Inorg. Chem. **1999,** *38,* 4139−4141 **4139**

Notes

First Investigation on the L Edges of the ^{249}Cf Aquo Ion by X-ray Absorption Spectroscopy

R. Revel,[*,†,‡] C. Den Auwer,[†] C. Madic,[§] F. David,[||] B. Fourest,[||] S. Hubert,[||] J.-F. Le Du,[||] and L. R. Morss[⊥]

CEA Marcoule, DCC/DRRV/SEMP Laboratoire de Chimie Théorique et Structurale, Bagnols-sur-Cèze Cedex, France, LURE, Université Paris Sud, Bâtiment 209D, BP34, 91898 Orsay Cedex, France, CEA/DCC/DIR, Saclay, Bâtiment 450, 91191 Gif sur Yvette, France, IPN Orsay, Université Paris-Sud, 91406 Orsay Cedex, France, and Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

Received February 23, 1999

Introduction

In the field of nuclear fuel reprocessing and nuclear waste treatment, solvent extraction is the preferred method to isolate long-lived radionuclides from short-lived ones and nonhazardous wastes. For example, solvent extraction is the basis of the PUREX[1] process for uranium and plutonium recovery from spent nuclear fuel. In order to develop the selective extraction of minor actinides such as americium and curium from the lanthanide fission products contained in high-activity wastes, meticulous characterization of the solvated adducts of trivalent 4f (lanthanide) and 5f (actinide) ions must be undertaken. Of course, as the mixture of trivalent ions is initially in aqueous solutions, the knowledge of the coordination geometry of the water molecules surrounding the trivalent lanthanides and actinides is essential for a comparison of the aquo ions (M^{3+}) of both series and the evaluation of their thermodynamic properties.[2] The data will be particularly relevant for the estimation of the covalent part of the bonds between M^{3+} and O of the water molecules.

To reach these goals, and for both structural and electronic characterization, X-ray absorption spectroscopy is one of the most suitable spectroscopic probes. Within the context of this research effort, we report here the first experimental data of which we are aware on L_{III}, L_{II}, and L_I edges and EXAFS data of the trivalent ^{249}Cf aquo ion.

Experimental Section

One milligram of ^{249}Cf in solution belonging to the team at Orsay University[3,4] was evaporated to dryness on a Teflon surface. The ^{249}Cf recovery was achieved by redissolution with HCl. Remaining ^{249}Cf γ radioactivity on the Teflon was found to be negligible in comparison with that contained in the recovered sample.

Table 1. L Edges of the Cf^{3+} Aquo Ion. Best Fit Parameters

	arctan			Gaussian	
edge	position (m[3]) (eV)	absorbance (m[2])	width (m[4]) (eV)	position (eV)	edge width (eV)
L_{III}	19 901.1 ± 0.5	0.005 87 ± 0.000 05	0.20 ± 0.02	19 911	20
L_{II}	25 095.2 ± 0.4	0.005 53 ± 0.000 03	0.31 ± 0.02	25 109	28
L_I	26 000.8 ± 0.9	0.005 65 ± 0.000 09	0.15 ± 0.02	26 028[a]	54

[a] No Gaussian curve could be incorporated in the fit, and the edge position was therefore determined by first spectrum derivative to be zero.

From the 0.6 mL of 1 M HCl(aq) containing 1 mg of ^{249}Cf starting solution, 0.4 mL was loaded into a room-temperature spectroscopic cell that had been adapted for radionuclide containment. Data were acquired at LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay, France) on the D44 experimental hutch at the DCI high-energy ring (1.8 GeV, $\lambda_c = 3.5$ keV) with a Si 311 double crystal monochromator (instrumental bandwidths were calculated to be 7.9, 12.5, and 13.4 eV for L_{III}, L_{II}, and L_I Cf edges, respectively). Argon-filled ionization chambers were used for signal detection in transmission mode, and in situ energy calibration was achieved by use of a third diode detector with Mo (for the L_{III} edge), Pd (for the L_{II} edge), and Ag (for the L_I edge) reference foils, respectively equal to 20 000, 24 350, and 25 514 eV.[5]

EXAFS data analysis was performed by standard methods using the set of programs " EXAFS pour le MAC".[6] After removal of the background absorption using a straight line, the Cf atomic absorption was modeled by a 6th degree polynomial and subtracted from experimental spectra. EXAFS oscillations were obtained using the Heitler−Eisenberger normalization. Fourier Transform (FT) of these oscillations was achieved between 3.15 and 12.3 Å^{-1} using a Kaiser window with $\tau = 2.5$.

Because there are no experimental reference spectra for Cf, EXAFS data were refined using theoretical phases and amplitudes calculated using the FeFF7.02 code.[7] Our approach consisted of (i) simulating the UO_2 structure from crystallographic data[8] by FeFF,[9] (ii) fitting the first shell of the $UO_{2.0}$ experimental spectrum to obtain the reduction factor S_0^2 for CfO_2, assuming that $S_0^2(CfO_2) \approx S_0^2(UO_2)$, and (iii) extracting CfO_2 phase, amplitude, and mean free path $\lambda(k)$ from FeFF using the same set of parameters as for UO_2. This calculation was carried out as follows: the FeFF7 code does not allow any calculation with an atomic number Z greater than 97 (Bk). Thus, from the crystallographic parameters of CfO_2, the Cf atomic potential was replaced by those of all the elements between U and Bk. Then, linear extrapolation up to Cf allowed us to approximate Cf electronic parameters (phases, amplitudes, electron mean free path, and inelastic losses).

---

[*] E-mail: renaud.revel@ifp.fr. Fax: 33 1 47 52 60 55.

[†] DCC/DRRV/SEMP Laboratoire de Chimie Théorique et Structurale and LURE, Université Paris Sud.

[‡] Present address: IFP, 1-4 Avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France.

[§] CEA/DCC/DIR.

[||] IPN Orsay, Université Paris-Sud.

[⊥] Argonne National Laboratory.

(1) Schulz, W. W.; Burger, L. L.; Navratil, J. D. *Science and Technology of Tributylphosphate*; CRC Press Inc.: Boca Raton, FL, 1990; Vol. III.

(2) David, F.; Fourest, B. *New J. Chem.* **1997**, *21*, 167.

(3) This isotope was lent by Argonne National Laboratory through the auspices of the U.S. Department of Energy.

(4) Fourest, B.; Morss, L. R.; Blain, G.; David, F.; M'Halla, J. *Radiochim. Acta* **1995**, *69*, 215.

(5) Bearden, J. A.; Burr, A. F. *Rev. Mod. Phys.* **1967**, *39* (1), 125.

(6) Michalowicz, A. *J. Phys. IV* **1997**, *7*, C2-235.

(7) Ankudinov, A. L.; Rehr, J. J. *Phys. Rev. B* **1997**, *56*, 1712.

(8) Katz, J. J., Seaborg, G. T., Morss, L. R., Eds. *The Chemistry of the Actinide Elements*; Chapman and Hall: London, 1986; Vol. 2.

(9) Potential is a partially nonlocal Dirac−Fock potential for core, Hedin−Lundqvist for valence electron and a constant imaginary part (EXCHANGE 5). Fermi level was decreased by 3 eV (Vr0 = 3). No overlap is taken into account (No AFOLP card). This input data was used by Ankudinov et al. (*Phys. Rev. B* **1998**, *57* (13), 7518).

10.1021/ic990214l CCC: $18.00

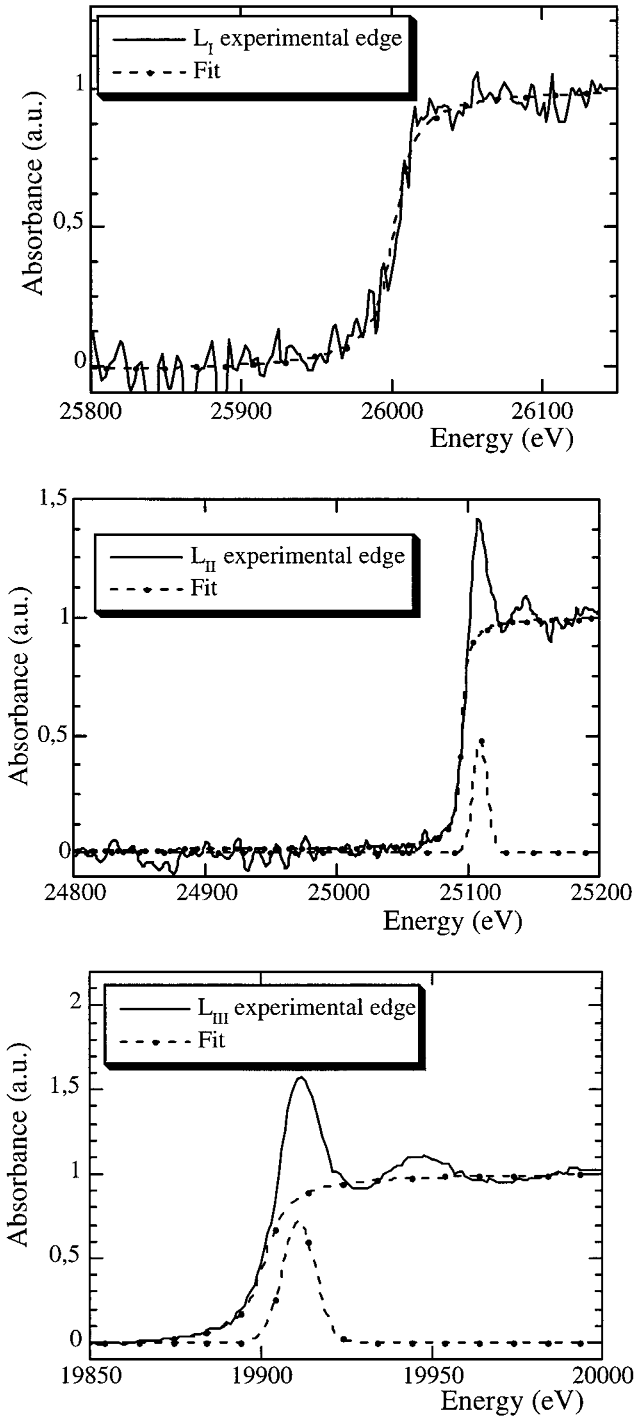

Figure 1. L$_I$, L$_{II}$, and L$_{III}$ edges of Cf^{3+} aquo ion in 1 M HCl aqueous solution at room temperature.

Results and Discussion

According to the dipolar approximation of the X-ray absorption process, the L edges of the Cf atom correspond to the following electronic transitions: $2p_{3/2} \rightarrow 6d_{3/2}$ for the L$_{III}$ edge, $2p_{1/2} \rightarrow 6d_{1/2}$ for the L$_{II}$ edge, and $2s_{1/2} \rightarrow 7p_{1/2}$ for the L$_I$ edge. The L$_I$, L$_{II}$, and L$_{III}$ edge experimental spectra and fits are shown in Figure 1. Edge positions reported in Table 1 have been determined as the value of the energy of the arctangent function in least-squares fits of the XANES region using an arctangent plus a Gaussian function.[10] The white line width is also given as twice the energy difference between the edge inflection point and the white line maximum. Interestingly, the edge positions differ significantly from the theoretical edge positions[11] on Cf^0, and these discrepancies (between 10 and 20 eV) are too large to be explained by the formal change of oxidation states (from III to 0). Such data are thus of primary importance as reference data for calculations on heavy actinide atoms and for future comparison with further actinide(III) coordination complexes, as already shown on other actinides.[12−15]

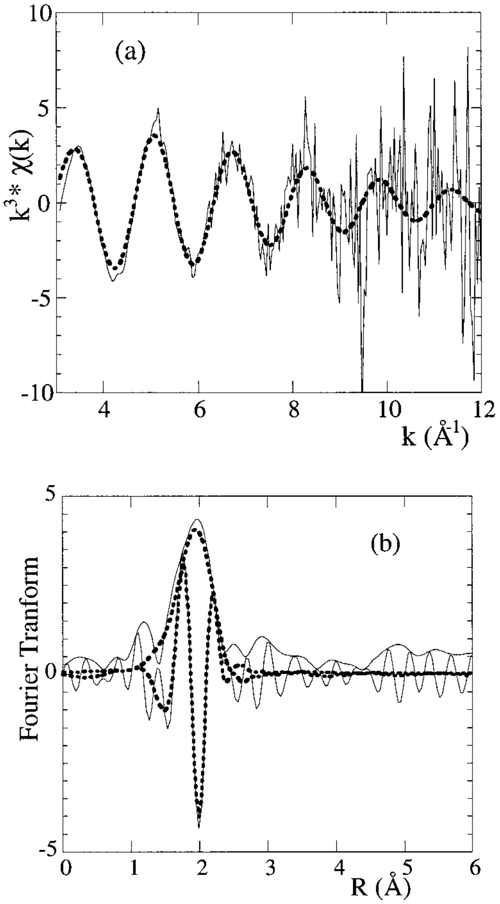

Figure 2. Cf L$_{III}$ edge k^3-weighted EXAFS data (a) and corresponding Fourier transform (b) (experimental data and theoretical fit).

Figure 2 shows the k^3-weighted EXAFS data and the corresponding FT spectrum. The FT spectrum shows a single peak that was fit by a single shell of 8.5 oxygen atoms[16] at 2.42 Å, as summarized in Table 2. This result shows that no formation of an inner-sphere chloro complex occurs for this Cl$^-$ concentration (1 M). This is consistent with previous data obtained at the same Cl$^-$ concentration for the Pu^{3+} aquo ion.[17] Furthermore, the Cf−O distance of 2.42 Å compares well with

---

(10) Fit = $m[1] + m[2]*(\arctan((x - m[3])*m[4])) + m[5]*\exp(-((x - m[6])^2)/(m[7]^2))$, where x is the X-ray energy in eV and the m's are the fit parameters (from ref 11).

(11) Indelicato, P.; Bouvard, S.; Lindroth, E. *Eur. Phys. J. D* **1998**, *3* (1), 29.

(12) Conradson, S. D.; Al Mahamid, I.; Clark, D. L.; Hess, N. J.; Hudson, E. A.; Neu, M. P.; Palmer, P. D.; Runde W. H.; Tait, C. D. *Polyhedron* **1998**, *17*, 599.

(13) Edelstein, N. M.; Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Sofield, C. D. *J. Am. Chem. Soc.* **1996**, *118*, 13115.

(14) Hudson, E. A.; Rehr, J. J.; Bucher, J. J. *Phys. Rev. B* **1995**, *52*, 13815.

(15) Kalkowski, G.; Kaindl, G.; Brewer, W. D.; Krone, W. *Phys. Rev. B* **1987**, *35*, 2667.

(16) This value is to be taken as indicative considering the large error bar associated with it.

(17) Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Edelstein, N. M.; Reich, T. *Inorg. Chem.* **1997**, *36*, 4676.

Table 2. EXAFS Structural Parameters for the Cf^{3+} Aquo Ion in 1M HCl at Room Temperature

	R_{Cf-O} (Å)[a]	N[a]	σ (Å)[a]	ΔE_0 (eV)[a]	S_0^2	χ_ν^2
Cf^{3+} in 1M HCl	2.42 ± 0.02	8.5 ± 1.5	0.095 ± 0.01	1.4 ± 1	0.924	0.4

[a] The signal over noise ratios are estimated by the filtering noise method.[21]

the distances given by Allen et al.[18] for the Pu^{3+}, Am^{3+}, and Cm^{3+} aquo ions (respectively 2.51, 2.48, and 2.45 Å) in chloride acidic solution. Here, the observed contraction is due essentially to the smaller size of Cf^{3+} compared to the other 3+ actinides.[19,20]

EXAFS measurements on the actinide(III) series (U^{3+}, Np^{3+}, Pu^{3+}, Am^{3+}, and Cm^{3+}) of aquo ions are presently being undertaken. In a future paper, results on this series of ions will be compared with data related to the trivalent lanthanide(III) aquo ions.

Acknowledgment. We thank H. Noël of Rennes 1 University, CSIM, for providing the $UO_{2.0}$ sample and Pr. A. Michalowicz for helpful discussion on the standard deviation. We are indebted for the loan of ^{249}Cf through the heavy isotopes production program of the U.S. Department of Energy, specifically the High Flux Isotope Reactor and Radioelement Development Centre of Oak Ridge National Laboratory.

IC990214L

---

(18) Allen, P. G.; Shuh, D. K.; Bucher, J. J.; Edelstein, N. M.; Reich, T. A Euroconference and NEA Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources, Grenoble, France, Oct 4−6, 1998.

(19) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.

(20) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1970**, *B26*, 1046.

(21) Newville, M.; Boyanov, B.; Sayers, D. The 10th International Conference on X-ray Absorption Fine Structure, Chicago, Aug 10−14, 1998.