Actinides

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Comparing the 2,2′-Biphenylenedithiophosphinate Binding of Americium with Neodymium and Europium

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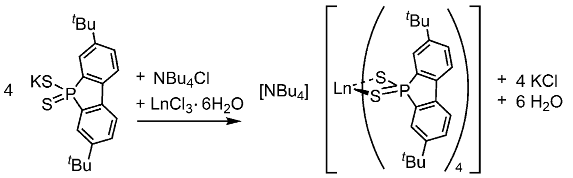
Abstract: *Advancing our understanding of the minor actinides (Am, Cm) versus lanthanides is key for developing advanced nuclear-fuel cycles. Herein, we describe the preparation of* $(NBu_4)Am[S_2P({}^tBu_2C_{12}H_6)]_4$ *and two isomorphous lanthanide complexes, namely one with a similar ionic radius (i.e.,* Nd^{III}*) and an isoelectronic one (*Eu^{III}*). The results include the first measurement of an Am–S bond length, with a mean value of 2.921(9) Å, by single-crystal X-ray diffraction. Comparison with the* Eu^{III} *and* Nd^{III} *complexes revealed subtle electronic differences between the complexes of* Am^{III} *and the lanthanides.*

The implementation of advanced nuclear-fuel cycles depends on developing methods to process spent fuel. One processing challenge is associated with separating the minor actinides (Am and Cm) from their 4f analogues. Owing to difficulties associated with conducting macroscopic experiments with Am and Cm, most insight into minor actinide/lanthanide separation chemistry comes from microchemical studies, where quantities are more conveniently determined by α-, β-, and γ-spectroscopy.[1] This leaves many macroscopic chemical concepts poorly understood as there are few structurally characterized trivalent pairs.[2]

Of the many separation strategies that have probability for success,[3] those that employ dithiophosphinate-based extractants are of particular interest. To advance our understanding of these dithiophosphinate separations, we have reported the synthesis of 4,4′-di-*tert*-butyl-2,2′-biphenylenedithiophosphinic acid, $HS_2P({}^tBu_2C_{12}H_6)$, whose aryl ring orientations were constrained through C–C linkages.[4,5] As $HS_2P({}^tBu_2C_{12}H_6)$ is air- and moisture-stable and soluble in common solvents, it provided an opportunity to compare and contrast the chemistry of minor actinide and lanthanide complexes with identical dithiophosphinate ligands. Herein, we compare the dithiophosphinate chemistry of Am^{III} ($5f^6$) with that of its electronic congener Eu^{III} ($4f^6$) and a size-matched 4f analogue, Nd^{III} (the ionic radii for Am^{III} and Nd^{III} are 1.109 and 1.108 Å).[2k,6,7] The isolation of the tetrakis(4,4′-di-*tert*-butyl-2,2′-biphenylenedithiophosphinato)metal(III) anions, $M[S_2P({}^tBu_2C_{12}H_6)]_4{}^{1-}$ (M = Am, Nd, or Eu), enabled the first single-crystal measurement of an Am–S bond distance. Moreover, the structural results, alongside the UV/Vis and fluorescence data, provocatively suggested that the $Am^{III}–S_2PR_2$ interaction is distinct from $Ln–S_2PR_2$ bonds within analogous environments.

The $(NBu_4)Ln[S_2P({}^tBu_2C_{12}H_6)]_4$ (Ln = Nd, Eu) complexes were prepared by salt metathesis reactions of $KS_2P({}^tBu_2C_{12}H_6)$ (potassium 4,4′-di-*tert*-butyl-2,2′-biphenylenedithiophosphinate),[4] with hydrated europium and neodymium trichlorides, $LnCl_3{\cdot}6\,H_2O$ (Ln = Eu, Nd), followed by addition of tetrabutylammonium chloride, NBu_4Cl [Eq. (1)]. As these synthetic procedures were robust and routinely provided single crystals on large (0.1 g) and small (> 0.01 g) scales, it seemed reasonable that similar methods would successfully afford an americium analogue. The importance of scaling down these reactions cannot be overstated as small-scale methods were necessitated by our limited inventory of ^{243}Am and the radioactivity associated with this isotope ($t_{1/2}$ = 7370(40) years). As anticipated, the salt metathesis reaction generated $(NBu_4)Am[S_2P({}^tBu_2C_{12}H_6)]_4$ (Scheme 1). The synthesis started by dissolving AmO_2 in aqueous HCl (6 M), upon which Am^{IV} was reduced to Am^{III}. The resulting Am^{III} solution was evaporated to a soft dryness, which left a peach-colored residue. The residue was suspended in ethanol and treated with $KS_2P({}^tBu_2C_{12}H_6)$ and NBu_4Cl.



(1)

For all complexes, crystalline blocks were obtained by slow evaporation of ethanol solutions. Figure 1 shows a thermal ellipsoid plot of $Am[S_2P({}^tBu_2C_{12}H_6)]_4{}^{1-}$. The structural metrics of the isomorphous $(NBu_4)M[S_2P({}^tBu_2C_{12}H_6)]_4$ (M =

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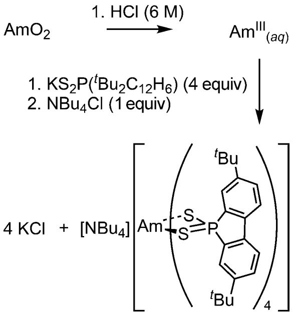


Scheme 1. Synthesis of $(NBu_4)Am[S_2P(^tBu_2C_{12}H_6)]_4$.

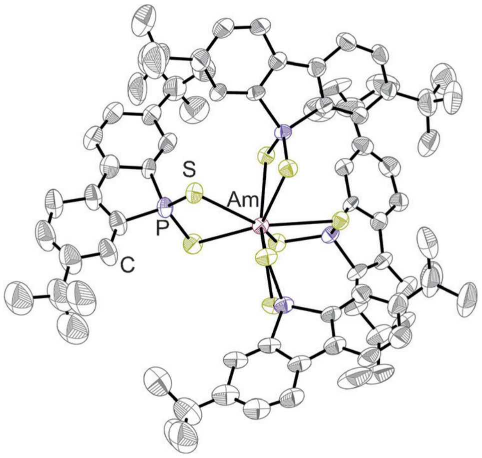


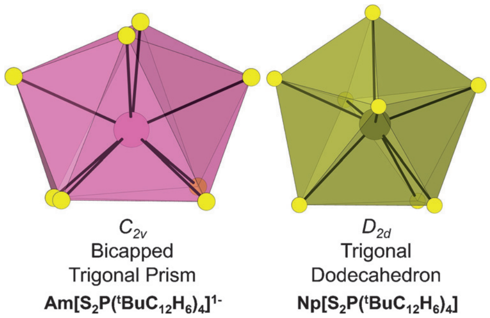
Figure 1. Thermal ellipsoid plot of $(NBu_4)Am[S_2P(^tBu_2C_{12}H_6)]_4$. Thermal ellipsoids set at 30% probability. NBu_4^{1+} and hydrogen atoms omitted for clarity.

Table 1: Average bond lengths and angles (with calculated standard errors)[9] in $(NBu_4)M[S_2P(^tBu_2C_{12}H_6)]_4$.

Average bond lengths [Å] and angles [°]	Nd	Eu	Am
M−S	2.941(8)	2.910(9)	2.921(9)
M−P	3.525(8)	3.498(8)	3.52(1)
S-M-S	68.6(5)	69.1(5)	68.3(3)
S-P-S	112.1(6)	111.4(6)	111.4(8)

Am, Eu, or Nd; Table 1) complexes indicated that the ligand geometries were different from those previously reported for the analogous +4 actinide compounds, $An^{IV}[S_2P(^tBu_2C_{12}H_6)]_4$ (An^{IV} = U, Np).[4] Raymond's Shape8 routine showed that the eight inner-sphere sulfur atoms for $M^{III}[S_2P(^tBu_2C_{12}H_6)]_4^{1-}$ (M = Eu, Nd, Am) form a distorted bicapped trigonal prism with approximate C_{2v} symmetry (Scheme 2).[8] In contrast, the +4 actinides adopted a distorted trigonal dodecahedral geometry with approximate D_{2d} symmetry.

The $Am[S_2P(^tBu_2C_{12}H_6)]_4^{1-}$ structure enabled the Am−S distance to be measured for the first time by single-crystal X-ray diffraction. The Am−S bond lengths varied by approximately 0.1 Å and ranged from 2.887(4) to 2.969(4) Å. Similar ranges were observed in the lanthanide structures. The Am^{III} bond lengths agree well with previously reported EXAFS data for Am^{III} extracted with bis(2,4,4-trimethylpentyl)dithiophosphinic acid, $HS_2P[C_8H_{17}]_2$ (Cyanex 301), into kerosene.[10] A plot of the mean M−S bond lengths in the $M[S_2P(^tBu_2C_{12}H_6)]_4^{x-}$ complexes (M = Eu, Nd, or Am: $x = 1$; M = U, Np: $x = 0$) versus the metal ionic radii[2k,6] (Figure 2) showed a linear relationship for Eu^{III}, Nd^{III}, U^{IV}, and Np^{IV}. The data was fit with a line whose slope approached unity, 0.89(2), and whose y intercept [1.95(2) Å] was approximately equal to the S^{2-} ionic radius (1.84 Å).[6] The average Am−S distance of 2.921(9) Å (uncertainty reported as error of the mean)[9] was 0.02 Å shorter than expected from this linear relationship. Plotting the normalized distribution of bond lengths against the observed M−S distances (M = Am^{III}, Nd^{III}; inset) demonstrates how the range of bond lengths varied as a function of metal identity. For example, replacing Nd^{III} with Am^{III} shifted the M−S distances—as a group—to shorter values by approximately 0.06 Å. While it is tempting to attribute the slightly shorter Am−S bond lengths to increased covalency, we refrained from doing so as the structural deviations were only marginally relevant. Instead, these results serve as motivation for future S K-edge X-ray absorption spectrosco-



Scheme 2. The first coordination environments of $Am[S_2P(^tBu_2C_{12}H_6)]_4^{1-}$ and $Np[S_2P(^tBu_2C_{12}H_6)]_4$.

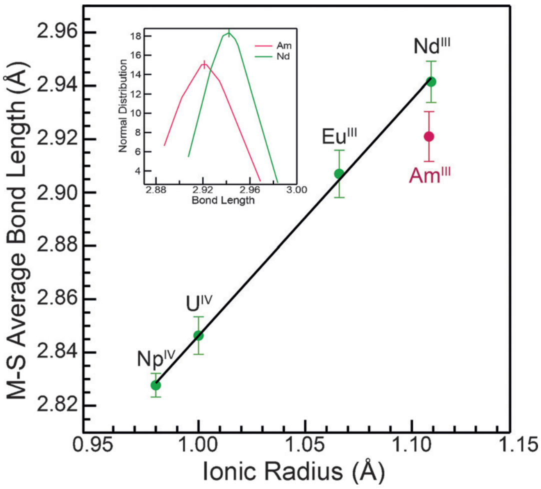


Figure 2. The M−S average bond lengths in $(NBu_4)M^{III}[S_2P(^tBu_2C_{12}H_6)]_4$ (M = Eu, Nd, Am) and $M^{IV}[S_2P(^tBu_2C_{12}H_6)]_4$ (M = U, Np).[4] Inset: Normal distribution of bond lengths versus the M−S bond length (M = Am, Eu).

py (XAS) measurements to determine the degree of S 3p and Am 5f/6d mixing.

Absorption spectra were recorded for single crystals of $M^{III}[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ (M = Eu, Nd, or Am; Figure 3). All spectra showed intense peaks at high energies, likely associated with charge-transfer transitions. For Nd^{III} and Am^{III}, weak, Laporte-forbidden f→f transitions were also present.[11] In contrast, for $Eu[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$, analogous transitions were engulfed in the high-energy charge transfer band, as observed previously for $(NEt_4)Eu[S_2P(C_6H_5)_2]_4$.[12]

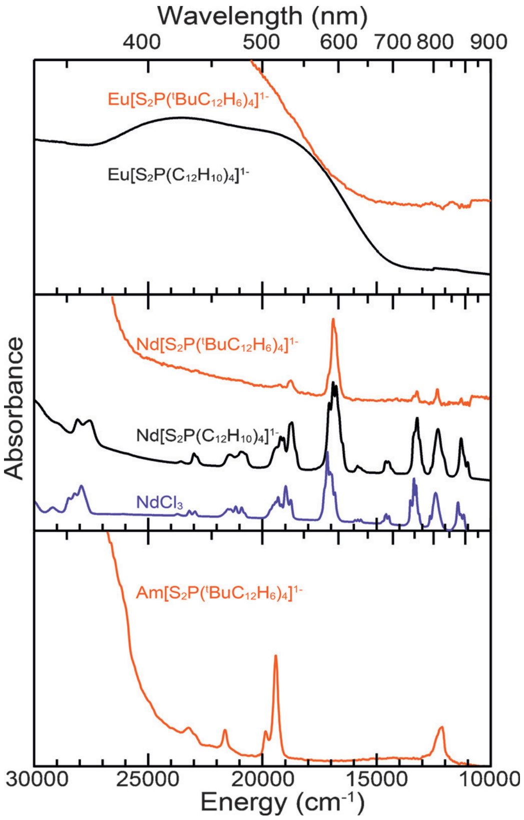


Figure 3. UV/Vis/NIR absorption spectra of single crystals of $(NBu_4)M[S_2P({}^tBu_2C_{12}H_6)]_4$ (M = Eu, Nd, Am; orange traces), $[Z]\{Ln[S_2P(C_6H_5)_2]_4\}$ (Ln = Eu, Z = PPh_4; Nd, Z = NEt_4; black traces), and $NdCl_3$ (purple trace). Spectra obtained from single crystals of $M[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ were recorded in transmission mode whereas the $Ln[S_2P(C_6H_5)_2]_4^{1-}$ and $LnCl_3$ data were acquired from powders by diffuse reflectance spectroscopy.

The absorption spectra of $Nd[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$, $(NEt_4)Nd[S_2P(C_6H_5)_2]_4$, and $NdCl_3$ are compared in Figure 3.[12] These spectra were similar and showed characteristic Nd^{III} 4f→4f transitions. Peaks were assigned based on previous interpretations and described from the perspective of the free ion.[11] We attributed the visible transitions to excitations from the Nd^{III} ${}^4I_{9/2}$ ground state to ${}^4G_{7/2}$, ${}^4G_{5/2}$, and ${}^2H_{9/2}$ excited states. Although a slight bathochromic shift (ca. 1 to 10 nm) was observed upon moving from $NdCl_3$ to $Nd[S_2P(C_6H_5)_2]_4^{1-}$, the $Nd[S_2P(C_6H_5)_2]_4^{1-}$ and $Nd[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ spectra were nearly superimposable. The similar energies for the 4f→4f transitions suggested that the ligand field contributions were small for $Nd[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$, $Nd[S_2P(C_6H_5)_2]_4^{1-}$, and $NdCl_3$.

The absorption spectrum of $Am[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ contained weak and narrow peaks at 428, 435, 461, 503, 514, and 818 nm, which were assigned to 5f→5f transitions (Figure 3). In accordance with previous interpretations,[13] the spectrum of $Am[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ involved excitations from the Am^{III} ${}^7F_0'$ ground state to the ${}^5H_4'$, ${}^2G_2'$, ${}^5D_2'$, ${}^5L_6'$, ${}^7F_6'$, and ${}^7F_4'$ excited states. While this interpretation was also described in terms of the free ion, all of the Am^{III} term symbols include a prime mark (′) as a reminder to treat the actinides using an intermediate coupling scheme. Under this designation, the orbital and spin angular momentum eigenvalues *L* and *S* are no longer "good" quantum numbers owing to the effects of *j–j* coupling.[13] The $Am[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ 5f→5f peak energies and line shapes substantially differed (> 100 nm) from those of other americium compounds, such as $Am(C_5H_5)_3$,[13b] AmX_3 (X = Cl, Br, I),[13a] $Am_2(HPO_3)_3(H_2O)$,[2k] and $Am[B_9O_{13}(OH)_4]\cdot H_2O$.[2g] Overall, these results suggested that the ligand field exerts a greater influence on the electronic structure of Am^{III} than for 4f ions, the latter exhibiting spectra that are essentially invariant from compound to compound (see above).

The luminescence spectra of single crystals of $(AsPh_4)S_2P({}^tBu_2C_{12}H_6)$ (prepared previously),[4] $Eu[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$, $Nd[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$, and $Am[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ are shown in Figure 4. The $S_2P({}^tBu_2C_{12}H_6)^{1-}$ free ligand luminesced when excited at $\lambda = 365$ and 420 nm. This ligand-based fluorescence persisted upon complexation with f-block elements and appeared alongside characteristic metal-based emission lines. For example, $Eu[S_2P({}^tBu_2C_{12}H_6)]^{1-}$ showed strong red emission with peaks centered at $\lambda = 590$, 612, 651, and 700 nm. From the free ion perspective, these features can be described as arising from relaxations of the ${}^5D_0$ state to the ${}^7F_1$, ${}^7F_2$, ${}^7F_3$, and ${}^7F_4$ states, respectively.[14]

Metal-based luminescence from $Nd[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ and $Am[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ was less intense than that from the Eu^{III} analogue. For $Nd[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$, excitation at $\lambda = 365$ and 420 nm generated a ${}^4F_{3/2}$ excited state that relaxed to the ${}^4I_{9/2}$ ground state by emission near $\lambda = 880$ nm.[15] Unfortunately, limitations associated with our spectrometer inhibited recording the complete spectrum, and the emission peak was only partially observed. The $Am[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ emission spectrum provided a rare example of americium-based luminescence. The spectrum contained an emission peak at $\lambda = 700$ nm and a weaker peak at 855 nm. The assignments of these peaks were based on interpretations of the limited number of other americium emission spectra.[2o,16] These features were attributed to relaxations from the ${}^5D_1'$ excited state to the ${}^7F_1'$ and ${}^7F_2'$ ground states, respectively. Additionally, a small feature near $\lambda = 600$ nm was also associated with americium-based emission, specifically the ${}^5D_1' \rightarrow {}^7F_0'$ transition.

Recycling the ${}^{243}Am$ sample for future studies was carried out using variations of published methods.[17] This involved digesting $Am[S_2P({}^tBu_2C_{12}H_6)]_4^{1-}$ with aqua regia in a sealed autoclave at 200 °C and subsequent purification using cation exchange chromatography. Samples were loaded onto the

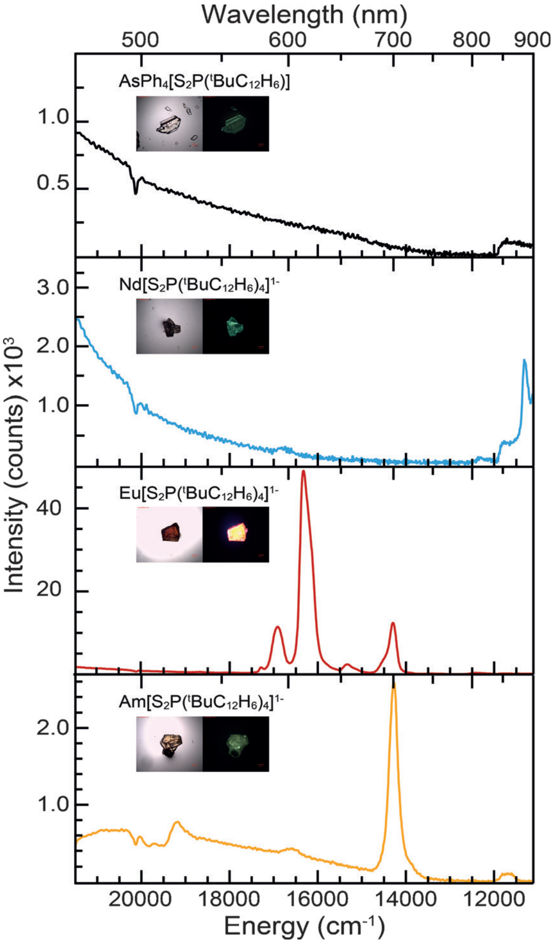


Figure 4. UV/Vis/NIR luminescence spectra of single crystals of (AsPh$_4$)[S$_2$P(^{t}Bu$_2$C$_{12}$H$_6$)]$_4$ (black), and (NBu$_4$)M[S$_2$P(^{t}Bu$_2$C$_{12}$H$_6$)]$_4$ (M = Eu: red; Nd: blue; Am: green). The visible colors of AsPh$_4$, Nd, and Am salts arise from ligand-based emission.

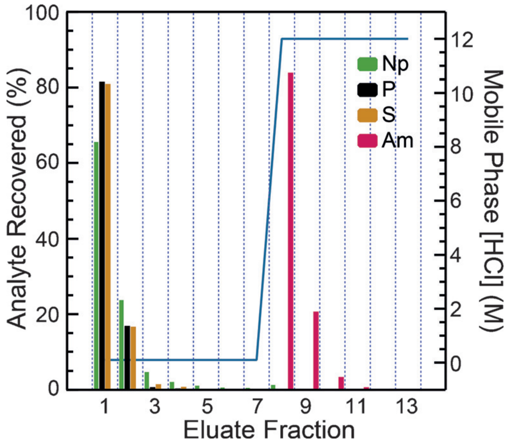


Figure 5. Representative elution profile of the americium recovery process using AG50W-X8 (100 to 200 mesh). Analyte recovery (in %; left axis) and the HCl concentration (in M; right axis, blue trace) in the mobile phase were plotted against the eluate fraction number. The amounts of ^{239}Np (green) and ^{243}Am (red) were quantified by γ-spectroscopy while S (yellow) and P (black) were measured by ICP-AES. Fraction 1 represents the load, fractions 2–7 are washes (HCl 0.1 M), and fractions 8–13 correspond to ^{243}Am elution (HCl 12 M).

column in dilute HCl, washed with HCl (0.1M), and Am^{III} was eluted with concentrated HCl (Figure 5). The column effluent was analyzed by γ-spectroscopy and ICP-AES, which showed that the majority of the S, P, and ^{239}Np (^{243}Am daughter nuclide) contaminates were removed in the first eight fractions. Americium was recovered in greater than >99% yield and in high purity.

In conclusion, the complexes described herein have afforded a rarely available opportunity to explore how the chemical and physical properties vary as a result of the 5f or 4f metal identity (Am^{III}, Nd^{III}, and Eu^{III}). These comparisons revealed differences between isomorphous complexes that contained isoelectronic metals (Eu 4f^6, Am 5f^6) and 5f and 4f metals of nearly identical radii (Am^{III} and Nd^{III}). Furthermore, the study enabled the first measurement of an Am–S bond length by single-crystal X-ray diffraction. The structural, optical absorption, and luminescence studies subtly suggested that the biphenylenedithiosphosphinate ligand field influenced the Am^{III} electronic structure to a greater extent than for lanthanide systems. These dithiophosphinate complexes constitute an excellent test bed for theoretical and spectroscopic studies to advance our understanding of f-element electronic structure and bonding. It is our hope that the anticipated advances in f-element chemistry will further our fundamental understanding in support of developing advanced nuclear-fuel cycles.

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[1] a) R. M. Diamond, K. Street, G. T. Seaborg, *J. Am. Chem. Soc.* **1954**, *76*, 1461; b) H. L. Smith, D. C. Hoffman, *J. Inorg. Nucl. Chem.* **1956**, *3*, 243; c) G. R. Choppin, *J. Less-Common Met.* **1983**, *93*, 323; d) K. L. Nash, R. E. Barrans, R. Chiarizia, M. L. Dietz, M. P. Jensen, P. G. Rickert, B. A. Moyer, P. V. Bonnesen, J. C. Bryan, R. A. Sachleben, *Solvent Extr. Ion Exch.* **2000**, *18*, 605; e) M. P. Jensen, A. H. Bond, *J. Am. Chem. Soc.* **2002**, *124*, 9870; f) M. Miguirditchian, D. Guillaneux, D. Guillaumont, P. Moisy, C. Madic, M. P. Jensen, K. L. Nash, *Inorg. Chem.* **2005**, *44*, 1404; g) D. Girnt, P. W. Roesky, A. Geist, C. M. Ruff, P. J. Panak, M. A. Denecke, *Inorg. Chem.* **2010**, *49*, 9627.

[2] a) J. H. Burns, J. R. Peterson, *Acta Crystallogr. Sect. B* **1970**, *26*, 1885; b) J. H. Burns, J. R. Peterson, J. N. Stevenson, *J. Inorg. Nucl. Chem.* **1975**, *37*, 743; c) J. H. Matonic, B. L. Scott, M. P. Neu, *Inorg. Chem.* **2001**, *40*, 2638; d) P. Lindqvist-Reis, C. Apostolidis, J. Rebizant, A. Morgenstern, R. Klenze, O. Walter, T. Fanghänel, R. G. Haire, *Angew. Chem. Int. Ed.* **2007**, *46*, 919; *Angew. Chem.* **2007**, *119*, 937; e) C. Apostolidis, B. Schimmelpfennig, N. Magnani, P. Lindqvist-Reis, O. Walter, R. Sykora, A. Morgenstern, E. Colineau, R. Caciuffo, R. Klenze, R. G. Haire, J. Rebizant, F. Bruchertseifer, T. Fanghänel, *Angew. Chem. Int. Ed.* **2010**, *49*, 6343; *Angew. Chem.* **2010**, *122*, 6487; f) A. E. Enriquez, J. H. Matonic, B. L. Scott, M. P. Neu, *Chem. Commun.* **2003**, 1892; g) M. J. Polinski, S. Wang, E. V. Alekseev, W. Depmeier, T. E. Albrecht-Schmitt, *Angew. Chem. Int. Ed.* **2011**, *50*, 8891; *Angew. Chem.* **2011**, *123*, 9053; h) M. J. Polinski, D. J. Grant, S. Wang, E. V. Alekseev, J. N. Cross, E. M. Villa, W. Depmeier, L. Gagliardi, T. E. Albrecht-Schmitt, *J. Am. Chem. Soc.* **2012**, *134*, 10682; i) M. J. Polinski, S. Wang, J. N. Cross, E. V. Alekseev, W. Depmeier, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2012**, *51*, 7859; j) M. J. Polinski, S. Wang, E. V. Alekseev, W. Depmeier, G. Liu, R. G. Haire, T. E. Albrecht-Schmitt, *Angew. Chem. Int. Ed.* **2012**, *51*, 1869; *Angew. Chem.* **2012**, *124*, 1905; k) J. N. Cross, E. M. Villa, S. Wang, J. Diwu, M. J. Polinski, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2012**, *51*, 8419; l) M. J. Polinski, K. A. Pace, J. Stritzinger, J. Lin, J. N. Cross, S. K. Cary, S. M. V. Cleve, E. V. Alekseev, T. E. Albrecht-Schmitt, *Chem. Eur. J.* **2014**, *20*, 9892; m) W. Runde, A. C. Bean, L. F. Brodnax, B. L. Scott, *Inorg. Chem.* **2006**, *45*, 2479; n) R. E. Sykora, Z. Assefa, R. G. Haire, T. E. Albrecht-Schmitt, *J. Solid State Chem.* **2004**, *177*, 4413; o) R. E. Sykora, Z. Assefa, R. G. Haire, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2005**, *44*, 5667; p) C. Tamain, B. Arab-Chapelet, M. Rivenet, X. F. Legoff, G. Loubert, S. Grandjean, F. Abraham, *Inorg. Chem.* **2016**, *55*, 51; q) S. K. Cary, M. Vasiliu, R. E. Baumbach, J. T. Stritzinger, T. D. Green, K. Diefenbach, J. N. Cross, K. L. Knappenberger, G. Liu, M. A. Silver, A. E. DePrince, M. J. Polinski, S. M. V. Cleve, J. H. House, N. Kikugawa, A. Gallagher, A. A. Arico, D. A. Dixon, T. E. Albrecht-Schmitt, *Nat. Commun.* **2015**, *6*, 6827.

[3] a) Z. Kolarik, *Chem. Rev.* **2008**, *108*, 4208; b) P. J. Panak, A. Geist, *Chem. Rev.* **2013**, *113*, 1199; c) M. J. Hudson, L. M. Harwood, D. M. Laventine, F. W. Lewis, *Inorg. Chem.* **2013**, *52*, 3414; d) Y. Zhu, J. Chen, R. Jiao, *Solvent Extr. Ion Exch.* **1996**, *14*, 61; e) C. Madic, M. J. Hudson, J.-O. Liljenzin, J.-P. Glatz, R. Nannicini, A. Facchini, Z. Kolarik, R. Odoj, *Prog. Nucl. Energy* **2002**, *40*, 523; f) B. Weaver, F. A. Kappelmann, *J. Inorg. Nucl. Chem.* **1968**, *30*, 263; g) M. Nilsson, K. L. Nash, *Solvent Extr. Ion Exch.* **2007**, *25*, 665.

[4] J. A. Macor, J. L. Brown, J. N. Cross, S. R. Daly, A. J. Gaunt, G. S. Girolami, M. T. Janicke, S. A. Kozimor, M. P. Neu, A. C. Olson, S. D. Reilly, B. L. Scott, *Dalton Trans.* **2015**, *44*, 18923.

[5] S. R. Daly, J. M. Keith, E. R. Batista, K. S. Boland, D. L. Clark, S. A. Kozimor, R. L. Martin, *J. Am. Chem. Soc.* **2012**, *134*, 14408.

[6] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *55*, 5135.

[7] F. H. David, *J. Less-Common Met.* **1986**, *121*, 29.

[8] a) A. E. Gorden, J. Xu, K. N. Raymond, *Chem. Rev.* **2003**, *103*, 4207; b) J. Xu, E. Radkov, M. Ziegler, K. N. Raymond, *Inorg. Chem.* **2000**, *39*, 4156.

[9] D. C. Harris in *Quantitative Chemical Analysis*, 8th ed., W. H. Freeman and Company, New York, **2010**, pp. 62–64.

[10] G. Tian, Y. Zhu, J. Xu, T. Hu, Y. Xie, *J. Alloys Compd.* **2002**, *334*, 86.

[11] K. Binnemans, C. Görller-Walrand, *Chem. Phys. Lett.* **1995**, *235*, 163.

[12] K. S. Boland, D. E. Hobart, S. A. Kozimor, M. M. MacInnes, B. L. Scott, *Polyhedron* **2014**, *67*, 540.

[13] a) R. G. Pappalardo, W. T. Carnall, P. R. Fields, *J. Chem. Phys.* **1969**, *51*, 1182; b) R. Pappalardo, W. T. Carnall, P. R. Fields, *J. Chem. Phys.* **1969**, *51*, 842.

[14] a) K. Binnemans, *Coord. Chem. Rev.* **2015**, *295*, 1; b) P. A. Tanner, *Chem. Soc. Rev.* **2013**, *42*, 5090.

[15] a) S. Yanagida, Y. Hasegawa, K. Murakoshi, Y. Wada, N. Nakashima, T. Yamanaka, *Coord. Chem. Rev.* **1998**, *171*, 461; b) R. Janicki, A. Mondry, *Eur. J. Inorg. Chem.* **2013**, 3429.

[16] a) A. B. Yusov, *J. Radioanal. Nucl. Chem.* **1990**, *143*, 287; b) Z. Assefa, K. Kalachnikova, R. G. Haire, R. E. Sykora, *J. Solid State Chem.* **2007**, *180*, 3121; c) W. H. Runde, W. W. Schulz in *The Chemistry of the Actinide and Transactinide Elements* (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger), Springer Netherlands, Dordrecht, **2011**, p. 1265; d) M. Sturzbecher-Hoehne, P. Yang, A. D'Aleo, R. J. Abergel, *Dalton Trans.* **2016**, *45*, 9912.

[17] a) R. A. Penneman, T. K. Keenan in *The Radiochemistry of Americium and Curium*, Technical Information Center, U.S. Atomic Energy Commission, Washington, D.C., **1960**, p. 15; b) J. Kleinberg, *Collected Radiochemical and Geochemical Procedures*, LA-1721 5th ed., Los Alamos National Laboratory, Los Alamos, **1990**, p. 203.

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