

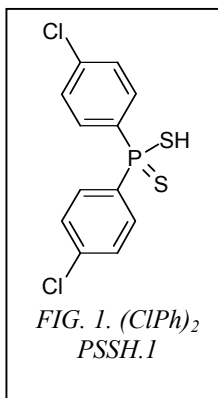
# Comparative EXAFS Study of Cm(III) and Eu(III) Complexed with Partitioning Relevant Ligands

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## Introduction

A comparative extended x-ray absorption fine structure (EXAFS) study of the coordination structures of Cm(III) and Eu(III) following extraction from 0.01 M nitric acid with di(chlorophenyl)-dithiophosphinic acid [(CIPh)<sub>2</sub>PSSH] (Fig. 1) and with differing neutral organophosphorus synergist compounds (tri-n-octyl-phosphine oxide [TOPO], tri-n-butylphosphate [TBP], and tris-(2-ethylhexyl)phosphate [T2EHP]) was performed. The goal of this study was to ascertain if there is a structural origin for the observed strong influence of the synergist on An(III)/Ln(III) separation factors. Specifically, Cm and Eu L3 EXAFS data were analyzed to obtain metric parameters describing the structure of the coordination sphere of the complexed Cm(III) and Eu(III) metal cations.



## Methods and Materials

Curium samples were prepared by extracting an aqueous solution of 5 mmol/L (1.23 mg/mL) Cm-248 in 0.01 M HNO<sub>3</sub> into 0.5 M (CIPh)<sub>2</sub>PSSH and different synergist compounds — TOPO, TBP or T2EHP (0.25 M) — dissolved in tert-butylbenzene. Europium samples were prepared by extracting an aqueous solution of 20 mmol/L Eu(III) in 0.01 M HNO<sub>3</sub> into 0.5 M (CIPh)<sub>2</sub>PSSH, containing TOPO or TBP (0.25 M) dissolved in tert-butylbenzene.

EXAFS measurements were performed with the APS ring running under top-up mode with a 104-mA current at BESSRC beamline 12-BM. Si(111) crystals were used in the double-crystal monochromator. The Cm L3 spectra were calibrated by defining the first inflection point of the first derivative XANES spectrum of a Zr foil as 17.998 keV, which was recorded at the beginning of the XAFS measurements and again at the end. No measurable energy shift between both measurements was observed. The Eu L3 spectra were calibrated in a similar manner by using an Fe foil as the energy reference (7.112 keV). The samples which were contained in sealed polyethylene vials and mounted in the Actinide Facility's sample changer, were measured in fluorescence mode by using a Canberra LGe 13-element solid-state detector. Three to four scans were averaged, and the EXAFS was extracted by using standard procedures and the WinXAS software [1]. Theoretical least squares fits to the EXAFS spectra

were performed in R-space by using the FEFFIT software [2] to obtain the metric parameters for the different coordination shells (indicated by i): coordination numbers (N<sub>i</sub>), interatomic distances (R<sub>i</sub>), mean square radial displacements or EXAFS Debye-Waller factors (σ<sup>2</sup><sub>i</sub>), and relative shifts in ionization potential (ΔE<sub>0</sub>). All fitting operations were performed in R-space. The amplitude reduction factor S<sub>0</sub><sup>2</sup> was fixed at 1. Single scattering phase shift and backscattering amplitude functions are calculated with FEFF8 [3].

## Results

The k<sup>2</sup>-weighted Cm and Eu L3 EXAFS for the (CIPh)<sub>2</sub>PSSH-synergist extracted complexes and their corresponding Fourier transform (FT) data are compared in Fig. 2. The comparison of the spectra with one another shows that the Cm sample spectra are significantly different than their Eu counterparts. The amplitude

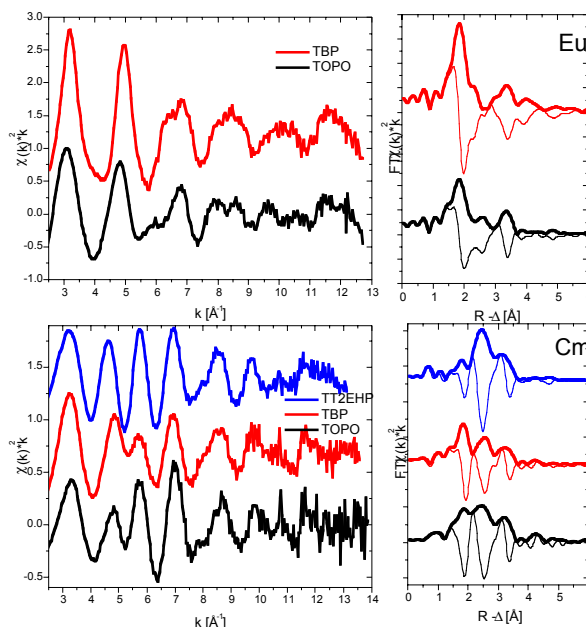


FIG. 2. k<sup>2</sup>-weighted L3 edge EXAFS (left) of the (CIPh)<sub>2</sub>PSSH-synergist extracted Eu<sup>3+</sup> (top) and Cm<sup>3+</sup> (bottom) complexes and their corresponding Fourier transform (FT) data (right). The different synergist compounds used are indicated.

differences cannot be solely explained by differences in their backscattering amplitude functions. This means that the Cm complexes have different coordination structures than do the corresponding Eu complexes. Furthermore, we find that all Cm and Eu complexes have oxygen,

sulfur, and phosphorus nearest neighbors. However, visual inspection of the spectra show them to differ in the intensities for each of these coordination shells. Results of fits of the Cm data to the EXAFS equation are given in Table 1. Also included are results from analysis of the Cm L3 EXAFS for the Cm<sup>3+</sup> aquo ion (data not shown).

TABLE 1. Metric parameters obtained from fits to the Cm L3 edge R-space data in Fig. 1.

Sample	Shell	N	R (Å)	$\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)
Cm <sup>3+</sup> aquo ion	O	8.7	2.47	0.0103	1.6
Cm-(CIPh) <sub>2</sub> PSSH - TOPO	O	2.4	2.32	0.004	3.3
	S	4.5	2.92	0.011	0.2
	P	2.6	3.57	0.004	7.3
Cm-(CIPh) <sub>2</sub> PSSH - TBP	O	2.9	2.34	0.004	-0.4
	S	3.0	2.96	0.011	4.5
	P	1.5	3.60	0.002	10.6
Cm-(CIPh) <sub>2</sub> PSSH - T2EHP	O	1.6	2.34	0.002	0.3
	S	4.8	2.93	0.010	0.8
	P	4.7	3.58	0.008	4.1

## Discussion

From the observed short curium-oxygen bond distance in the extracted complexes, we conclude that the oxygen shell is from synergist molecules directly coordinated to the cation and not from legating water molecules. The Cm-O distance in the extracted samples is more than 0.2 Å shorter than the Cm-O distance observed in the Cm<sup>3+</sup> aquo ion. Time-resolved laser fluorescence spectroscopy (TRLFS) results on these extraction systems support this conclusion. This is experimental evidence for theoretical results reported in Ref. 4, which propose coordination of both dithiophosphinate and synergist molecules in the extracted complex. Comparison of the Cm-S and Cm-P distances with those reported by Jensen et al. [5] indicates bidentate complexation of Cm by (CIPh)<sub>2</sub>PSSH.

General trends in the different FT intensity ratios of the S (near 2.5 Å) and O (near 1.8 Å) peaks in Fig. 2 and N(S)/N(O) from the results in Table 1 are observed. We find upon comparing spectra for Cm and Eu samples extracted with the same synergist that the S/O intensity ratio is always higher for Cm. We also observe the S/O intensity ratio and N(S)/N(O) values decrease in the order T2EHP > TOPO > TBP for spectra of Cm samples with different synergists and in the order TOPO > TBP for Eu sample spectra.

We draw two conclusions from these observed trends. First, the Eu complexes have different coordination spheres than their corresponding Cm counterparts, with Eu being more favorably complexed by oxygen atoms from the synergist (Cm less favorably by oxygen) or with Eu being less favorably complexed by sulfur from (CIPh)<sub>2</sub>PSSH (Cm more favorably by sulfur). This is in accord with results from equilibrium data (compare with Ref. 6), where the slope of log*D* versus log[*synergist*] is shown to be higher for Ln(III) than for An(III). Note, however, the slope analysis does not yield information on whether additional synergist molecules in the Ln(III) complexes are directly coordinated to the metal cation in the inner sphere. The second conclusion is that a high separation factor between An(III) and Ln(III) seems to be generally correlated with a high S/O intensity ratio in the complex EXAFS spectra. *SF*<sub>Cm/Eu</sub> is in the range of 100 when T2EHP is used as synergist, whereas it is near 10 for TOPO and TBP.

The coordination numbers are 6 to 7. These are lower than expected values in the range of 9. We believe that destructive interference due to small distortions in the complex coordination structure (i.e., a spread of bond lengths) is the reason for the relatively low coordination numbers observed. Further study is needed to check this hypothesis.

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