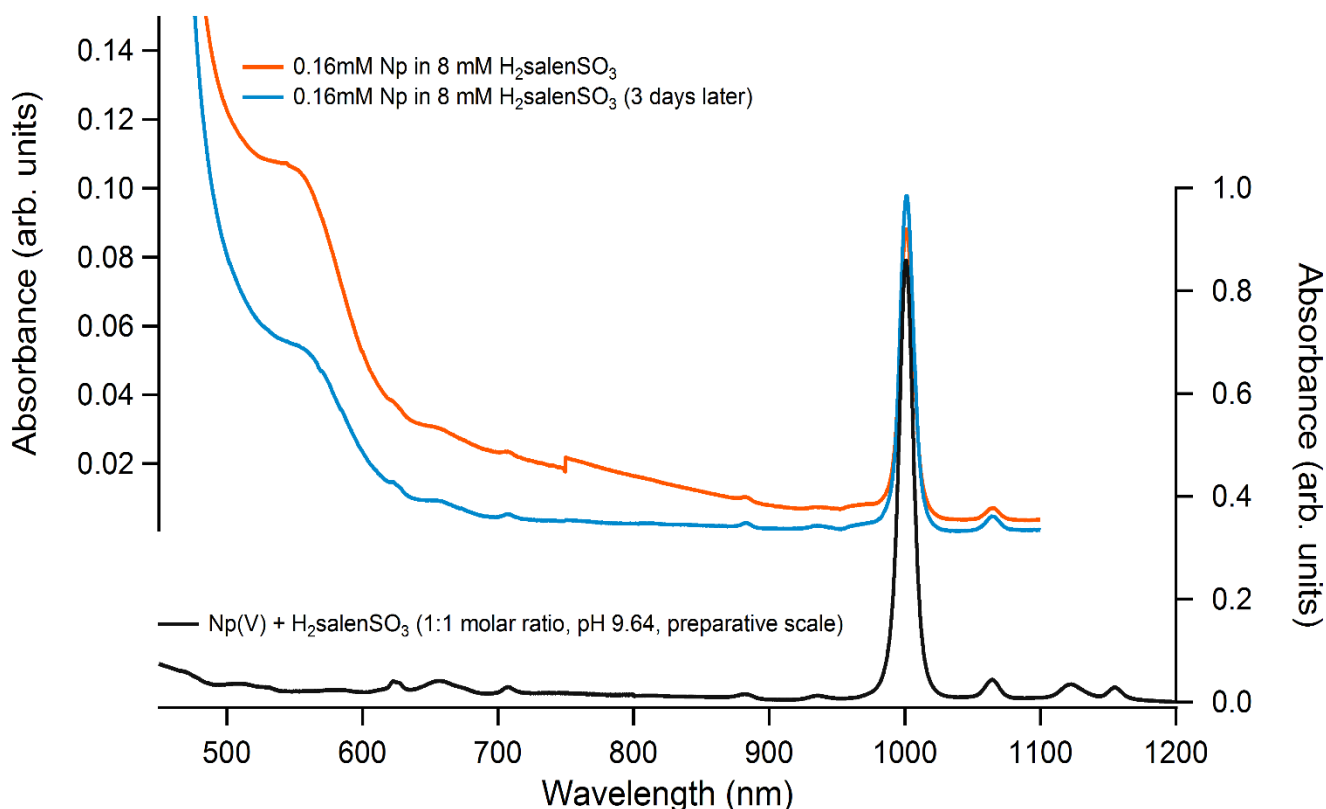


Fig. 4 Visible/nIR spectra of 0.16 mM Np in an 8×10^{-3} M solution of $\text{H}_2\text{salenSO}_3$ in 0.1 M KNO_3 at pH 7.69 at the time of preparation (orange) and 3 days later (yellow). For reference, a definitive Np(V)-salen SO_3 spectrum from the 1:1 combination of Np and $\text{H}_2\text{salenSO}_3$ in aqueous solution at pH 9.64 (black) is overlaid.

Interestingly, upon dissolution of the working stock in the ligand solution an initially intense, greenish-brown colour was observed, but quickly vanished upon mixing. This fleeting colour change is presumably associated with a $[\text{Np(VI)O}_2(\text{salenSO}_3)]^{2-}$ complex prior to reduction to $[\text{Np(V)O}_2(\text{salenSO}_3)]^{3-}$ and is consistent with a broad charge transfer feature observed in the initial solution in Fig. 4 that extends from the visible into the near-IR region (ca. 550-900 nm). Therefore, the three day gap in these first two spectra is deceiving, as these observations indicate that the ligand-to-metal charge transfer and reduction may be complete within minutes, and the remaining spectral features between 550-900 nm associated with excess $\text{H}_2\text{salenSO}_3$.

Extraction studies of neptunium

Trends in the extraction behaviour of neptunium (Fig. 2) by HDEHP in the presence and absence of $\text{H}_2\text{salenSO}_3$ can be explained in terms of the redox speciation of the metal ion elucidated by visible-NIR spectroscopy. Np has the lowest distribution ratios of the metal ions examined in the absence of the aqueous $\text{H}_2\text{salenSO}_3$. At this acidity,

neptunyl(V) is expected to be the most thermodynamically stable species.⁴¹ Our spectroscopic results indicate slow reduction from Np(VI) to Np(V) in the absence of the Schiff base. The predominant form in the working stock solution within the one hour timeframe in which it was used to spike the aqueous phase is expected to be Np(VI), which is less extractable than U(VI).³⁷ In the presence of H₂salenSO₃, D_{Np} was diminished by a factor of ~~80-300~~ 5 30 minutes and remains below one up to 32 hours of phase contact. According to the visible-NIR spectroscopic results in this study, the most prevalent species in the presence of the Schiff base is the NpO₂⁺ ion, which due to its lower charge density is less extractable than NpO₂²⁺.^{36,37} A relatively flat kinetic curve is consistent with these observations. The general trend of D_{Np} differs from that of D_U, in that the increase in extraction is more gradual. A ~~seven~~ 10 ~~eighteen~~-fold increase in extraction of neptunium is observed by 32 hours, whereas uranium extraction increases by 400-fold in the same timeframe. ~~At this point, U is greater than 97% extracted and Np is less than 1% extracted. Therefore, in the case of Np~~ These difference reflect, that H₂salenSO₃ not only binds the ~~actinyl-neptunyl~~ cation to reduce extractability but also causes rapid reduction, which also facilitates hold-back as the less extractable +V oxidation state. A practical implication of these trends is the three to four orders of magnitude separation factors with respect to Np observed at 32 hours of mixing (see Table 1), where U, Eu, and Cm are well 15 extracted (D_M > 10). Combined with early time points, where both U and Np are not extracted and trivalent metal ions are well-extracted, these later time points may provide a means to separate the two actinyl ions from trivalent ions and from each other.

¹H NMR titration of U(VI) with aqueous H₂salenSO₃

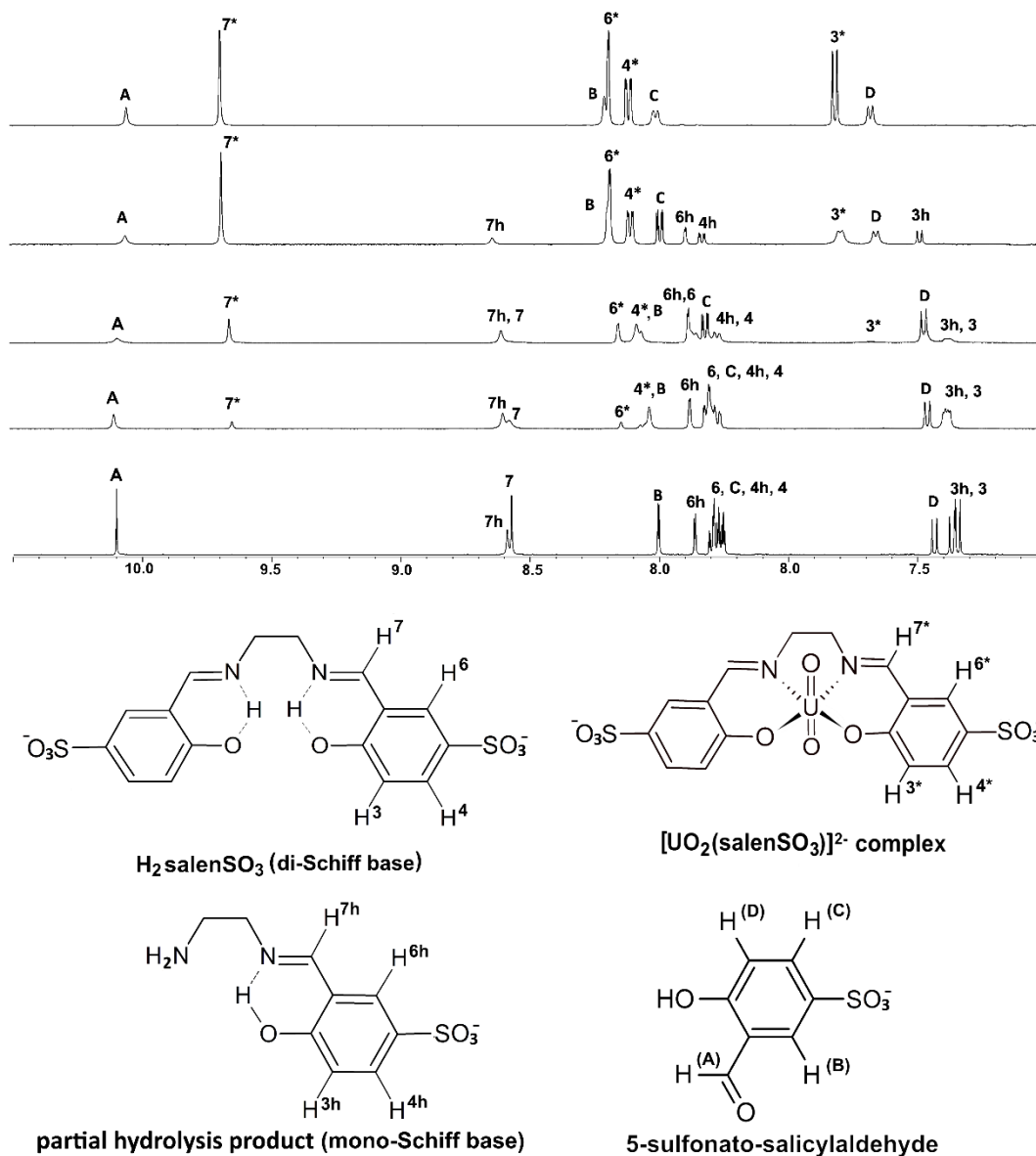
Preliminary NMR spectroscopic data from our previous report suggests that the structure of the aqueous solution 20 U(VI)-salenSO₃ complex is consistent with the solid state structure, behaving as an N₂O₂ donor ligand around the equatorial plane of the linear dioxo uranyl moiety, with an additional coordinated water molecule.²⁴ The intent of these experiments was to probe in more detail the aqueous equilibria that influence the phase transfer of both U(VI) and Eu(III) observed in Fig. 2 and verify the stoichiometry of the U(VI) solution phase complex.

¹H NMR Spectroscopy titration of U(VI) with aqueous H₂salenSO₃. Proton NMR spectroscopy was employed to 25 evaluate the effect of the uranyl ion on the speciation of H₂salenSO₃ in solutions resembling those of the aqueous phase described in the extraction. Fig. 5 contains the downfield portion (6.5 ppm to 10.5 ppm) of representative ¹H NMR spectra during the titration of 7.5 mM (formal concentration) H₂salenSO₃ by UO₂(NO₃)₂.

For two reasons, the spectrum for the ligand alone (bottom trace) is more complex than expected. Firstly, partial hydrolysis results in the production of the 5-sulfonato-salicylaldehyde and ethylenediamine (not shown in Fig. 5) 30 precursors of the Schiff base. The presence of the 5-sulfonato-salicylaldehyde resonance (A) is observed at 10.1 ppm. Secondly, the azomethine (7) resonance remains sharp and split into two singlets indicate that partial hydrolysis occurred upon dissolution. The resonances denoted by “h” are attributed to the mono-Schiff base, an assignment supported by the pH titration ¹H NMR spectra in Fig. S4 and Fig. S5, and by the COSY and NOESY spectra in Fig. S8 and Fig. S9.[†] The azomethine (7, 7h) protons are correlated with two states of the ethylene bridge 35 protons, those observed in one environment associated with the di-Schiff base and those observed in two environments of the methylene groups of the mono-Schiff base.

Intact ligand signals are best identified by the phenyl proton doublets at both 6.75 ppm (3) and 7.8 ppm (6), and the azomethine singlet (7) near 8.6 ppm. With increasing U(VI) concentration these resonances shift downfield, and after equivalence, they remain at 7.3, 8.2, and 9.7 ppm, respectively, indicating one state for the complex, the 40 1:1 [UO₂(salenSO₃)]₂²⁺. Complexation of UO₂²⁺ by the intact ligand is most apparent in the shift of the azomethine signal (7 to 7*) downfield by 1.1 ppm. In fact, all of the H₂salenSO₃ resonances in this region shift downfield due

to the deshielding effect of the LMCT. When the U(VI) concentration exceeds equivalence, the signals of the complex are sharp, consistent with one state of the complex. Further verification of the proton assignments and the 1:1 stoichiometry are permitted by the increasing symmetry observed post-equivalence (5.0 mM U(VI)).



5 **Fig. 5** Downfield region of ^1H NMR spectra in the titration of 4.4 mM (7.5 mM (formal concentration) $\text{H}_2\text{salenSO}_3$) by (bottom to top) $0, 0.5, 1.5, 3.75,$ and 5.0 mM $\text{UO}_2(\text{NO}_3)_2$ in 0.1 M KNO_3 with 10% D_2O , pH was $7.56, 7.39, 7.10, 6.00,$ and 4.36 , in the same order. The label convention for the resonances is provided in the legend below, where the protonation states are based on the model described in the supplementary data. For simplicity, only one half of the labelled protons in di-Schiff base structures are shown. All spectra are on the same scale.

10 It is important to point out that ~~because~~ the $\text{H}_2\text{salenSO}_3$ disodium salt was dissolved directly in the $\text{UO}_2(\text{NO}_3)_2$ solutions, ~~the trend of decreasing ligand hydrolysis with increasing U(VI) concentration indicates that complexation is faster than hydrolysis and thereby promotes ligand stability.~~ Under none of these conditions does the mono-Schiff base appear to complex with U(VI) and its disappearance from the latter spectra is further

evidence that the di-Schiff base is protected by complexation with excess metal ion. In the presence of U(VI), signals of 5-sulfonato-salicylaldehyde are broader, suggesting that chemical exchange equilibria with the aldehyde may be weak and dynamic on the NMR timescale (*i.e.*, approximately 100 μ s with respect to line-broadening and relaxation times). Ultimately, six dominant proton environments account for the six mutually degenerate Ph-H resonances of $[\text{UO}_2(\text{salenSO}_3)]^{2-}$ and three Ph-H signals from 5-sulfonato-salicylaldehyde.

Confirmation of the U:ligand stoichiometry in solution was provided by the graphical analysis of the chemical shift *versus* the U/ $\text{H}_2\text{salenSO}_3$ mole-ratio of the complex and the quantitative NMR experiment provided in Fig. 6. the assumption of a constant total $\text{H}_2\text{salenSO}_3$ concentration is based on the linearity of the mole ratio plot using a single di-Schiff base concentration (4.4 mM, by proton integral analysis of the ligand solution alone). Negligible hydrolysis of the ligand with increasing U(VI) concentration and decreasing pH indicates that complexation is faster than hydrolysis and thereby promotes ligand stability.

~~This~~ The spectrum in Fig. 6 includes resonances of $[\text{UO}_2(\text{salenSO}_3)]^{2-}$ complex and ethylenediamine, which were used to estimate the concentrations and stoichiometry of these species. Due to formation of the *gem*-diol in aqueous solution, the aldehyde integral is less than that expected from stoichiometry. Calculated concentrations of ethylenediamine (en) and $[\text{UO}_2(\text{salenSO}_3)]^{2-}$ (average of 7*, 6*, and 3*) were 2.70 mM and 4.06 ± 0.09 mM, respectively. The sum of these (6.76 mM), is 106% of the formal $\text{H}_2\text{salenSO}_3$ concentration, thus confirming the 1:1 stoichiometry of the complex. Based on the similar actinyl ion chemistry, we postulate that the Np(V/VI) complexes resemble that of U(VI).

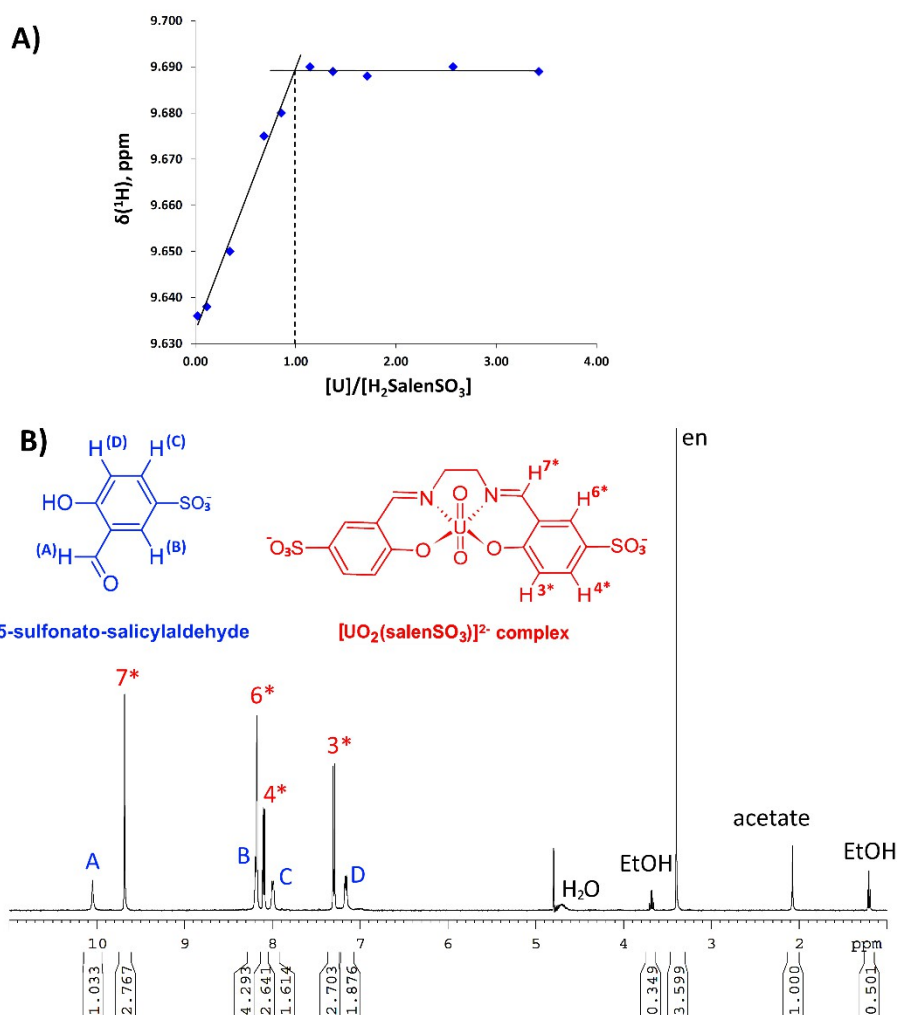


Fig. 6 A) Mole-ratio plot of the NMR chemical shift change of the azomethine (7/7*) proton resonance from the titration of **4.4 M** (7.5 mM formal concentration) $\text{H}_2\text{salenSO}_3$ (formal concentration) by $\text{UO}_2(\text{NO}_3)_2$. The ligand concentrations used for calculations were compensated by the contribution to ligand salt weight from residual ethanol and the extent of hydrolysis by the ratio of the integrals of the ethylene bridge protons to the ethylenediamine protons. B) Proton NMR spectrum of 4.06 mM $\text{H}_2\text{salenSO}_3$ in 5.00 mM $\text{UO}_2(\text{NO}_3)_2$ with 0.1 mM KNO_3 , 1 mM ammonium acetate (internal standard), and 10% (v/v) D_2O . The methyl integral of acetate was used to calibrate the spectrum. The labels, "en" and "EtOH" are resonances of ethylenediamine and residual ethanol (0.1% w/w), respectively.

^1H NMR studies of Eu(III) complexation with aqueous $\text{H}_2\text{salenSO}_3$

10 Assessment of the interaction of Eu(III) with $\text{H}_2\text{salenSO}_3$ and hydrolysis products in the solvent extraction aqueous phase was undertaken by the NMR paramagnetic shift and band signal broadening that accompanies contact and pseudo-contact of the paramagnetic lanthanide metal cation with nuclei of the constituents in solution. Fig. 7 contains a stack of three proton spectra, where a 5 mM (formal) solution of $\text{H}_2\text{salenSO}_3$ was prepared with 0.1 M KNO_3 at pH 5.7 (to avoid metal ion hydrolysis) and spiked with increasing amounts of $\text{Eu}(\text{NO}_3)_3$.

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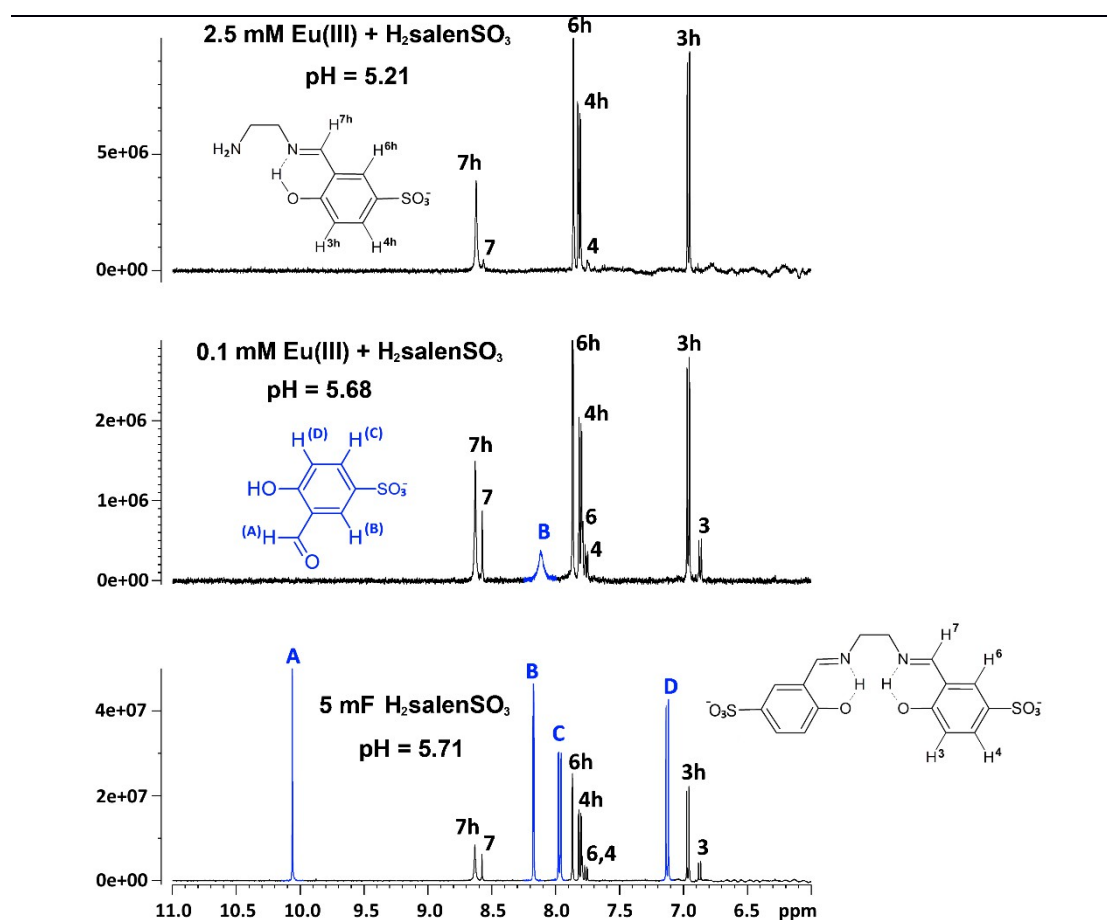


Fig. 7 Proton spectra of 5 mM (formal) $\text{H}_2\text{salenSO}_3$ in the absence and presence of $\text{Eu}(\text{NO}_3)_3$ in 0.1 M KNO_3 .

The spectra reveal no significant chemical shifts associated with complexation of $\text{Eu}(\text{III})$ with salenSO_3 , and opposite to $\text{U}(\text{VI})$ behaviour, there is strong evidence that $\text{Eu}(\text{III})$ instead binds to the aldehyde decomposition product. Consistent with this hypothesis, through pseudo-contact shift only the isolated (B) phenyl proton signal of the aldehyde remains and is significantly broadened after addition of just 0.1 mM $\text{Eu}(\text{III})$. Decreased $\text{H}_2\text{salenSO}_3$ signals are expected due to hydrolysis at the lower pH that follows addition of the more acidic $\text{Eu}(\text{NO}_3)_3$ stock solution, with aldehyde promoting ligand decomposition. According to the trends in Fig. 2, it appears that the aldehyde complex extractable, whether or not the aldehyde is substituted by HDEHP during phase transfer. Because of the similar chemistry of $\text{Cm}(\text{III})$ and $\text{Eu}(\text{III})$, we can predict that $\text{Cm}(\text{III})$ will also preferentially complex with the aldehyde.

Effect of 5-sulfonato-salicylaldehyde on extractions

According to the trends in Fig. 2 and the $\text{Eu}(\text{III})$ complexation results, it appears that the aldehyde complex could render the metal ion more extractable, regardless of what complex is involved in phase transfer. To assess the effect of the presence of the 5-sulfonato-salicylaldehyde hydrolysis product on extraction of $\text{U}(\text{VI})$ and $\text{Eu}(\text{III})$, as representative metal ions, 30 minute solvent extraction experiments were performed in the same fashion as those with $\text{H}_2\text{salenSO}_3$, by substituting 5-sulfonato-salicylaldehyde (10 mM) for the aqueous ligand. The results of these

experiments were $D_U = 135(5)$ and $D_{Eu} = 8.5(0.1)$, which are similar to those without the aqueous ligand. Therefore, it appears that the aldehyde hydrolysis product has a negligible effect on the extraction of either the actinyl or trivalent ions.

[UO₂(salenSO₃)]²⁻ aqueous complex stability constant by absorption spectrophotometry

5 Quantification of the stability of the [UO₂(salenSO₃)]²⁻ complex was carried-out using UV-visible spectrophotometric experiments with variation of the ligand concentration under conditions similar to the extraction aqueous phase. A 0.05 M ammonium acetate buffer was used to avoid large pH excursions due to addition of increasing amounts of a pH 7.8 ligand stock solution. As previously discussed, ¹H NMR could be, and was, used to determine the actual concentration of the di-Schiff base stock solution. Representative spectra are
10 shown in Fig. 8B, where the absorption band centred on 460 nm is assigned to a LMCT transition in [UO₂(salenSO₃)]²⁻. An absorption band attributed to the ligand hydrolysis product, the aldehyde (Fig. 6A), is centred near 370 nm (Fig. S14). This feature is the primary contribution to the increased absorption observed across metal-to-ligand ratios greater than one. Nevertheless, because the 460 nm LMCT band is sufficiently resolved from the much more intense transitions up to equivalence, this band was employed in the calculation of a
15 conditional stability constant. A plot of absorbance at 460 nm as a function of ligand:metal ratio is shown in Figure Fig. 8B and is consistent with a 1:1 stoichiometry of the complex.

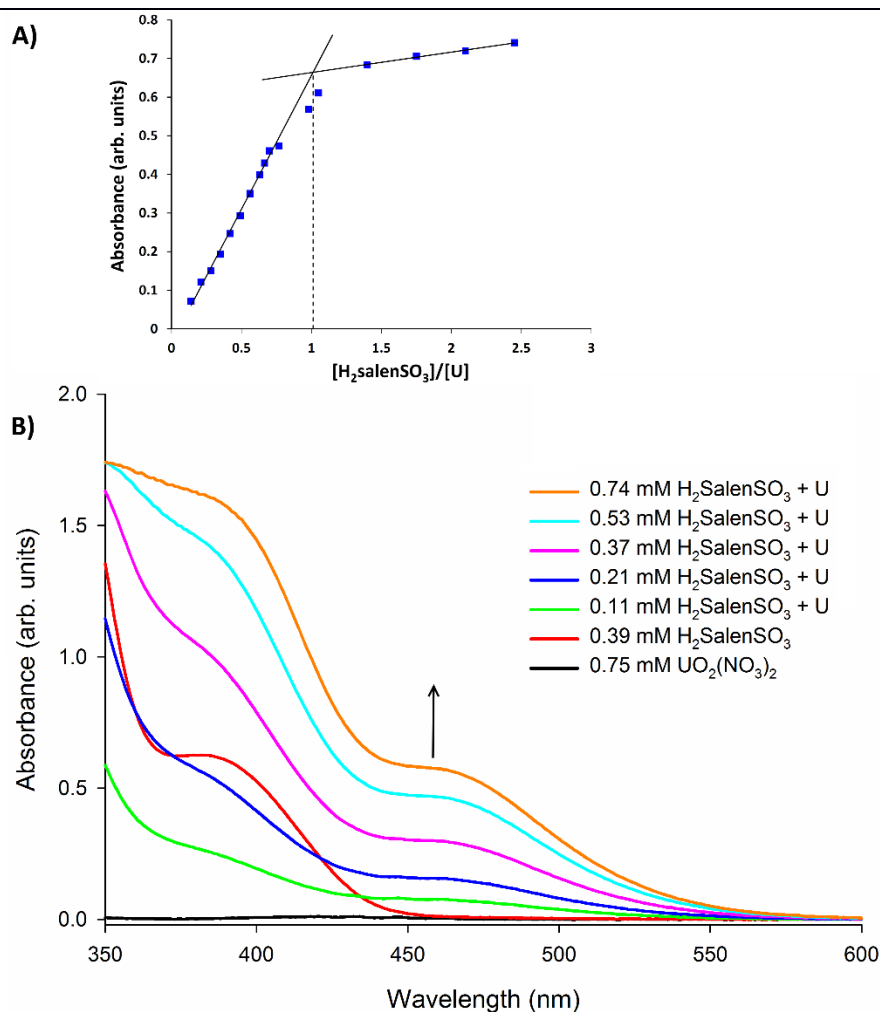


Fig. 8 A) Titration of U(VI) by $\text{H}_2\text{salenSO}_3$ using visible spectrophotometry of the the LMCT band centred at 460 nm. The actual concentration of the ligand was measured in the stock solution by proton NMR spectroscopy. **B)** UV-visible spectra of samples in the titration of 0.75 mM UO_2^{2+} by $\text{H}_2\text{salenSO}_3$ in solutions comprising 0.1 M KNO_3 and 0.05 M ammonium acetate buffer (pH 5.5). The arrow indicates increasing absorbance of the LMCT with increasing ligand concentration. Spectra of ligand and metal ion solutions alone are provided for perspective.

Using a data range of 450-600 nm for 17 spectra and the pertinent equilibria in Table S3,[†] a $\log \beta_{1,1}$ of 25.80 ± 0.08 was calculated for the aqueous $[\text{UO}_2(\text{salenSO}_3)]^{2-}$ complex by the HypSpec program. The estimated error is a combination of standard deviations of absorbance readings and that calculated by the HypSpec program, all of which may be higher than those for typical complexometric titrations due to variations in extent of hydrolysis and interference from nearby transitions. This sizeable conditional stability constant for the $[\text{UO}_2(\text{salenSO}_3)]^{2-}$ complex is consistent with the complete chelation of U(VI) in the aqueous phase, in which the aldehyde and ethylenediamine concentrations are at least an order of magnitude higher without the stronger buffer.

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Conclusions

In the course of our research we have purposely added a Schiff base ligand, which can accommodate the steric demands of actinyl cations, thus introducing a known steric effect. Combined with the complexometric and spectroscopic data, the extraction experiments in this study confirm that selective complexation of An(V/VI) ions by a quasiplanar tetradentate Schiff base alters the order of extraction dramatically and greatly enhances separation factors for trivalent Ln/An cations *versus* An(V/VI). Spectroscopic data suggest that Eu(III) forms weak complexes with 5-sulfonato-salicylaldehyde, which masks possible interactions with H₂salenSO₃ and corroborates the extraction trends. Rapid, ligand mediated reduction of Np(VI) to a stable Np(V)-salenSO₃ complex was confirmed by optical spectroscopy and accounts for the difference in extraction kinetic behaviour between U and Np. Although this ligand displays poor stability in aqueous solution, rendering quantification of the intact ligand particularly challenging, these results demonstrate its effectiveness as a prototype, actinyl-selective solvent extraction hold-back reagent. Provided the strong chelating nature of these complexes, similar compounds could also prove useful on other separation platforms (*e.g.*, extraction chromatography or selective adsorption of uranium from natural waters). Such advances in the chemistry of this family of Schiff bases could offer ways to separate and quantify *f*-elements under conditions not commonly considered.

Acknowledgements

This work was supported by the University of California under the UCOP Grant ID# 12-LF-237294, awarded jointly to UC Irvine and Los Alamos National Laboratory. C.G.B. acknowledges the support of the Los Alamos National Laboratory Seaborg Institute for Summer Research Fellowships. Los Alamos National Security, LLC, operates Los Alamos National Laboratory for the National Nuclear Security Administration of the Department of Energy under contract DE-AC52-06NA25396.

Notes and references

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† Electronic Supplementary Information (ESI) available: Fourteen figures, one scheme, three tables, and more detailed experimental descriptions are included in the ESI. See DOI: 10.1039/b000000x/
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