



Figure S1. XANES spectra of each complex normalized to a unit edge step for HC272 (dashed line), HC302 (dotted line), and HC301 (solid line) for the (A) Nd L_3 , (B) Nd L_2 , (C) Sm L_3 , (D) Sm L_2 , and (E) Cm L_3 edges.

Preparation and Assay of the Actinide Stock Solutions. The ^{243}Am was obtained from a laboratory stock solution and chemically purified by fluoride precipitation followed by cation exchange chromatography on Biorad Dowex-50X2. Assay for radiochemical purity by α - and γ -spectroscopy gave an Am composition of 99.86 atom % ^{243}Am and 0.14 atom % ^{241}Am (with 0.0071 atom % ^{244}Cm). The specific activity was 4.65×10^8 dpm α /mg Am. Curium (96.766 atom % ^{248}Cm , 3.161 atom % ^{246}Cm , 0.057 atom % ^{245}Cm , and 0.016 atom % ^{247}Cm), obtained from the Oak Ridge National Laboratory Radiochemical Engineering Development Center as CmO_2 , was dissolved in sufficient HCl to make a 0.035 M Cm(III)/0.1 M HCl stock solution. The specific activity of the curium was 3.47×10^7 dpm α /mg Cm.

Estimation of the Expected Covalent Contraction in An-S Bonds Relative to Ln-S Bonds in HC301 Complexes. Our approach to estimating the expected contraction in the An-S bond lengths relates the free energy of An/Ln separation observed for HC301 complexes to the free energy of intra-lanthanide separations and the differences in Ln(III) cation radii. The estimate is based on primarily ionic bonds, but it has been shown that empirical bond strength-bond length correlations developed for primarily ionic bonds can also be applied to more covalent bonds.¹ In making this comparison, we assume that the degree of covalence does not change significantly across the Ln series, that the shape and depth of the potential well of *f*-element ionic and covalent bonds for these complexes are similar, and that steric constraints imposed by the ligands do not have an important effect on the metal-ligand bond lengths for the metals ions and ligands used in the comparison. This approach also uses the free energy of separation as a proxy for the more meaningful enthalpy of separation.

The free energy of separation by HC301 reported for the separation of Am(III) and Nd(III) is -19.4 kJ/mol.² Using simple ratios, and correcting for the 0.008 Å difference in the Nd(III) and Am(III) radii³ one can estimate the covalent contraction of the Am-S bonds relative to the Nd-S bonds, $\Delta r_{\text{covalent}}$, from the equations

$$\Delta r_{Am-Nd} = \Delta G_{Am-Nd} \frac{\Delta r_{Ln-Ln'}}{\Delta G_{Ln-Ln'}} \quad (1S)$$

and

$$\Delta r_{covalent} = \Delta r_{Am-Nd} - 0.008 \text{ \AA} \quad (2S)$$

where Ln and Ln' are the two lanthanide cations used for comparison, Δr is the difference in hexacoordinate Shannon crystal radii of the two cations, and ΔG is the difference in the free energy of extraction of the two cations. The free energy of Ce/La separation is -3.1 kJ/mol,⁴ while the difference in the radii of hexacoordinate La(III) and Ce(III) is 0.022 Å,³ which gives $\Delta r_{covalent} = 0.13 \text{ \AA}$. Another way of looking at the calculation is that the thermodynamic strength of the Am(III)-HC301 complex is the same as would be expected for a Ln(III)-HC301 complex with a cation crystal radius of 0.985 Å rather than the 1.115 Å reported for hexacoordinate Am(III).³ Similar calculations using $\Delta G_{Ln-Ln'}$ from HC272⁵ and HC302⁶ complexes give similar results for the expected covalent contraction of the Am-S bonds in the Am-C301 complex (0.14 Å and 0.09 Å, respectively) even though HC272 and HC302 contain oxygen donor atoms and adopt different coordination geometries than HC301 complexes. Taken together with the 0.07 - 0.11 Å contraction in the bond lengths of the uranium- π -acid ligand complexes reported by Brennan,⁷ 0.1 Å appears to be a reasonable upper limit for the covalent contraction of an An-S bond as compared to a Ln-S bond when variations in the ionic radii of the An(III) and Ln(III) are considered.

When equations 1S and 2S are coupled with the results of quantum mechanical calculations on $\text{Ln}(\text{S}_2\text{PMe}_2)_3$ complexes,⁸ a much smaller An-S bond contraction is obtained: $\Delta r_{covalent} = 0.024 \text{ \AA}$. Moreover, it has been reported that $\Delta r_{covalent} \approx 0.04 \text{ \AA}$ in compounds with Zn^{2+} , Cd^{2+} , In^{3+} , and Tl^+ , which are closed shell d^{10} cations that form more covalent bonds than do either Ln(III) or An(III) cations, when a softer

sulfide ligand replaces a harder oxide ligand.³ Taken together, these results indicate a reasonable lower bound on An-S bond contraction of ca. 0.02 Å. This value approaches the experimental uncertainty in bond distances determined by EXAFS.

- (1) Brown, I. D.; Shannon, R. D. *Acta Cryst.* **1973**, *A29*, 266.
- (2) Zhu, Y.; Xu, J.; Chen, J.; Chen, Y. *J. Alloys Compd.* **1998**, 271-273, 742.
- (3) Shannon, R. D. *Acta Cryst.* **1976**, *A32*, 751.
- (4) Chen, J.; Zhu, Y.; Jiao, R. *Sep. Sci. Technol.* **1996**, *31*, 2723.
- (5) Linrud, C., Unpublished results.
- (6) Li, D.; Luo, A.; Wang, C.; Yuan, M. In *Value Adding Solvent Extraction*; Shallcross, D. C.; Paimin, R.; Prvcic, L. M.; Eds.; University of Melbourne: Melbourne, Australia, 1996, pp 165-170.
- (7) Brennan, J. G.; Stults, S. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chim. Acta* **1987**, *139*, 201.
- (8) Boehme, C.; Wipff, G. *Chem. Eur. J.* **2001**, *7*, 1398.