



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<sub>3</sub>, (B) Nd L<sub>2</sub>, (C) Sm L<sub>3</sub>, (D) Sm L<sub>2</sub>, and (E) Cm L<sub>3</sub> edges.

**Preparation and Assay of the Actinide Stock Solutions.** The  $^{243}\text{Am}$  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  $\alpha$ - and  $\gamma$ -spectroscopy gave an Am composition of 99.86 atom %  $^{243}\text{Am}$  and 0.14 atom %  $^{241}\text{Am}$  (with 0.0071 atom %  $^{244}\text{Cm}$ ). The specific activity was  $4.65 \times 10^8$  dpm  $\alpha$ /mg Am. Curium (96.766 atom %  $^{248}\text{Cm}$ , 3.161 atom %  $^{246}\text{Cm}$ , 0.057 atom %  $^{245}\text{Cm}$ , and 0.016 atom %  $^{247}\text{Cm}$ ), obtained from the Oak Ridge National Laboratory Radiochemical Engineering Development Center as  $\text{CmO}_2$ , 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  $3.47 \times 10^7$  dpm  $\alpha$ /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.<sup>1</sup> 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.<sup>2</sup> Using simple ratios, and correcting for the 0.008 Å difference in the Nd(III) and Am(III) radii<sup>3</sup> 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,  $\Delta r$  is the difference in hexacoordinate Shannon crystal radii of the two cations, and  $\Delta G$  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,<sup>4</sup> while the difference in the radii of hexacoordinate La(III) and Ce(III) is 0.022 Å,<sup>3</sup> 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).<sup>3</sup> Similar calculations using  $\Delta G_{Ln-Ln'}$  from HC272<sup>5</sup> and HC302<sup>6</sup> 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- $\pi$ -acid ligand complexes reported by Brennan,<sup>7</sup> 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 Ln(S<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub> complexes,<sup>8</sup> 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<sup>2+</sup>, Cd<sup>2+</sup>, In<sup>3+</sup>, and Tl<sup>+</sup>, 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.<sup>3</sup> 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.

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