

Supplemental Information

Extraction of the Trivalent Transplutonium Actinides Americium through Einsteinium by the Sulfur Donor Cyanex 301

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Table S1. Emission wavelengths of lanthanides used in ICP-OES.

| Metal | Wavelength (nm) | Metal | Wavelength (nm) |
|-------|--------------------|-------|--------------------|
| La | 398.852 | Dy | 353.171 |
| Pr | 422.293 | Ho | 345.600 |
| Nd | 430.358 | Er | 337.271 |
| Sm | 443.432 | Tm | 384.802 |
| Eu | 393.048 | Yb | 328.937 |
| Gd | 342.247 | Lu | 547.669 |

Table S2. Calculated thermodynamic parameters for the reaction
$$M(C301)_3 + NO_3^- \rightleftharpoons M(C301)_2(NO_3) + C301^-$$

. ΔG is calculated at a temperature of 298.15 K.

| Metal | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol·K) |
|------------|------------------------|------------------------|-------------------------|
| Lanthanide | | | |
| Ce | 15.82 | 18.58 | 9.25 |
| Pr | 12.97 | 15.48 | 8.41 |
| Pm | 16.40 | 20.96 | 15.27 |
| Sm | 12.80 | 31.30 | 61.97 |
| Eu | 19.54 | 30.96 | 38.20 |
| Tb | 17.28 | 31.34 | 47.11 |
| Dy | 15.23 | 26.44 | 37.57 |
| Ho | 8.24 | 30.96 | 76.27 |
| Er | 6.90 | 27.20 | 67.95 |
| Tm | 4.48 | 31.34 | 90.17 |
| Lu | 6.95 | 26.19 | 64.68 |
| Actinide | | | |
| Am | 19.04 | 21.84 | 9.29 |
| Cm | 18.62 | 22.51 | 13.01 |
| Bk | 23.22 | 29.16 | 20.04 |
| Cf | 21.09 | 27.07 | 20.08 |
| Es | 23.81 | 31.05 | 24.31 |

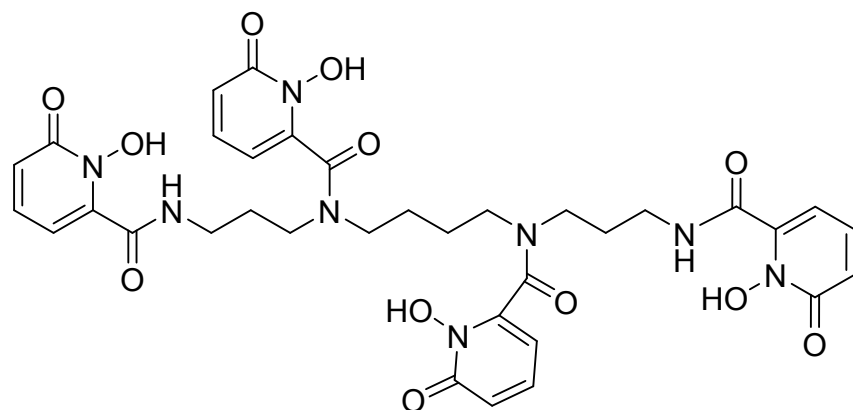
Figure S1. Structure of 3,4,3-LI(1,2-HOPO).

Figure S2. The pH corrected distribution ratio of the lanthanides Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu with 0.5024 M HC301 at an average pC_{H^+} of 4.46. The value for n_{H^+} (1.13) was obtained from radiotracer experiments with Eu.

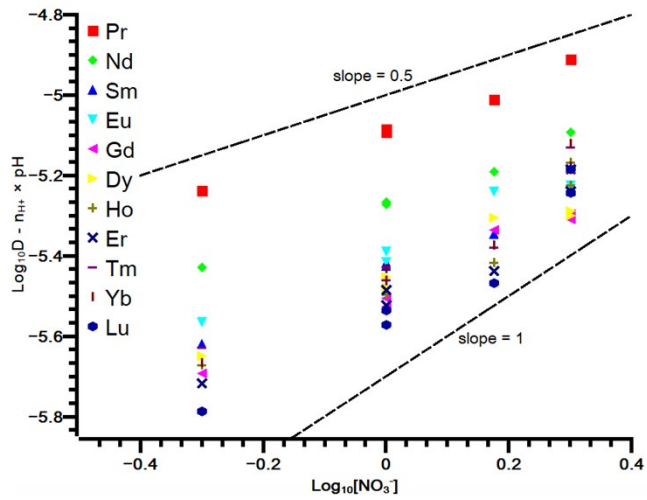
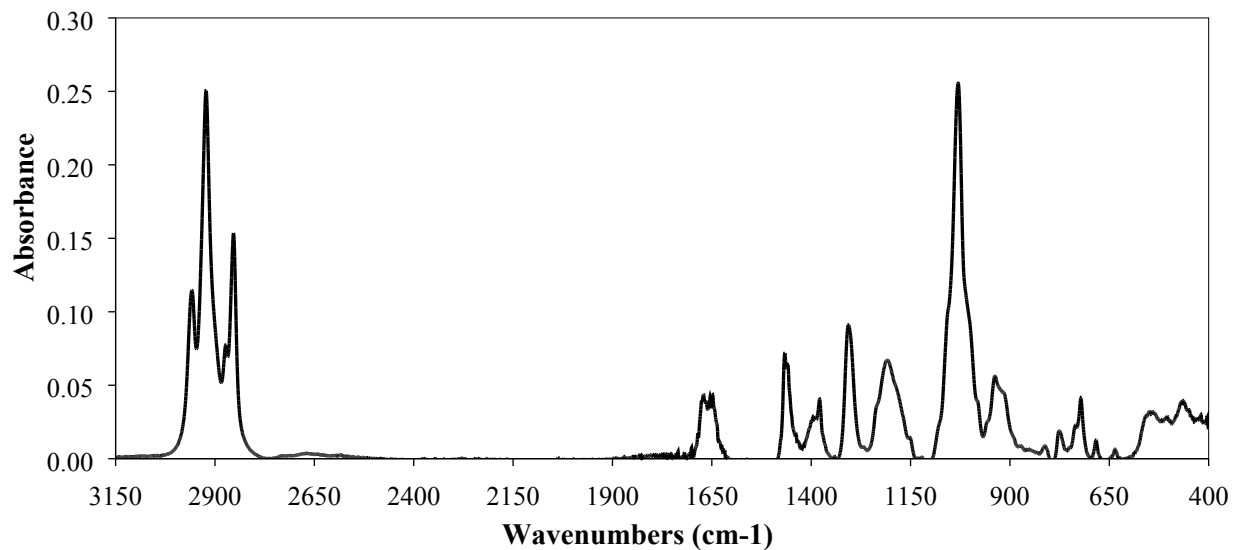


Figure S3. FTIR spectra of 20% tributyl phosphate (TBP) dissolved in n-dodecane following contact with 15 M HNO₃. The TBP organic phase contains 0.17 M H₂O in this system. No broad -OH stretch around 3000 cm⁻¹ is observed. The band at 1648 cm⁻¹ is from the TBP·HNO₃ species and no -OH stretch around 3000 cm⁻¹ is observed. Water content was determined by Karl Fischer titration.



[1] Ferraro, J.R., Borkowski, M., Chiarizia, R. and McAlister, D.R., 2001. FT-IR spectroscopy of nitric acid in TBP/octane solution. *Solvent Extraction and Ion Exchange*, 19(6), pp.981-992.

Optimized Geometries.

Coordinates are representative of the optimized structures of all lanthanide and actinide complexes modeled.

Am(C301)₃

| | | | |
|----|-------------|-------------|-------------|
| C | -3.34540759 | -2.90041902 | 0.80716076 |
| S | 2.44053787 | -0.81160548 | -1.48082444 |
| Am | 0.17554057 | -0.00000000 | -0.00000000 |
| S | 2.44053787 | 0.81160548 | 1.48082444 |
| S | -0.27618505 | 2.42071506 | -1.38337778 |
| S | -1.75162280 | -1.42866993 | -1.48995462 |
| S | -1.75162280 | 1.42866993 | 1.48995462 |
| S | -0.27618505 | -2.42071506 | 1.38337778 |
| P | -1.71980314 | -2.82918494 | -0.00364666 |
| P | -1.71980314 | 2.82918494 | 0.00364666 |
| P | 3.59035078 | -0.00000000 | -0.00000000 |
| C | 4.68474461 | 1.27289595 | -0.69646039 |
| C | -1.44489696 | -4.47974795 | -0.71433944 |
| C | -3.34540759 | 2.90041902 | -0.80716076 |
| C | -1.44489696 | 4.47974795 | 0.71433944 |
| C | 4.68474461 | -1.27289595 | 0.69646039 |
| H | -3.32497382 | -3.67550359 | 1.58562711 |
| H | -4.10999205 | -3.14000985 | 0.05556288 |
| H | -3.56102288 | -1.92437908 | 1.25910754 |
| H | 5.31075974 | 1.68282731 | 0.10785318 |
| H | 4.07270692 | 2.07017125 | -1.13521300 |
| H | 5.31654123 | 0.81759495 | -1.47115287 |
| H | -0.47477649 | -4.49393937 | -1.22550142 |
| H | -2.24814063 | -4.69827238 | -1.43117171 |
| H | -1.45141463 | -5.22076609 | 0.09693026 |
| H | -3.32497382 | 3.67550359 | -1.58562711 |
| H | -4.10999205 | 3.14000985 | -0.05556288 |
| H | -3.56102288 | 1.92437908 | -1.25910754 |
| H | -0.47477649 | 4.49393937 | 1.22550142 |
| H | -2.24814063 | 4.69827238 | 1.43117171 |
| H | -1.45141463 | 5.22076609 | -0.09693026 |
| H | 5.31075974 | -1.68282731 | -0.10785318 |
| H | 4.07270692 | -2.07017125 | 1.13521300 |
| H | 5.31654123 | -0.81759495 | 1.47115287 |

Am(C301)₂(NO₃)

| | | | |
|---|-------------|-------------|-------------|
| O | -2.08009326 | -3.99843583 | 0.40082905 |
| S | 2.18503174 | -1.06214484 | -1.43257272 |

| | | | |
|----|-------------|-------------|-------------|
| Am | -0.22581121 | -0.33847483 | -0.18537492 |
| S | 1.81115292 | 0.61258194 | 1.47816941 |
| S | -0.42862827 | 2.02988095 | -1.69289553 |
| O | -2.07550158 | -1.98287868 | -0.49752654 |
| S | -2.12141053 | 1.27884741 | 1.11901539 |
| O | -0.40104486 | -2.61139321 | 0.76577400 |
| N | -1.54344889 | -2.90751348 | 0.22868136 |
| P | -1.61680622 | 2.75740601 | -0.20119486 |
| P | 3.12959341 | -0.00910651 | 0.04456802 |
| C | 3.97320927 | 1.43349830 | -0.67198059 |
| H | 4.94116695 | -0.43405572 | 1.57194302 |
| C | -3.11924119 | 3.49887800 | -0.90255620 |
| C | -0.75991216 | 4.09689564 | 0.67904529 |
| C | 4.43131120 | -1.02668117 | 0.80018601 |
| H | -3.67090351 | 2.73459940 | -1.46272703 |
| H | 0.16662852 | 3.70022558 | 1.11260115 |
| H | -1.41284028 | 4.47829379 | 1.47587948 |
| H | 4.49913692 | 1.97177275 | 0.12854954 |
| H | 3.22460969 | 2.08941724 | -1.13273979 |
| H | 4.69094063 | 1.09174139 | -1.42983871 |
| H | -0.52709858 | 4.90033821 | -0.03287213 |
| H | 5.14594848 | -1.32513548 | 0.02091284 |
| H | 3.97664751 | -1.91690877 | 1.25133182 |
| H | -2.83074773 | 4.32038971 | -1.57261928 |
| H | -3.73985718 | 3.88419863 | -0.08201920 |

Nd(C301)₃

| | | | |
|----|-------------|-------------|-------------|
| C | -3.43167915 | -3.09919259 | 0.62759237 |
| S | 2.37064894 | -0.65924721 | -1.55212679 |
| Nd | 0.08229736 | -0.00000000 | -0.00000000 |
| S | 2.37064894 | 0.65924721 | 1.55212679 |
| S | -0.50374026 | 2.31632678 | -1.53587528 |
| S | -1.68989403 | -1.59942057 | -1.54110284 |
| S | -1.68989403 | 1.59942057 | 1.54110284 |
| S | -0.50374026 | -2.31632678 | 1.53587528 |
| P | -1.73044472 | -2.92027327 | 0.01701285 |
| P | -1.73044472 | 2.92027327 | -0.01701285 |
| P | 3.52405082 | -0.00000000 | -0.00000000 |
| C | 4.61646956 | 1.33571405 | -0.56576223 |
| C | -1.23073930 | -4.56859465 | -0.55986451 |
| C | -3.43167915 | 3.09919259 | -0.62759237 |
| C | -1.23073930 | 4.56859465 | 0.55986451 |
| C | 4.61646956 | -1.33571405 | 0.56576223 |
| H | -3.44229504 | -3.82804748 | 1.44939736 |

| | | | |
|---|-------------|-------------|-------------|
| H | -4.07041458 | -3.44969504 | -0.19454435 |
| H | -3.78812902 | -2.12657711 | 0.98777975 |
| H | 5.24215518 | 1.66563980 | 0.27453171 |
| H | 4.00389783 | 2.17136438 | -0.92469667 |
| H | 5.24878762 | 0.95946486 | -1.38125829 |
| H | -0.20384353 | -4.51751827 | -0.94127244 |
| H | -1.91114049 | -4.88751262 | -1.36120420 |
| H | -1.28281311 | -5.27357326 | 0.28082098 |
| H | -3.44229504 | 3.82804748 | -1.44939736 |
| H | -4.07041458 | 3.44969504 | 0.19454435 |
| H | -3.78812902 | 2.12657711 | -0.98777975 |
| H | -0.20384353 | 4.51751827 | 0.94127244 |
| H | -1.91114049 | 4.88751262 | 1.36120420 |
| H | -1.28281311 | 5.27357326 | -0.28082098 |
| H | 5.24215518 | -1.66563980 | -0.27453171 |
| H | 4.00389783 | -2.17136438 | 0.92469667 |
| H | 5.24878762 | -0.95946486 | 1.38125829 |

Nd(C301)₂(NO₃)

| | | | |
|----|-------------|-------------|-------------|
| O | -1.99653200 | -3.46276900 | 0.05279800 |
| S | 2.32270100 | -0.52985600 | -1.54692900 |
| Nd | 0.05199000 | 0.12449100 | -0.00637000 |
| S | 2.27862100 | 0.40235400 | 1.69382900 |
| S | -0.79490500 | 2.19237700 | -1.72250200 |
| O | -1.30872800 | -1.66254000 | -1.02562600 |
| S | -1.59892900 | 1.82262600 | 1.53178000 |
| O | -0.79647600 | -1.92393400 | 1.08672400 |
| N | -1.39324500 | -2.39628400 | 0.03918500 |
| P | -1.84212400 | 2.96636000 | -0.14489100 |
| P | 3.45252400 | -0.16141200 | 0.11684000 |
| C | 4.66790300 | 1.13819400 | -0.23954900 |
| H | 5.02132300 | -1.42238700 | 1.43626400 |
| C | -3.60344300 | 3.07343800 | -0.56995500 |
| C | -1.29550500 | 4.66585900 | 0.18221900 |
| C | 4.40252700 | -1.64418100 | 0.55637100 |
| H | -3.98452600 | 2.06635800 | -0.77667500 |
| H | -0.23051000 | 4.65747500 | 0.44254100 |
| H | -1.88167700 | 5.07304900 | 1.01709400 |
| H | 5.28257500 | 1.30660800 | 0.65499000 |
| H | 4.13884200 | 2.06021500 | -0.50852600 |
| H | 5.30059700 | 0.81285400 | -1.07634700 |
| H | -1.45510000 | 5.27091900 | -0.72059000 |
| H | 5.04172100 | -1.92327000 | -0.29201000 |
| H | 3.70740000 | -2.46091800 | 0.78487900 |
| H | -3.71585000 | 3.70650700 | -1.46039800 |
| H | -4.14914400 | 3.51410300 | 0.27542200 |