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Challenging Conventional f-Element Separation Chemistry – Reversing Uranyl(VI)/Lanthanide(III) Solvent Extraction Selectivity

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The water soluble tetradentate Schiff base, *N,N'*-bis(5-sulfonatosalicylidene)-diaminoethane ($H_2salen-SO_3$), will readily coordinate to the uranyl(VI) cation, but not to the same extent to trivalent lanthanide cations. This allows for the reversal of conventional solvent extraction properties and opens the possibility for novel separation processes.

Developing new separation strategies for the actinide elements is essential if many of the challenges related to spent nuclear fuel (SNF) processing and nuclear waste management are to be addressed.^[1] In most chemical separation processes relevant to the nuclear industry uranium is the most abundant actinide element, and the uranyl(VI) dication (UO_2^{2+}) the most stable species in solution.^[2] Despite decades of research into uranium separations there is still considerable activity directed towards the application of complexants for the selective extraction of uranyl(VI) from an aqueous to an organic phase.^[3] Conventional PUREX (Plutonium and Uranium Reduction Extraction) based solvent extraction processes rely on the extraction of uranyl(VI) nitrate by tri-*n*-butyl phosphate into an organic phase as the first step of the separation flowsheet.^[4] However, keeping the bulk of the uranium out of the solvent phase could significantly reduce the volume of solvent required for SNF processing operations. A good example of such an approach is the development of technologies related to the initial crystallization of $UO_2(NO_3)_2 \cdot 6H_2O$ prior to subsequent solvent extraction processes used to separate transuranic and fission product elements.^[5]

The concept of selectively retaining ions in an aqueous phase during a solvent extraction process has been shown to hold great promise in processes for An(III)/Ln(III) separation such as TALSPEAK (Trivalent Actinide – Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes) and Reverse TALSPEAK, as well as more recent innovative SANEX (Selective Actinide Extraction) process concepts.^[6]

Complexation of uranyl cations by Schiff base ligands has received considerable recent attention due to their ability to stabilize uranyl(V),^[7] catalytic properties, utility for ion-pair recognition, and potential application as chemical sensors.^[8] The capacity of 4 or 5 dentate Schiff base ligands to accommodate the steric demands of the linear dioxo uranyl moiety has, not surprisingly, led to interest in their application as extractants for uranyl(VI) cation, with extraction from aqueous to organic solutions.^[9]

With the aim of reversing standard uranyl solvent extraction chemistry we have initiated studies into the complexation of $\{UO_2\}^{2+}$ by Schiff base ligands functionalized with sulfonato groups, complexants which are known to bind to transition metals.^[10-14] We chose this approach as a means of preparing a water soluble uranyl(VI) complex, which we hypothesized

would not extract into an organic phase. Our preliminary work has focused on a sulfonated salen ligand (Fig. 1), with structural, spectroscopic and separation chemistry studies presented here.

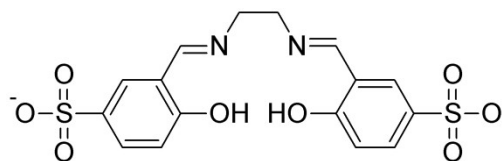
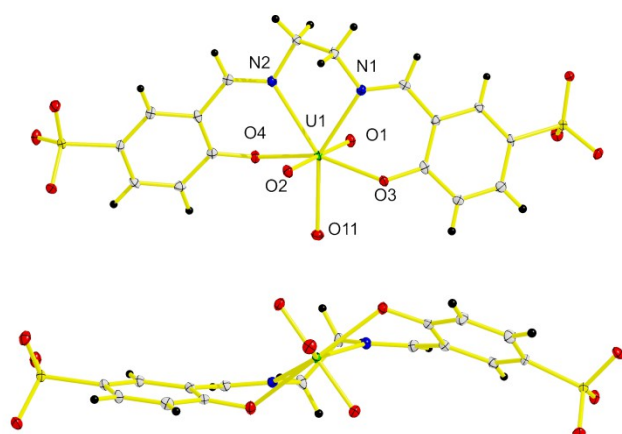


Figure 1. *N,N'*-bis(5-sulfonatosalicylidene)-diaminoethane ($H_2salen-SO_3$), synthesized as the disodium salt.

Crystals of Disodium [*N,N'*-ethylenebis(5-sulfonato salicylidene)iminato](aqua)dioxouranium nonahydrate, $Na_2[UO_2(salen-SO_3)(OH_2) \cdot 9H_2O]$, suitable for single crystal X-ray diffraction were grown by slow evaporation of an aqueous solution of 1:1 $H_2salen-SO_3$ and $UO_2(NO_3)_2$ at a starting pH of 7.6. In the anion, $[UO_2(salen-SO_3)(OH_2)]^{2-}$, the linear dioxo uranyl(VI) moiety (UO_2^{2+}) is coordinated to the two imine nitrogens and two deprotonated phenolic oxygens of the salen- SO_3 ligand, and a water molecule. This ligand environment results in distorted pentagonal bipyramidal coordination around the central uranium atom, by far the most common geometric arrangement for 7-coordinate uranyl complexes.^[15] The two imine nitrogen atoms are positioned respectively above and below the equatorial plane around the uranyl moiety ($O1-U1-N1 = 85.22(8)^\circ$ and $O1-U1-N2 = 99.04(8)^\circ$), resulting in the sulfonated salicylidene units also siting above and below the equatorial plane in a ‘stepped’ conformation. This tetradentate ligand binding and stepped conformation has also been observed for three previously structurally coordinated salen complexes, $UO_2(salen)(MeOH)$, $UO_2(salen)(EtOH)$ and $UO_2(salen)(TPPO)$ (TPPO = triphenylphosphine oxide).^[16-18] This indicates that the addition of sulfonate groups to the aromatic ring has negligible impact on either the coordination environment around the uranium atom, or complex conformation. The bond lengths and angles associated with the central uranyl moiety and the N_2O_2 -donor ligand in $[UO_2(salen-SO_3)(OH_2)]^{2-}$ are comparable to those previously reported for $UO_2(salen)(MeOH)$, $UO_2(salen)(EtOH)$, $UO_2(salen)(TPPO)$ and $UO_2(salen)(OH_2)$ (see ESI).^[16-19] The bond length of the coordinated water, $U-O = 2.3957(18)$ Å, is only slightly shorter than the values reported for the coordinated water molecule in $UO_2(salen)(OH_2)$, $U-O = 2.430(5)$ Å.^[19]

Figure 2. Structural representations of $[UO_2(salen-SO_3)(OH_2)]^{2-}$ highlighting both the main connectivity around the uranium atom (top) and the stepped conformation of the deprotonated and coordinated $H_2salen-SO_3^{2-}$ ligand (bottom). Atom colors are C (white), H (black), N (blue), O (red), S (yellow), and U (green).



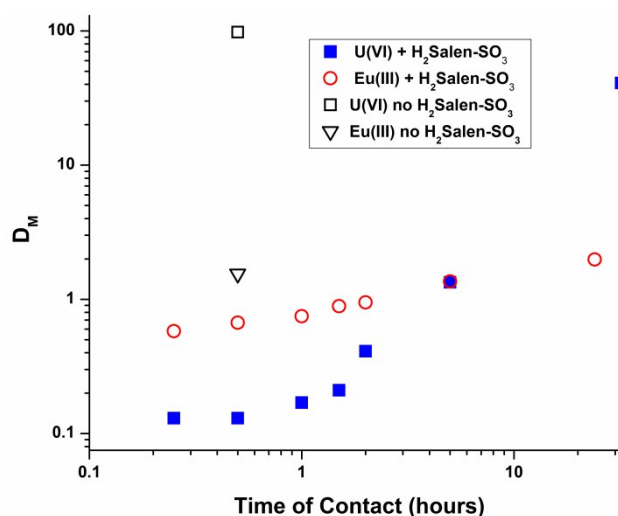
There are numerous structural studies that show that N_2O_2 -donor Schiff base ligands can bind to trivalent lanthanide cations. Multifarious structural motifs have been observed, including tetradentate coordination through all four donor atoms and coordination just through phenolic oxygens.^[20] However, there is also evidence that, under comparable reaction conditions, uranyl(VI) will more readily coordinate to such ligand sets than Ln(III).^[21] Taken in conjunction with the observation that U(VI) tends to form more stable complexes in solution than Ln(III),^[22] and our preliminary spectroscopic studies indicating that U(VI) more readily coordinates to $\text{H}_2\text{salen-SO}_3$ than Nd(III) or Eu(III),^[23] it would appear that $\text{H}_2\text{salen-SO}_3$ could be applied to f-element separation chemistry.

To explore the use of $\text{H}_2\text{salen-SO}_3$ as a holdback reagent, selective for U(VI) vs. Ln(III), competitive extraction experiments were conducted in a biphasic system comprising 0.01 mol L^{-1} di(2-ethylhexyl)phosphate (HDEHP) in toluene and 0.01 mol L^{-1} $\text{H}_2\text{salen-SO}_3$ in 0.1 mol L^{-1} KNO_3 at a pC_H of 5.3. The mild acidity was chosen based on spectrophotometric and potentiometric titrations that established a range of pK_a values between 5 and 9 for the phenolic protons of this and analogous Schiff bases,^[24] and that f-element metal ions tend to hydrolyze to insoluble products above pH 6.^[25] Europium(III) was chosen as a representative Ln(III) ion for which a high specific activity radiotracer was readily available. HDEHP was chosen as a reagent demonstrated to effectively extract both Eu(III) and U(VI) from aqueous mineral acid solutions.^[6a,26-28]

The U(VI) and Eu(III) extraction in absence of $\text{H}_2\text{salen-SO}_3$, at 30 min contact time, is shown in Fig. 3 as an open square (U(VI)) and an open triangle (Eu(III)). The data are consistent with previously published work in similar systems demonstrating that,

in the absence of holdback reagent in the aqueous phase, D_U is nearly two orders of magnitude higher than D_{Eu} .^[25,26] The addition of $\text{H}_2\text{salen-SO}_3$ into the aqueous phase causes a dramatic decrease in U(VI) extraction over the same 30 min contact time, an almost 3 orders of magnitude decrease in D_U (Fig. 3, Table 1). Clearly UO_2^{2+} is readily complexed by deprotonated $\text{H}_2\text{salen-SO}_3$ under these conditions as evidenced by the deep red coloration of the aqueous solution, post-contact. Conversely, the addition of $\text{H}_2\text{salen-SO}_3$ leads to a decrease in D_{Eu} by only a factor of three, suggesting that Eu(III) exhibits weaker complexation with $\text{H}_2\text{salen-SO}_3$ (vs. U(VI)). The extractability of the respective f-element cations by HDEHP has therefore been *completely reversed* by the presence of the aqueous soluble salen ligand.

Fig. 3 and Table 1 also show the extraction of U(VI) and Ln(III) by HDEHP into toluene, with $\text{H}_2\text{salen-SO}_3$ in the aqueous phase, at various phase contact times. As the contact time is increased the ability of $\text{H}_2\text{salen-SO}_3$ to hold-back U(VI) (and Eu(III)) in the aqueous phase diminishes. Aqueous salen ligand degradation could certainly be a component of this increased organic phase extraction,^[29] but the ligand is stabilized somewhat by the presence of uranyl(VI) - as indicated by preliminary solution state NMR studies (see ESI). Phase transfer kinetics are likely also an important contributing factor to increase U(VI) and Eu(III) extraction as a function of time.^[30] Future studies will focus on designing aqueous soluble back extractants which do not have hydrolysable imine functionalities to allow for a more detailed investigation of the impact of phase transfer kinetics.



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Figure 3. Competitive extraction of uranyl(VI) (10^{-4} mol L $^{-1}$), and Eu(III) (10^{-5} mol L $^{-1}$ total) in the presence of uranyl(VI) (10^{-4} mol L $^{-1}$), from 0.01 mol L $^{-1}$ H₂salen-SO₃ in 0.1 mol L $^{-1}$ KNO₃ and 0.01 mol L $^{-1}$ acetic acid at equilibrium pC_H of 5.5 by 0.01 M HDEHP in toluene.

Timepoint (hours)	D _U	%E _U	D _{Eu}	%E _{Eu}
0.25	0.13 (0.03)	12%	0.58 (0.02)	37%
0.5	0.13 (0.01)	11%	0.67 (0.01)	40%
1	0.17 (0.01)	15%	0.75 (0.01)	43%
1.5	0.21 (0.03)	17%	0.89 (0.02)	47%
2	0.41 (0.07)	29%	0.95 (0.01)	49%
5	1.34 (0.2)	57%	1.36 (0.03)	58%
24			1.98 (0.03)	66%
32	41 (23)	98%		
No H ₂ salen-SO ₃	98 (25)	99%	1.55 (0.03)	61%

Table 1. Summary of competitive extraction results: metal ion distribution ratios (D_M), percent extraction (%E), and separation factors (D_{Eu}/D_U). Numbers in parentheses are the uncertainties from the combination of counting error and standard deviations of triplicate analysis at the 95% confidence interval.

Conclusions

We have structurally and spectroscopically characterized an aqueous soluble uranyl salen complex, [UO₂(salen-SO₃)(OH₂)]²⁺. Under most conditions U(VI) is readily extracted from aqueous solution by HDEHP into toluene, but when H₂salen-SO₃ is added to the aqueous solution, U(VI) is held back in the aqueous phase, with a ca. 3 order magnitude decrease in distribution coefficient. Additionally, under the same conditions the extraction of Eu(III) is held back to a much lesser extent in the aqueous phase by H₂salen-SO₃, reversing conventional U(VI)/Eu(III) solvent extraction chemistry. These results hold promise for the application of aqueous Schiff base ligands in the development of novel lanthanide/actinide separation schemes that defy conventional trends in f-element cation extraction properties.

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