J|A|C|S
ARTICLES

Comparison of Covalency in the Complexes of Trivalent Actinide and Lanthanide Cations

Mark P. Jensen* and Andrew H. Bond†

Contribution from the Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439

Received December 21, 2001

Abstract: The complexes of trivalent actinide (Am(III) and Cm(III)) and lanthanide (Nd(III) and Sm(III)) cations with bis(2,4,4-trimethylpentyl)phosphinic acid, bis(2,4,4-trimethylpentyl)monothiophosphinic acid, and bis(2,4,4-trimethylpentyl)dithiophosphinic acid in *n*-dodecane have been studied by visible absorption spectroscopy and X-ray absorption fine structure (XAFS) measurements in order to understand the chemical interactions responsible for the great selectivity the dithiophosphinate ligand exhibits for trivalent actinide cations in liquid−liquid extraction. Under the conditions studied, each type of ligand displays a different coordination mode with trivalent f-element cations. The phosphinate ligand coordinates as hydrogen-bonded dimers, forming $M(HL_2)_3$. Both the oxygen and the sulfur donor of the monothiophosphinate ligand can bind the cations, affording both bidentate and monodentate ligands. The dithiophosphinate ligand forms neutral bidentate complexes, ML_3, with no discernible nitrate or water molecules in the inner coordination sphere. Comparison of the Cm(III), Nd(III), and Sm(III) XAFS shows that the structure and metal−donor atom bond distances are indistinguishable within experimental error for similarly sized trivalent lanthanide and actinide cations, despite the selectivity of bis(2,4,4-trimethylpentyl)dithiophosphinic acid for trivalent actinide cations over trivalent lanthanide cations.

Introduction

Although lanthanide-like actinide(III) species have been reported for all of the actinides, the chemical similarity of the lanthanide (Ln) and actinide (An) elements becomes most apparent for actinides heavier than Pu, where the energy and spatial extension of the actinide 5f orbitals is sufficiently smaller than the energies and spatial extension of the 6d, 7s, and 7p orbitals to make the trivalent oxidation state the most stable oxidation state in aqueous solution (except for No). Because they are hard cations of identical charge and similar ionic radii, the coordination chemistry of Ln(III) and An(III) cations with hard donor ligands is nearly indistinguishable.[1] These similarities make the chemical separation of Am(III) and Cm(III) (minor products of the neutron irradiation of U or Pu) from the light lanthanides (abundant products of U or Pu fission) a difficult problem in nuclear waste management.[2]

One important solution to the problem of Ln(III)/An(III) separations exploits the ability of ligands containing donor atoms that are soft compared to oxygen (e.g., N, S, or Cl^-) to discriminate between similarly sized Ln(III) and An(III),[2−5] an effect attributed to a modest enhancement of covalency in actinide−ligand bonding as compared to the lanthanides.[3,5,14] The origin and magnitude of the covalent contribution to f-element bonding remains a subject of continuing scientific investigation, and the s,[7] p,[8,9] d,[10,11] and f orbitals[3,9,12] all have been suggested as contributors to covalent bonding in various f-element compounds.

Of all the soft donor ligands studied for Ln(III)/An(III) separations, organodithiophosphinates ($R_2PS_2^-$) have shown the greatest selectivity for An(III) over Ln(III), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HC301, Figure 1), the major component of the commercial extractant Cyanex 301,[13]

---

[*] Address correspondence to this author. E-mail: mjensen@anl.gov.

[†] Present address: PG Research Foundation, 8205 S. Cass Ave., Suite 111, Darien, IL 60561.

(1) Choppin, G. R. *J. Less-Common Met.* **1983**, *93*, 323.

(2) Nash, K. L. *Solvent Extr. Ion Exch.* **1993**, *11*, 729.

(3) Diamond, R. M.; Street, K., Jr.; Seaborg, G. T. *J. Am. Chem. Soc.* **1954**, *76*, 1461.

(4) (a) Weaver, B.; Kappelmann, F. A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 263. (b) Muscatello, A. C.; Horwitz, E. P.; Kalina, D. G.; Kaplan, L. *Sep. Sci. Technol.* **1982**, *17*, 859. (c) Smith, B. F.; Jarvinen, G. D.; Miller, G. G.; Ryan, R. R.; Peterson, E. J. *Solvent Extr. Ion Exch.* **1987**, *5*, 895. (d) Ensor, D. D.; Jarvinen, G. D.; Smith, B. F. *Solvent Extr. Ion Exch.* **1988**, *6*, 439. (e) Zhu, Y. *Radiochim. Acta* **1995**, *68*, 95. (f) Hagström, I.; Spjuth, L.; Enarsson, Å.; Liljenzin, J. O.; Skålberg, M.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Cordier, P.-Y.; Hill, C.; Francois, N. *Solvent Extr. Ion Exch.* **1999**, *17*, 221. (g) Drew, M. G. B.; Iveson, P. B.; Hudson, M. J.; Liljenzin, J. O.; Spjuth, L.; Cordier, P.-Y.; Enarsson, Å.; Hill, C.; Madic, C. *J. Chem. Soc., Dalton Trans.* **2000**, 821.

(5) (a) Musikas, C.; Cuillerdier, C.; Livet, J.; Forchioni, A.; Chachaty, C. *Inorg. Chem.* **1983**, *22*, 2513. (b) Musikas, C. In *Proceedings of the International Symposium on Actinide/Lanthanide Separations*; Choppin, G. R., Navratil, J. D., Schulz, W. W., Eds.; World Scientific: Philadelphia, 1985; pp 19−30.

(6) Wietzke, R.; Mazzanti, M.; Latour, J.-M.; Pècaut, J. *J. Chem. Soc., Dalton Trans.* **2000**, 4167.

(7) Lewis, W. B.; Jackson, J. A.; Lemons, J. F.; Taube, H. *J. Chem. Phys.* **1962**, *36*, 694.

(8) Tatsumi, K.; Hoffman, R. *Inorg. Chem.* **1980**, *19*, 2656.

(9) Pyykkö, P.; Laakkonen, L. J.; Tatsumi, K. *Inorg. Chem.* **1989**, *28*, 1801.

(10) (a) Jørgensen, C. K. *Isr. J. Chem.* **1980**, *19*, 174. (b) Bursten, B. E.; Rhodes, L. F.; Strittmatter, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 2758. (c) Denning, R. G. *Struct. Bonding* **1992**, *79*, 215.

(11) Iversen, B. B.; Larsen, F. K.; Pinkerton, A. A.; Martin, A.; Darovsky, A.; Reynolds, P. A. *Inorg. Chem.* **1998**, *37*, 4559.

(12) Depaoli, G.; Russo, U.; Valle, G.; Grandjean, F.; Williams, A. F.; Long, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 5999.

10.1021/ja0178620 CCC: $22.00

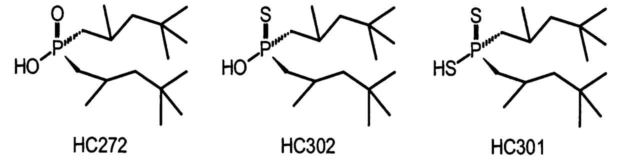

Figure 1. Derivatives of bis(2,4,4-trimethylpentyl)phosphinic acid used in this study.

is among the most selective. The equilibrium constant for the liquid−liquid extraction of Am(III) by HC301 in kerosene is 5900 times larger than that of Eu(III), the homologous lanthanide.[14] The importance of covalence in the Am−S bonds is evident[15] from the −25.6 kJ/mol difference between the enthalpies of Am(III) and Eu(III) extraction by HC301 into kerosene.[16]

The difference in metal−ligand bond lengths has been suggested as a relative measure of the degree of covalence in bonding, with stronger, more covalent bonds being shorter.[17,18] Thus, studies of the solution structures of Ln(III) and An(III) complexes could be used to examine the relative covalence of the metal−ligand interactions. Two structural manifestations of the greater thermodynamic stability of the An(III)−HC301 complexes are possible: more An−S bonds and shorter An−S bonds. We used measurements of the X-ray absorption fine structure (XAFS) and visible absorption spectroscopy to examine the solution structures of Ln(III) (Nd and Sm) and An(III) (^{243}Am and ^{248}Cm) complexes with a series of O- and S-substituted phosphinic acid ligands (Figure 1), bis(2,4,4-trimethylpentyl)phosphinic acid, bis(2,4,4-trimethylpentyl)monothiophosphinic acid (HC302), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid, to probe structural manifestations of enhanced covalence in An−S bonding. The f-element cations selected for this study have similar crystal radii (differing by ≤0.025 Å),[18] which reduces uncertainty introduced by cation radii corrections. The ligands employed in this work also permit an examination of changes in the solution stoichiometries of Ln(III) and An(III) complexes as the ligand donor arrays change from hard O donor to soft S donor sets.

Experimental Section

Sample Preparation. Solutions of the f-element complexes were prepared by extracting the appropriate Ln(III) or An(III) from 1.0 M NaNO$_3$/0.05 M (Na/H)OAc between $-\log [\mathrm{H}^+] = 3.0$ and 5.1 into *n*-dodecane solutions containing 1.0 M concentrations of 99% HC272, 97% HC302, or 99% HC301. The purification and assay of the reagents used and the general procedures for extraction have been described previously.[19] The metal ion concentration of each organic phase ($[\mathrm{M}]_{\mathrm{org}}$, Table 1) was determined spectrophotometrically using the Arsenazo III complex[20] (Nd and Sm) or by liquid scintillation counting with α/β discrimination (Am and Cm). Isotopic compositions of the actinide samples are given in the Supporting Information.

Spectroscopic Measurements. UV−visible absorption spectra of the organic phases were collected in solvent-welded 1.00 cm path length poly(methyl methacrylate) cuvettes (Am and Cm) or 1.000 cm path length quartz cuvettes (Nd) with a computer-controlled Cary-14 spectrophotometer (OLIS, Inc.).

Organic phases containing Nd or Sm for XAFS measurements were placed in X-ray fluorescence cells (SPEX Certiprep) with 7.5 μm Kapton film windows. The Cm samples in the poly(methyl methacrylate) cuvettes were heat-sealed in polyethylene bags. The resulting lanthanide and actinide samples were then mounted in separate sealed aluminum boxes outfitted with Kapton X-ray windows.

The BESSRC-CAT bending magnet beamline 12BM-B[21] at the Advanced Photon Source, with a Si⟨111⟩ double-crystal monochromator and a Pt mirror for harmonic rejection, was used to collect L$_2$ (Nd and Sm) and L$_3$ (Nd, Sm, and Cm) X-ray absorption spectra in the fluorescence mode using a flow-type fluorescent ion chamber detector (EXAFS Co.) without filters. The monochromator energy was calibrated against the first inflection point of the K-edges of a Nb foil (18.986 keV) or an Fe foil (7.112 keV). The fluorescence detector was filled with Ar for Nd and Sm and with Xe for Cm. Lanthanide spectra were collected with a focused 1.5 mm^2 point beam, while Cm spectra were collected with an unfocused 0.5 mm × 16 mm beam. Four (Nd and Cm) or six (Sm) scans were averaged for each sample.

The spectra were analyzed by standard methods[22] using the programs EXAFSPAK[23] and WinXAS97[24] to fit the unfiltered EXAFS function, $k^3\chi(k)$, to the theoretical phase and amplitude functions calculated for single scattering paths by FEFF8.00.[25] All error estimates or uncertainties are reported at the 95% confidence level. The amplitude reduction factor for each cation, S_0^2, was fixed at the values obtained from fitting the HC272 data using $N_\mathrm{O} = 6$[19,26] (0.90 for Nd, 0.98 for Sm, and 0.92 for Cm). The X-ray absorption near-edge structure (XANES) region of each spectrum was fit using a combination of Lorentzian and arctangent functions. The value of E_0 used in the conversion of the extended X-ray fine structure (EXAFS) region of the data from energy to momentum space was set equal to the L$_2$- or L$_3$-edge energy of the absorbing element (for Nd, L$_2$ = 6.721 keV, L$_3$ = 6.208 keV; for Sm, L$_2$ = 7.312 keV, L$_3$ = 6.716 keV; and for Cm, L$_3$ = 18.970 keV). The “coordination number”, *N*, of each shell of atoms was fixed for each fit on the basis of structural models derived from liquid−liquid extraction[19] and crystallographic[27,28] data, though different models and geometries were tested for each of the complexes. The bond distances derived for all of the complexes were independent (±0.005 Å) of the coordination geometry and coordination number.

Results

The L$_3$-edge EXAFS of the Sm(III) and Cm(III) complexes with each ligand and the magnitude of the Fourier transformations (which are not phase shift corrected) are shown in Figures 2 and 3, respectively. The results from nonlinear least-squares fitting of the experimental L$_3$ EXAFS data are summarized in Table 1 for each of the species. Similar results were obtained at the L$_2$-edges of Sm and Nd. A broad glitch in the Sm L$_3$ EXAFS required the data to be truncated at 10 Å^{-1}, but the

---

(13) Sole, K. C.; Hiskey, J. B. *Hydrometallurgy* **1992**, *30*, 345.
(14) Chen, J.; Zhu, Y.; Jiao, R. *Sep. Sci. Technol.* **1996**, *31*, 2723.
(15) Rizkalla, E. N.; Sullivan, J. C.; Choppin, G. R. *Inorg. Chem.* **1989**, *28*, 909.
(16) Zhu, Y.; Chen, J.; Jiao, R. *Solvent Extr. Ion Exch.* **1996**, *14*, 61.
(17) (a) Shannon, R. D. *Chem. Commun.* **1971**, 881. (b) Raymond, K. N.; Eigenbrot, C. W. Jr. *Acc. Chem. Res.* **1980**, *13*, 276. (c) Sockwell, S. C.; Hanusa, T. P. *Inorg. Chem.* **1990**, *29*, 76. (d) Brown, I. D.; Shannon, R. D. *Acta Crystallogr.* **1973**, *A29*, 266. (e) Shannon, R. D.; Vincent, H. *Struct. Bonding* **1974**, *19*, 1.
(18) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(19) Jensen, M. P.; Bond, A. H. *Radiochim. Acta* **2002**, *90*, 205.
(20) Marczenko, Z. *Separation and Spectrophotometric Determination of Elements*; Halsted: New York, 1986; pp 468−470.
(21) Beno, M. A.; Engbretson, M.; Jennings, G.; Knapp, G. S.; Linton, J.; Kurtz, C.; Rütt, U.; Montano, P. A. *Nucl. Instrum. Methods A* **2001**, *467−468*, 699.
(22) O’Day, P. A.; Rehr, J. J.; Zabinsky, S. I.; Brown, G. E., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 2938.
(23) Pickering, I. J.; George, G. N. *Inorg. Chem.* **1995**, *34*, 3142.
(24) Ressler, T. *J. Phys. IV* **1997**, *7*, C2.
(25) Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D. *Phys. Rev. B* **1998**, *58*, 7565.
(26) Beitz, J. V.; Sullivan, J. C. *J. Less-Common Met.* **1989**, *148*, 159.
(27) (a) Pinkerton, A. A.; Schwarzenbach, D. *J. Chem. Soc., Dalton Trans.* **1976**, 2464. (b) Spiliadis, S.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chim. Acta* **1983**, *75*, 115.
(28) Meseri, Y.; Pinkerton, A. A.; Chapuis, G. *J. Chem. Soc., Dalton Trans.* **1977**, 725.

Table 1. Parameters Used in the Curve Fitting of the L_3-Edge $k^3\chi(k)$ EXAFS of the Cm(III), Sm(III), and Nd(III) Complexes, with the Uncertainties in the Parameters Varied in the Fit Given at $\pm 2\sigma$

	$[M]_{org}$ (mmol/L)	coordination number	M–L (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Cm 1.11 Å[a]					
HC272	6.7	6 O	2.32 ± 0.01	0.005 ± 0.001	8.2 ± 1.4
HC302	6.7	3.4 ± 0.4 O	2.33 ± 0.01	0.0047	4.7 ± 1.5
		1.2 ± 0.4 S	2.79 ± 0.03	0.0083	
HC301	6.6	6 S	2.826 ± 0.008	0.0083 ± 0.0006	8.3 ± 1.0
		3 P	3.45 ± 0.01	0.007 ± 0.003	
Sm 1.098 Å[a]					
HC272	14.1	6 O	2.301 ± 0.003	0.0067 ± 0.0005	10.4 ± 0.2
		6 P	3.83 ± 0.01	0.015 ± 0.002	
HC302	16.3	3.8 ± 0.2 O	2.326 ± 0.004	0.0067	10.5
		0.9 ± 0.2 S	2.79 ± 0.02	0.0087	
		0.9 ± 0.2 P[b]	3.27 ± 0.03	0.010	
		2 P	3.81 ± 0.02	0.010	
HC301	8.7	6 S	2.803 ± 0.006	0.0087 ± 0.0005	10.6 ± 0.6
		3 P	3.40 ± 0.01	0.005 ± 0.001	
Nd 1.123 Å[a]					
HC272	11.2	6 O	2.345 ± 0.004	0.0063 ± 0.0005	12.6 ± 0.2
		6 P	3.91 ± 0.01	0.0135 ± 0.0002	
HC302	20.0	3.6 ± 0.2 O	2.365 ± 0.009	0.0063	12.5
		1.0 ± 0.2 S	2.83 ± 0.02	0.0070	
		1.0 ± 0.2 P[b]	3.32 ± 0.02	0.010	
		2 P	3.84 ± 0.02	0.010	
HC301	9.9	6 S	2.852 ± 0.007	0.0070 ± 0.0005	12.4 ± 0.7
		3 P	3.48 ± 0.01	0.006 ± 0.001	

[a] Shannon crystal radius of the cation for CN = 6, ref 18. [b] Varied parameter set equal to the value of the varied parameter immediately above.

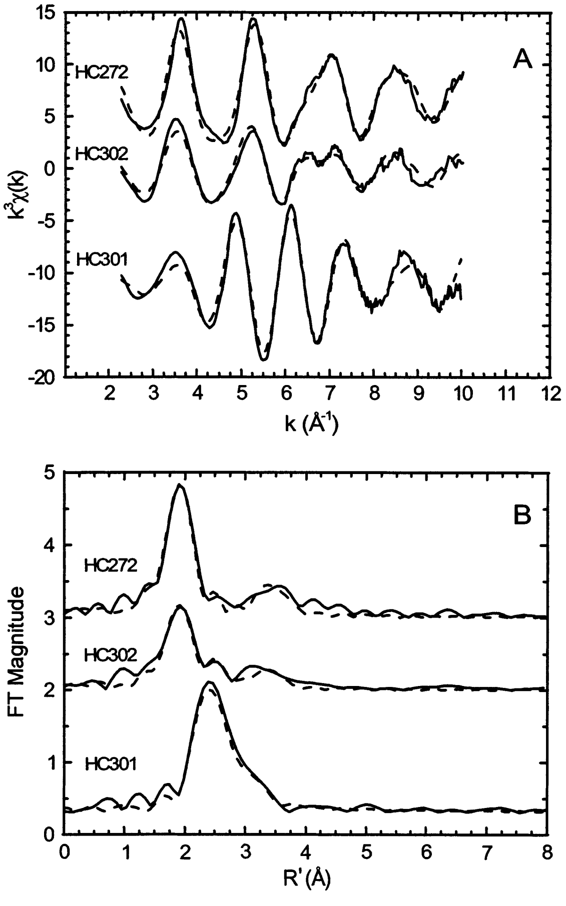

Figure 2. Sm L_3-edge k^3-weighted EXAFS (A) and the associated Fourier transformations taken over the full range of 2.3−10 Å^{-1} (B), showing the experimental data (solid line) and the best fit (dashed line).

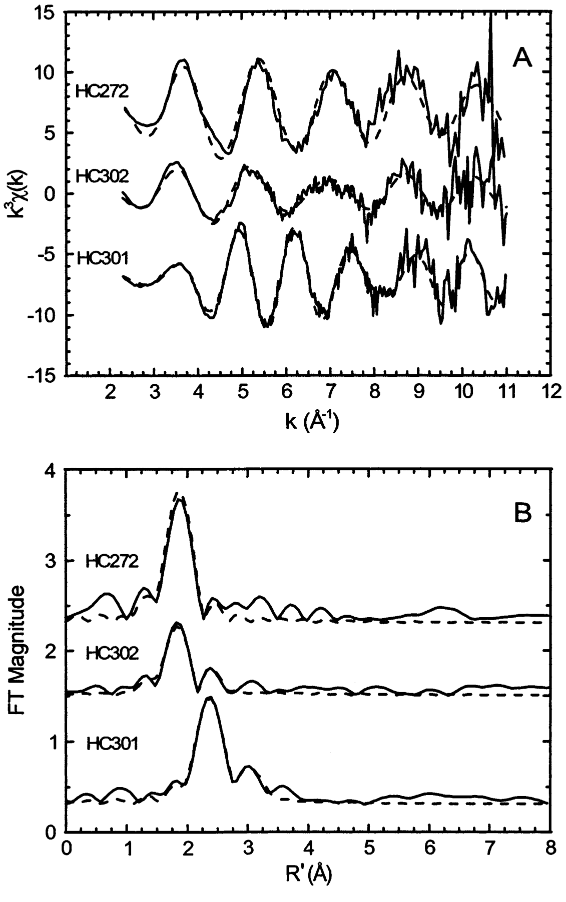

Figure 3. Cm L_3-edge k^3-weighted EXAFS (A) and the associated Fourier transformations taken over the full range of 2.3−11 Å^{-1} (B), showing the experimental data (solid line) and the best fit (dashed line).

Cm and Nd L_3 EXAFS were well defined to 11 Å^{-1} at the L_3-edge. The greater noise of the Cm data diminishes the significance of any contribution of the shells of P atoms to the Cm−HC272 and Cm−HC302 EXAFS to the point where the fit to the Cm data is not improved by the inclusion of P atoms. Despite this, the compositions of the Ln(III) and An(III) inner

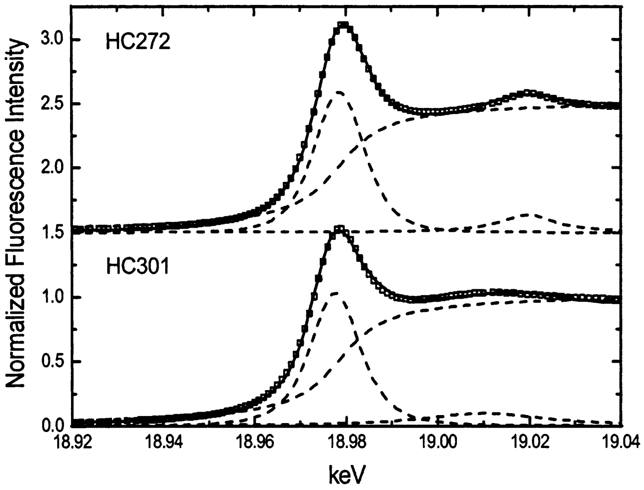

Figure 4. XANES spectra of the HC272 and HC301 complexes of Cm(III), showing the experimental data (solid line), the best-fit Lorentzian and arctangent functions (dashed lines), and the sum of the best-fit functions (squares).

coordination spheres derived from the curve fitting are indistinguishable for complexes involving the same ligand. Attempts to account for possible multielectron excitations[29] by removing the weak features at $k \approx 6.5$ Å^{-1} from the Nd and Sm EXAFS were deemed unnecessary because this changed the fitted bond distances of the coordinated O and S atoms by less than 0.005 Å.

The inner coordination spheres of the HC272 (R_2PO_2H) and HC301 (R_2PS_2H) complexes each contain a single type of donor atom, O for HC272 and S for HC301. The HC302 (R_2PSOH) complexes, on the other hand, contain both O and S atoms bound to the metal center. Initial attempts to model the EXAFS of the HC302 complexes used fixed coordination shells of $N_O = 3-6$, or $N_O = 3$, $N_S = 3$ (and in the case of Nd and Sm, $N_P = 3$) with varying Debye−Waller factors (σ^2), which account for thermal and structural disorder in the complexes. This approach reproduced the experimental data poorly for all shells of atoms and gave Debye−Waller factors for the O shell that were smaller (0.003−0.006 Å^2) than those obtained for the HC272 complexes with the same M−O distance, while σ^2 for the S shell was unusually large, at 0.02−0.03 Å^2. However, the data were well fit when the Debye−Waller factors of O, S, and P in the HC302 complexes were fixed at the average values found in the corresponding HC272 and HC301 complexes and the coordination number of each shell of atoms in the HC302 complexes was allowed to vary, as summarized in Table 1.

The XANES portion of each X-ray absorption spectrum (Figure 4 and Supporting Information) was analyzed to determine the area and position of the white line, the prominent peak that appears immediately after the absorption edge. It arises from 2p → $(n + 1)$d electronic transitions in these experiments. The same pattern is observed for the Nd, Sm, and Cm samples: the white line height decreases in the order HC302 $\gtrsim$ HC272 > HC301, while the *apparent* white line width decreases in the order HC272 $\gtrsim$ HC302 > HC301. Despite these visual observations, the results of least-squares fitting of the XANES to a combination of Lorentzian and arctangent functions show that the *actual* area of the white line does not change significantly if the same arctangent is used for each complex of an element at a particular absorption edge (Table 2). Although the experimental edge energy, taken as the first maximum of the first derivative of the XANES, is constant, there is a small shift in the energy of the white line when the two O donors of HC272 are replaced by the two S donors of HC301. The average value of this shift at the L_3-edges of the f-elements studied is -0.8 ± 0.4 eV, which is similar to the shift observed between the fluoride and iodide complexes of Ln(III) or U(IV).[30]

Optical spectra of the most intense f−f absorption bands of the Nd−HC301 complex are depicted in Figure 5, while those of each Am and Cm complex appear in Figure 6. The measured spectrum of the Nd−HC272 complex matches the spectrum previously reported for $Nd[H(DEHP)_2]_3$ in 1.5 M HDEHP/dodecane (DEHP = bis(2-ethylhexyl)phosphate anion).[31] As S donors are substituted for O donors in the phosphinate ligands, the spectra of each metal ion show stronger band intensities and a shift of the absorption bands to longer wavelengths due to the nephelauxetic effect. Both of these observations are consistent with an increase in the covalent character[32] of the M−S bonds relative to M−O bonds for both the Nd(III) and An(III) complexes. Intense charge-transfer bands, which also indicate some degree of covalence, are observed in the spectra of the HC301 complexes below ~380 nm.

Discussion

Structure and Stoichiometry of the Complexes. A modest amount of work has been reported on the coordination chemistry of the f-element complexes of acidic organodithiophosphorus ligands, and only cursory studies of the comparable monothiophosphorus complexes exist. In contrast, great attention has been paid to the dialkylphosphoric, -phosphonic, and -phosphinic acid complexes of f-element cations in organic solvents, and spectroscopic[26,33,34] and thermodynamic methods[35] have firmly established the stoichiometry and solution structures of these complexes. All of our results for the trivalent f-element complexes of the phosphinic acid extractant HC272 are consistent with this literature. When a large excess of ligand is present, HC272 behaves like other R_2PO_2H extractants, forming Ln(III)/An(III) complexes with the formula $M[H(C272)_2]_3$, where three $H(C272)_2^-$ hydrogen-bonded dimers[36] act as "bidentate" ligands (Figure 7) that completely dehydrate Ln(III) or An(III) cations extracted into nonpolar organic solvents.[26]

With the exception of the Nd(III) hypersensitive band centered at 595 nm, the integrated intensities of the strongest absorption bands of the Nd, Am, and Cm complexes with HC272 are 6 times smaller than the corresponding bands in the aquo cations. These low-intensity f−f transitions are nearly as

---

(29) Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Edelstein, N. M.; Craig, I. *Inorg. Chem.* **2000**, *39*, 595.

(30) (a) Hu, Z.; Kaindl, G.; Meyer, G. *J. Alloys Compd.* **1997**, *246*, 186. (b) Hu, Z.; Kaindl, G.; Meyer, G. *J. Alloys Compd.* **1998**, *274*, 38.

(31) Jensen, M. P.; Chiarizia, R.; Urban, V. *Solvent Extr. Ion Exch.* **2001**, *19*, 865.

(32) Henrie, D. E. *Mol. Phys.* **1974**, *28*, 415.

(33) Barbanel, Y. A.; Mikhailova, N. K. *Russ. J. Inorg. Chem.* **1973**, *18*, 365.

(34) Takahashi, T.; Suzuki, Y.; Yamasaki, A. In *Solvent Extraction 1990: Proceedings of the International Solvent Extraction Conference*; Sekine, T., Kusakabe, S., Eds.; Elsevier: New York, 1992; Vol. A, pp 189−193.

(35) Sekine, T.; Hasegawa, Y. *Solvent Extraction Chemistry*; Marcel Dekker: New York, 1977.

(36) (a) Danesi, P. R.; Vandegrift, G. F. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 109. (b) Peppard, D. F.; Mason, G. W.; Lewey, S. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2065. (c) Nakamura, S.; Sato, A.; Akiba, K. *J. Radioanal. Nucl. Chem.* **1994**, *178*, 63. (d) Sella, C.; Bauer, D. *Solvent Extr. Ion Exch.* **1988**, *6*, 819. (e) Sastre, A. M.; Miralles, N.; Martinez, M. *Monatsh. Chem.* **1995**, *126*, 401.

Table 2. Position and Area of the L-Edge White Lines from Fitting Lorentzian and Arctangent Functions to the XANES Data

	white line center (eV)[a]			white line area (eV)[b]			normalized area
	HC272	HC302	HC301	HC272	HC302	HC301	A_{HC301}/A_{HC272}
Cm L_3	18 979	18 978	18 978	16.4	16.3	16.3	1.00
Sm L_2	7 325.9	7 325.9	7 325.3	19.2	18.6	18.4	0.96
Sm L_3	6 728.3	6 728.1	6 727.5	18.8	18.1	18.3	0.97
Nd L_2	6 734.0	6 733.9	6 733.4	20.7	20.1	19.9	0.96
Nd L_3	6 221.0	6 220.8	6 220.0	18.0	18.1	17.7	0.98

[a] Error relative to standard ±0.6 eV. [b] Estimated uncertainty ±2%.

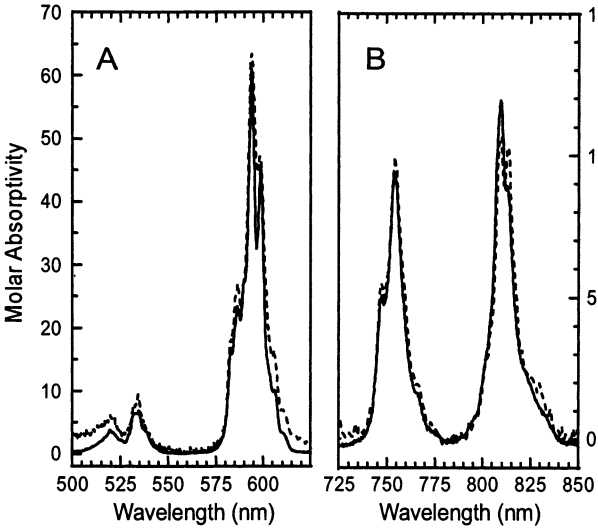

Figure 5. Optical absorption spectra of the Nd(III) $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ (A) and $^4I_{9/2} \rightarrow {}^4S_{3/2}, {}^4F_{7/2}$ and $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$ (B) transitions of the Nd–HC301 complex in dodecane (dashed line) and of Nd(C301)$_3$ in toluene (solid line).

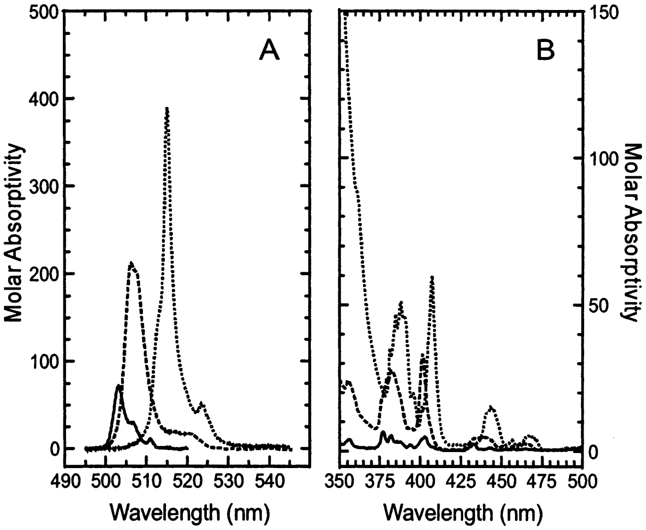

Figure 6. Effect of changing the donor atoms from oxygen to sulfur on the optical absorption spectra of the solution-phase Am (A) and Cm (B) complexes of HC272 (solid line), HC302 (dashed line), and HC301 (dotted line).

weak as those observed for the octahedral $LnCl_6^{3-}$ and $AnCl_6^{3-}$ complexes,[37] suggesting that the f–f transitions of the M[H(C272)$_2$]$_3$ complexes are symmetry forbidden by the presence of an inversion center. Given the presence of an inversion center and the number of donor atoms ($N_O = 6$), the O donors of the Ln(III) and An(III) complexes with HC272 would appear to adopt O_h point symmetry. Previous analysis of the Stark splitting induced in the spectrum of Eu[H(DEHP)$_2$]$_3$ by the ligand field also led to the conclusion that this closely related complex has nearly O_h symmetry.[33]

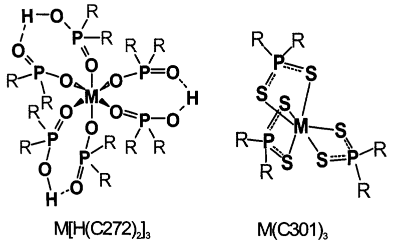

Figure 7. Structures of the trivalent f-element complexes deduced from EXAFS and absorption spectroscopy.

The EXAFS of the HC272 complexes with Ln(III) and An(III) fully support the distorted O_h symmetry deduced from the optical spectroscopy and further demonstrate the nearly identical structural behavior of similarly sized An(III) and Ln(III) cations in highly ionic coordination complexes. The M–O bond distances derived from the EXAFS data (Table 1) are in excellent agreement with those derived from EXAFS or diffraction studies of hexacoordinate Ln(III) or Cm(III) ions in crystalline or amorphous solids.[38] Moreover, the M–O bond distances in Table 1 closely resemble the distances expected from the sum of the cation and O crystal radii (i.e., 2.33, 2.31, and 2.32 Å for hexacoordinate Nd(III), Sm(III), and Cm(III), respectively).[18] The M–P separations measured for the Ln–HC272 complexes also are consistent with the coordination geometry depicted in Figure 7.

In contrast to that of the extensively studied R_2PO_2H complexes, the f-element coordination chemistry of monothiophosphinic acids is relatively unknown. Several crystal structures of Ln(III) complexes with bis(methyl)- or bis(cyclohexyl)-monothiophosphinic acid have been published,[39] and a dinuclear Nd$_2$(C302)$_6$ complex was recently reported in toluene solution.[31] Liquid–liquid extraction data indicate a 1:3 M:C302 ratio and hint at an An–S interaction.[19] Speciation calculations show that the hydrogen-bonded dimer (HC302)$_2$ is the dominant form of the uncomplexed ligand under our experimental conditions,[40] but the M:L ratio of 1:3 indicates that metal complexation

---

(37) (a) Ryan, J. L.; Jørgensen, C. K. *J. Phys. Chem.* **1966**, *70*, 2845. (b) Marcus, Y.; Bomse, M. *Isr. J. Chem.* **1970**, *8*, 901. (c) Barbanel, Y. A. *Sov. Radiochem.* **1975**, *17*, 279. (d) Barbanel, Y. A.; Kotlin, V. P.; Kolin, V. V. *Sov. Radiochem.* **1977**, *19*, 406.

(38) (a) Ponader, C. W.; Brown, G. E., Jr. *Geochim. Cosmochim. Acta* **1989**, *53*, 2893. (b) Liu, G. K.; Zhorin, V. V.; Antonio, M. R.; Li, S. T.; Williams, C. W.; Soderholm, L. *J. Chem. Phys.* **2000**, *112*, 1489. (c) Ellison, A. J. G.; Loong, C. K.; Wagner, J. *J. Appl. Phys.* **1994**, *75*, 6825. (d) Lebedev, V. G.; Palkina, K. K.; Maksimova, S. I.; Lebedeva, E. N.; Galaktionova, O. V. *Russ. J. Inorg. Chem.* **1982**, *27*, 1689. (e) Huang, C.; Yi, T.; Lu, Y.; Xu, G.; Ling, H.; Ma, Z. *Chin. Chem. Lett.* **1992**, *13*, 947. (f) Zeng, G.; Guo, X.; Wang, C.; Lin, Y.; Li, H. *Jiegou Huaxue* **1994**, *13*, 24.

(39) (a) Mühlsiepen, K. M.; Mattes, R. *Z. Anorg. Allg. Chem.* **1983**, *506*, 115. (b) Mühlsiepen, K. M.; Mattes, R. *Z. Anorg. Allg. Chem.* **1983**, *506*, 125.

(40) Almela, A.; Elizalde, M. P. *Anal. Proc.* **1995**, *32*, 145.

disrupts the ligand dimers to afford monomeric $C302^-$ as the active ligand.

Despite the strong preference of the trivalent f-elements for hard O donor atoms, our results for the HC302 complexes demonstrate that both O and S atoms in the same ligand are capable of simultaneously coordinating the Ln(III) and An(III) metal centers in organic media. The bond distances of the Nd−, Sm−, and Cm−HC302 complexes measured by EXAFS (Table 1) are considerably shorter than those expected for crystalline hepta- and octacoordinate dinuclear $Ln(III)-R_2POS^-$ complexes, which correspond to average Sm−O bond lengths of 2.35 (CN = 7) and 2.43 Å (CN = 8) and average Sm−S bond lengths of 2.90 (CN = 7) and 2.98 Å (CN = 8).[39] However, the bond distances of the HC302 complexes are close to those measured for the hexacoordinate $R_2PO_2^-$ and $R_2PS_2^-$ complexes.

While the M−L bond lengths of the HC302 complexes are consistent with those measured for the hexacoordinate HC272 and HC301 complexes, the coordination numbers of the HC302 complexes of Ln(III) and An(III) cations derived from the EXAFS measurements are unusual. Previous liquid−liquid extraction and neutron scattering studies imply a M:C302 ratio of 1:3, affording a maximum of three O and three S atoms from the HC302 molecules in the inner coordination sphere. Assuming that the Debye−Waller factors of the O, S, and P atoms in the HC272, HC301, and HC302 complexes are similar led to an average total coordination number ($N_O + N_S$) for the three HC302 complexes of 4.6 (Table 1). With only one S atom and more than three O atoms in the inner coordination sphere, the additional O in the inner coordination sphere of the $M(C302)_3$ complexes most likely comes from extracting one water molecule with the metal cation. (Nitrate and acetate anions are not extracted into the organic solvent during complex formation.[19]) This conclusion is supported by fluorescence lifetime measurements[41] of *n*-dodecane solutions of the Eu(III)−HC302 complex that suggest one water molecule is present in the Eu inner coordination sphere ($k_{H_2O} = 2.98\ ms^{-1}$, $k_{D_2O} = 2.17\ ms^{-1}$, $N_{H_2O} = 0.9 \pm 0.5$). The resulting mononuclear complex would consist of a cation surrounded by two monodentate $C302^-$ molecules bound only through their O atoms, one bidentate $C302^-$ molecule bound through both the O and S atoms, and one water molecule. Such an arrangement includes one short and two long M−P distances, consistent with the EXAFS of the Sm− and Nd−HC302 complexes. This general structure of the HC302 complexes is similar to those observed for Ln(III)−R_2PSOH complexes in the solid state, which manifest each of these coordination modes.[39]

Although the $M(C302)_3(H_2O)$ species described above is consistent with the existing liquid−liquid extraction data, gives the best fit of the EXAFS results, does not contradict the optical absorption measurements, and is related to the monothiophosphinate complexes found in the solid state, a coordination number between 4 and 5 is unusually low for f-element cations. Complexes of Ln(III) and An(III) ions with such low coordination numbers (CN = 3−5) are observed only in organometallic compounds or complexes with sterically demanding ligands.[42] The low coordination number could be an artifact of our approach to data modeling (fixing the Debye−Waller factors at the values obtained from HC272 and HC301), but the results of the other experimental techniques give no concrete direction otherwise. These results clearly show that an HC302 ligand is capable of forming bidentate complexes with Ln(III) and An(III) cations in solution using both O and S donors. Similar observations with d-transition metal complexes of R_2POS^- ligands[43] have been reported.

The symmetry and general structure of the f-element complexes with HC301 are different from those of both the HC272 and HC302 complexes. Yet the absorption spectra and EXAFS of the An(III) and Ln(III) complexes demonstrate the structural equivalence of the dithiophosphinate complexes of trivalent 4f and 5f cations. Previous work has suggested that the absorption spectra of the Nd− and Am−HC301 complexes are most consistent with $N_S = 8$ and a cubic geometry.[44] In contrast to those findings, Figure 5 shows that the number of absorption bands, the band energies, and the intensity patterns of the Nd−HC301 complex in *n*-dodecane that was used for the EXAFS measurements closely match those of the known spectrum of $Nd(C301)_3$ in toluene.[31]

The Nd−HC301 absorption spectrum is helpful in understanding the EXAFS because the experimental data for each cation are equally well fit by models with $N_S = 6$, $N_P = 3$ or $N_S = 8$, $N_P = 4$. The only differences between these two models are the values obtained for the Debye−Waller factors. However, the distances between the metal centers and both the S and P atoms derived from the EXAFS (Table 1) are in excellent agreement with those expected for hexacoordinate $Ln(S_2PR_2)_3$ complexes from X-ray crystallography,[28,45] and the M−S distances are approximately 0.1 Å shorter than those found in crystalline, octacoordinate $Ln(S_2PR_2)_4^-$ complexes.[27,46] The M−P separations are consistent with bidentate coordination of each $R_2PS_2^-$ group. As with HC302, the formation of f-element−S bonds disrupts the hydrogen bonding of the $(HC301)_2$ dimers. Unlike the HC302 complexes and despite the presence of O-bearing NO_3^-, OAc^-, and H_2O ligands in the liquid−liquid extraction system, the EXAFS data are most consistent with the presence of only S donors in the inner coordination spheres of both the Ln(III)− and An(III)−HC301 complexes under these extraction conditions. All of the metal cations studied show similar structures and coordination numbers, and a hexacoordinate model that resembles the D_3 symmetry of the solid-state $Ln(S_2PR_2)_3$ complexes (Figure 7) is likely under the solution conditions studied. The Sm(III), Nd(III), and Cm(III) complexes with HC301 each have a 1:3 M:C301 ratio with $N_S = 6$. The greater thermodynamic stability of the An−HC301 complexes is not reflected in a change in the number of S donor atoms in the inner coordination sphere of the Ln(III) and An(III) complexes.

---

(41) Horrocks, W. D., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334.

(42) (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021. (b) Stewart, J. L.; Andersen, R. A. *Polyhedron* **1998**, *17*, 953. (c) Aspinall, H. C.; Bradley, D. C.; Sales, K. D. *J. Chem. Soc., Dalton Trans.* **1988**. (d) Rabe, G. W.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5378. (e) Edelmann, F. T.; Steiner, A.; Stalke, D.; Gilje, J. W.; Jagner, S.; Hakansson, M. *Polyhedron* **1994**, *13*, 539. (f) Shao, P.; Berg, D. J.; Bushnell, G. W. *Inorg. Chem.* **1994**, *33*, 3452.

(43) Calligaris, M.; Ciana, A.; Meriani, S.; Nardin, G.; Randaccio, L.; Ripamonti, A. *J. Chem. Soc. A* **1970**, 3386.

(44) Zhu, Y.; Xu, J.; Chen, J.; Chen, Y. *J. Alloys Compd.* **1998**, *271−273*, 742.

(45) Pinkerton, A. A.; Schwarzenbach, D. *J. Chem. Soc., Dalton Trans.* **1980**, 1300.

(46) (a) Pinkerton, A. A.; Meseri, Y.; Rieder, C. *J. Chem. Soc., Dalton Trans.* **1978**, 85. (b) Pinkerton, A. A.; Storey, A. E.; Zellweger, J.-M. *J. Chem. Soc., Dalton Trans.* **1981**, 1475. (c) Pinkerton, A. A.; Schwarzenbach, D. *J. Chem. Soc., Dalton Trans.* **1981**, 1470.

Bond Lengths as a Measure of Enhanced Covalence in the Actinide Complexes. Since the stoichiometry and geometry of the HC272, HC302, and HC301 complexes do not change when the Ln(III) are replaced by An(III), is the greater strength of the An−HC301 complexes manifested in shorter M−S bonds? The general question of covalent contraction in An−ligand bonds has been investigated for Ln(III) and An(III) complexes containing N or S donor ligands with 500−1000 times less selectivity than HC301 for the An(III) cations, but only small contractions (≤0.01−0.05 Å) in the An−ligand bond lengths were observed.[6,47] Given the much greater selectivity of HC301, covalent contractions in the An−S bonds as large as 0.1 Å might be expected (Supporting Information).

To minimize the impact of systematic errors introduced from the published crystal radii, we have adopted the methodology of Brennan et al.,[48] who computed the covalent contraction in specific actinide−ligand bonds relative to those in homologous lanthanide compounds. The method contains an inherent correction for differences in the radii of Cm(III) and Ln(III). Moreover, it has the advantage of using EXAFS data that have been collected and analyzed in a uniform fashion, thus reducing the importance of errors introduced by data collection, uncertainties in the theoretical phase and amplitude calculations, and fitting of the EXAFS data. The M−O bonds in the HC272 complexes are taken as prototypical electrostatic bonds for f-element complexes, and the covalent contraction of the Cm−S bond relative to a Ln−S bond, $\Delta r_{\text{covalent}}$, is calculated from the equation

$$\Delta r_{\text{covalent}} = (r_{\text{Cm-O}} - r_{\text{Cm-S}}) - (r_{\text{Ln-O}} - r_{\text{Ln-S}}) \qquad (1)$$

Positive values of $\Delta r_{\text{covalent}}$ indicate a covalent contraction in the Cm−S bond length. Using eq 1, we find $\Delta r_{\text{covalent}} = 0.00 \pm 0.02$ Å for Ln = Nd and Sm. Consequently, there is no structural evidence for a covalent contraction in the An−S bonds relative to the Ln−S bonds, despite the enhanced covalence in the An−S bonds implied by the −25.6 kJ/mol[16] difference in the Am(III) and Eu(III) conditional extraction enthalpies.

Participation of the d Orbitals in Bonding. The XANES portion of the XAFS spectra also contains potentially useful information about the degree of covalency in metal−ligand bonds. While other mechanisms can affect the white line intensity,[49] the L_2- and L_3-edge white lines can be used to probe the covalency of metal−ligand bonds because the peak position, bandwidth, and oscillator strength of these $2p \rightarrow (n + 1)d$ transitions is influenced by the energy and occupancy of the final d-states in transition metal[50] and f-element compounds.[51] For dioxomolybdenum(VI) complexes, substituting a single O-bearing phenoxide ligand with a S-bearing benzylthiolate ligand caused a 27% decrease in the area (oscillator strength) of the Mo L_3 white line, which was correlated with the degree of covalency of the Mo−ligand bonds.[52] To a first approximation, if the Cm 6d orbitals are significantly more involved in the formation of M−S bonds than the Nd or Sm 5d orbitals are, then the white line of $Cm(C301)_3$, normalized to the $Cm[H(C272)_2]_3$ white line, should be less intense than the normalized white lines of $Nd(C301)_3$ and $Sm(C301)_3$.

Comparison of the areas and heights of the normalized L_2 and L_3 white lines of the $M(C301)_3$ complexes does not show a consistent change in the height or area of the white line (Table 2). In contrast to the dioxomolybdenum(VI) results described above, exchanging six O donors for six S donors in the f-element complexes causes at most a 4 ± 3% decrease in the intensity of the white line, with no significant difference between the normalized areas of the lanthanide and actinide samples. The change in the shape of the white line that occurs when the six S donors of three $C301^-$ molecules are substituted for the six O donors of $H(C272)_2^-$ suggests a different splitting of the d orbitals in the two species, which is consistent with a change in symmetry from O_h to D_3, but the change in the areas of the white lines provides no evidence for greater participation of the Cm 6d orbitals in M−S bonding. This is in agreement with an X-ray diffraction study of $Th(S_2PMe_2)_4$,[11] which reported no significant electron density in the 6d or 5f orbitals. However, substantial polarization of the Th electron density was observed and attributed to charge polarization of the Th 5d orbitals.

Conclusions

The high selectivity of organodithiophosphinic acid ligands for An(III) cations over Ln(III) cations does not result in shortened An−S bonds or variations in the structures or composition of the $M(C301)_3$ complexes extracted into 1.0 M solutions of HC301 in *n*-dodecane from aqueous solutions of 1.0 M $NaNO_3$/0.05 M (Na,H)OAc. This suggests that the origin of the preference for the An(III) cations is an increased covalence in the An−S bonds that is not reflected in significantly shorter An−S bonds, perhaps in this particular case because of steric interaction between the ligands or because covalence is a minor component in both An−S and Ln−S bonding. In addition, the thermodynamic preference of An(III) for softer donor atoms does not favor a greater number of An−S bonds in these complexes. Like the HC301 complexes, the structures and stoichiometries of the phosphinic acid (HC272) complexes, $M[H(C272)_2]_3$, and monothiophosphinic acid (HC302) complexes, $M(C302)_3(H_2O)$, extracted into dodecane are the same for the Ln(III) and An(III) cations studied and are in agreement with our previous work. The differences between the structures of complexes of HC272, HC302, and HC301 with the trivalent f-element cations are mostly due to differences in the basicity of the O and S donor atoms in these ligands and the ability of the ligands to form hydrogen-bonded dimers.

---

(47) (a) Yaita, T.; Tachimori, S.; Edelstein, N. M.; Bucher, J. J.; Rao, L.; Shuh, D. K.; Allen, P. G. *J. Synchrotron Radiat.* **2001**, *8*, 663. (b) Rivière, C.; Nierlich, M.; Ephritikhine, M.; Madic, C. *Inorg. Chem.* **2001**, *40*, 4428. (c) Karmazin, L.; Mazzanti, M.; Pécaut, J. *Chem. Commun.* **2002**, 654. (d) Mazzanti, M.; Wietzke, R.; Pécaut, J.; Latour, J.-M.; Maldivi, P.; Remy, M. *Inorg. Chem.* **2002**, *41*, 2389.

(48) Brennan, J. G.; Stults, S. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chim. Acta* **1987**, *139*, 201.

(49) (a) Materlik, G.; Müller, J. E.; Wilkins, J. W. *Phys. Rev. Lett.* **1983**, *50*, 267. (b) de Groot, F. M. F.; Hu, Z. W.; Lopez, M. F.; Kaindl, G.; Guillot, F.; Tronc, M. *J. Chem. Phys.* **1994**, *101*, 6570. (c) Michels, G.; Junk, S.; Schlabitz, W.; Holland-Moritz, E.; Abd-Elmeguid, M. M.; Dünner, J.; Mewis, A. *J. Phys.: Condens. Matter* **1994**, *6*, 1769.

(50) (a) Lytle, F. W. *J. Catal.* **1976**, *43*, 376. (b) Mansour, A. N.; Cook, J. W., Jr.; Sayers, D. E. *J. Phys. Chem.* **1984**, *88*, 2330. (c) Rao, C. N. R.; Thomas, J. M.; Williams, B. G.; Sparrow, T. G. *J. Phys. Chem.* **1984**, *88*, 5769. (d) Choy, J.-H.; Kim, D.-K.; Hwang, S.-H.; Demazeau, G.; Jung, D.-K. *J. Am. Chem. Soc.* **1995**, *117*, 8557.

(51) (a) Röhler, J. *J. Magn. Magn. Mater.* **1985**, *47&48*, 175. (b) Malterre, D. *Phys. Rev. B* **1991**, *43*, 1391. (c) Moghe, N. V.; Sapre, V. B. *X-ray Spectrom.* **1995**, *24*, 241. (d) Loeffen, P. W.; Pettifer, R. F.; Müllender, S.; van Veenendaal, M. A.; Röhler, J.; Sivia, D. S. *Phys. Rev. B* **1996**, *54*, 14877. (e) Espeso, J. I.; Sal, J. C. G.; Chaboy, J. *Phys. Rev. B* **2000**, *63*, 14416. (f) d'Acapito, F.; Mobilio, S.; Bruno, P.; Barbier, D.; Philipsen, J. *J. Appl. Phys.* **2001**, *90*, 265.

(52) Izumi, Y.; Glaser, T.; Rose, K.; McMaster, J.; Basu, P.; Enemark, J. H.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1999**, *121*, 10035.

Acknowledgment. P. Rickert purified the ligands, J. Beitz made the Eu fluorescence measurements, K. Nash, L. Soderholm, and M. Denecke participated in fruitful discussions, and BESSRC-CAT and the ANL Chemistry Division's Actinide Facility for Synchrotron Radiation Research provided the infrastructure for the EXAFS measurements. The ^{248}Cm used in the experiments is on loan from the Radiochemical Engineering Development Center at Oak Ridge National Laboratory as part of the Transuranium Element Program. This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Chemical Sciences, through Contract No. W-31-109-ENG-38.

Supporting Information Available: XANES spectra of each Nd, Sm, and Cm complex; preparation and composition of the actinide solutions; and estimation of the covalent contraction in actinide−sulfur bonds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0178620