ELSEVIER

Journal of Alloys and Compounds 271–273 (1998) 184–188

Journal of ALLOYS AND COMPOUNDS

Structural study of holmium (III) and uranium (VI) organic ligand complexes by extended X-ray absorbtion fine-structure spectroscopy

Tsuyoshi Yaita[a,*], Hirokazu Narita[a], Shinichi Suzuki[a], Shoichi Tachimori[a], Hideaki Shiwaku[b], Haruhiko Motohashi[b]

[a]*Department of Chemistry and Fuel Research, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki, 319–11, Japan*

[b]*Department of Synchrotron Radiation Facilities Project, Japan Atomic Energy, Research Institute, Spring-8, Akoh-gun, Hyogo, 678–12, Japan*

Abstract

The structures of holmium-organophosphorus mono- and bidentate ligands and uranium-monoamide ligand complexes in solutions were determined by extended X-ray absorption fine-structure spectroscopy. The diphosphine dioxide coordinates directly to holmium with symmetric bidentate mode, while the carbamoyl phosphine oxide with asymmetric bidentate mode. The structure for uranium-*N*,*N*-dihexyl-3-ethylhexanamide complex is very similar to that for the aqua nitrato uranyl complex in bond distance and coordination number.

Keywords: EXAFS; Lanthanide; Uranium; Complex structure in solution; Diphosphine dioxide; CMPO; Amide

---

1. Introduction

Trivalent lanthanide and actinide ions are efficiently extracted from aqueous nitrate and chloride solutions by bidentate organophosphorus compounds such as calbamoyl phosphine oxides (CMPO) [1] and diphosphine dioxides (DPDO) [2]. Studies regarding the trivalent lanthanides and actinides extractions with the bidentate ligands have been reported and several mechanisms have been proposed by many researchers [3–5]. The differences in the extraction properties were, however, not completely clarified solely by the extraction studies. Siddall [6,7] first studied the extraction mechanism for lanthanide–carbamyl phosphonate (CMP) complexes based on equilibrium measurements, and concluded that tris-bidentate chelate complexes, $M(CMP)^{3+}$ were formed in organic phases during the extraction processes. Furthermore, Stewart and Siddall [8] isolated several lanthanide–CMP complexes from the ethanol solutions and their compositions were deduced from the elemental analyses. Structural study is very important, since it yields direct information about coordination properties and steric effects. However, as single crystals for some complexes often cannot be isolated from solution, single crystal X-ray and neutron diffraction studies are not always possible and very few are possible for extractant systems related to nuclear waste reprocessing. In contrast, extended X-ray absorption fine-structure (EXAFS) spectroscopy can be used to probe a local structure around a specific metal of interest, and does not need single crystals. Therefore, the EXAFS method is very useful for structural studies of organometallic complexes in solution, and recently has begun to be applied to studies regarding nuclear waste reprocessing. The purpose of this study is to understand local structures for lanthanide and actinide–organic ligand complexes in solutions. The extractants used in this study are the mono- and bidentate organophosphorus compounds for trivalent lanthanide extraction, and the amide compound for hexavalent uranium extraction. Amide compounds have recently been noticed as a substitute for tributyl phosphate (TBP) in the nuclear reprocessing fields. We will discuss the coordination properties of mono- and bidentate ligands to lanthanide and actinide ions.

2. Experimental

The solution samples for lanthanide complexes were prepared by dissolving holmium chloride salt into ethanol solution containing a ligand. These sample solutions were stirred for one night at room temperature. Complexations were confirmed using ^{31}P and ^{13}C NMR measurement at 223 K. Additionally, coordination numbers of ligands were also confirmed by area integration of ^{31}P NMR peaks for

---

[*] Corresponding author.

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(98)00051-6

complexed and free ligand (see N for Ho-O_1 in Table 1). The concentrations of the metals (Ho and U) were 0.1–0.2 mol/l. The organophosphorus ligands used in this study were DPDOs (TTMDPDO: tetra *p*-tolylmethylene diphosphine dioxide, and TOMDPDO: tetraoctylmethylene diphosphine dioxide), CMPO: *n*-octylphenyl-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide), and TBP: tributyl phosphate. The solution samples for uranium complexes were prepared by extraction from an aqueous 3 mol/l nitric acid solution with DH3EHA: *N*,*N*-dihexyl-3-ethylhexanamide in dodecane at room temperature.

L_{III} edge X-ray absorption spectra of the holmium and uranium were measured in transmission mode at the BL27B station of the Photon Factory at the High Energy Accelerator Organization (KEK). Synchrotron radiation from a storage ring operated at 2.5 GeV with a beam current of 100–250 mA was monochromatized with a Si (111) double crystal monochromator. We analyzed the data as following. Background adsorption was estimated by a least-squares fitting procedure with a Victorian function and a constant term, and was subtracted from the total adsorption. The smooth L_{III}-shell adsorption (μ0) was removed by a four-section cubic spline.

The EXAFS signal $\chi(k)$ was extracted and normalized as follows:

$$\chi(k) = [\mu(k) - \mu_0(k)]/\mu_0(k) \tag{1}$$

where k is the photoelectron wave vector given as $\sqrt{2m(E - E_0)/\hbar^2}$ (E denotes the energy of the incident X-rays and E_0 is the threshold energy for the liberation of the photoelectron wave). In this study, E_0 was the maximum value of a first-order derivative for the edge jump. The k^3-weighted EXAFS signals: $k^3\chi(k)$ were Fourier transformed from k space into r space to give a radial structural function (RSF):

$$\Phi(r) = \left(\frac{1}{2\pi}\right)^{1/2} \int_{k\,\min}^{k\,\max} k^3\chi(k)W(k)\exp(2ikr)dk \tag{2}$$

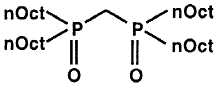
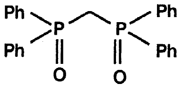
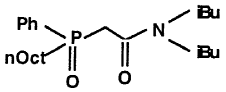
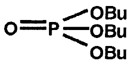
where $W(k)$ is a Hanning window function applied to the first and last 5% of the k-space data to smooth the finite transform. $k_{\min}$ and $k_{\max}$ are the lower and upper k values of the EXAFS data, which were 2.5 and 12 $Å^{-1}$ for holmium, and 4.0 and 14 $Å^{-1}$ for uranium, respectively. Peaks in the RSF represent a contribution due to ordering of the nearest neighbor of the metals. In quantitative study, the raw k^3-weighted filtered data were fitted to the single-scattering EXAFS equation,

$$k^3\chi(k) = k^2N_j\exp(-2\sigma_j^2k^2 - 2r_j/\lambda)F_j(k)\sin[2kr_j + \alpha_j(k)]/r_j^2 \tag{3}$$

where $F_j(k)$ is the backscattering amplitude from each of N_j scattering j atom, at distance r_j from an X-ray absorbing

Table 1

EXAFS structural parameters for holmium organophosphorus complexes in ethanol

Ligand \ Distance	Ho-O1 (O=P) (O=C)*			Ho-O2 (Water)			Ho--P (P=O) Ho--C** (C=O)		
	r / Å	N$^{1)}$	σ^2	r$^{3)}$/ Å	N	σ^2	r / Å	N	σ^2
 TOMDPDO	2.28	2 (1)$^{2)}$	0.004	2.37	4	0.006	3.60	2	0.009
 TTMDPDO	2.32	4 (2)$^{2)}$	0.006	2.37	4	0.01	3.61	4	0.01
 CMPO	2.31 2.51*	2 2* (2)$^{2)}$	0.003 0.003*	2.37	4	0.006	3.51 3.70**	2 2**	0.004 0.01**
 TBP	2.55	2	0.003	2.37	6	0.01	3.81	2	0.008

r: Bond distance, N: Coordination number, σ: Debye–Waller factor.

[a] All the coordination numbers of ligands based on NMR results, held constant during fit.

[b] The numbers in parenthesis are the coordination numbers as a bidentate ligand.

[c] $r = 2.37$ Å, held constant during fit.

atom. $\alpha_j(k)$ is the total scattering phase shift experienced by the photoelectron. Theoretical values of $F_j(k)$ and $\alpha_j(k)$ calculated by Mackale [9] for holmium, and from FEFF 5 of Rehr et al. for uranium were used [10].

3. Results and discussion

3.1. Lanthanides complexes

The radial structural function (RSF) obtained by the absolute values of Fourier transforms of k^3-weighted EXAFS are shown in Fig. 1. The RFS's phase shifts associated with the absorber–scatterer interactions were not corrected (0.2–0.5 Å). The RSF apparently consist of 2 shells. Taking the single crystal data for diisopropyl *N*,*N*-diethylcarbamylmethylenephosphonate (CMP)–lanthanide complexes [11] into account, the first shells, at about 2.0 Å in the RSF, represent contributions from the oxygen of the ligands, while, the second shells, at about 3.2 Å in the RSF for the bidentate complexes and 3.4 Å in the RSF for TBP complexes, arise from phosphorous of phosphoryl group and carbon of carbonyl group. In this study, there are no significant differences in the RSF patterns between holmium–DPDO and –CMPO complexes. In contrast, the shell position of the TBP complex shows a different pattern with about 0.2-Å longer distances of phosphorous for TBP than for bidentate ligands. This result indicated that the bidentate ligands coordinate more strongly to lanthanides by chelation than the monodentate one.

Fig. 2 shows the raw EXAFS signals weighted with k^3 and the fitting results for the holmium complexes, demonstrating the fitting quality over the *k*-range. The Ho-O$_1$ distances for the TTMDPDO, TOMDPDO, CMPO and TBP complexes are listed in Table 1. For the DPDO complexes, the interatomic distances shorten in the order of TTMDPDO: 2.32 Å>TOMDPDO: 2.28 Å. This order agreed with the reverse order of magnitude for basicity [12] [pK_a: TOMDPDO (8.6)>TTMDPDO (6.5)]. Accordingly, this result reasonably demonstrated that the ligands having higher basicity interact strongly with lanthanides. Additionally, the coordination number (CN) of ligands also decreased in the same order as the interatomic distance: TTMDPDO (CN=2)>TOMDPDO (CN=1): These CNs for bidentate coordination are the numbers in parenthesis in Table 1. Rozen et al. [12] first reported the AAS effect (Anomalous Aryl Strengthening effect), and explained that this effect was due to the transmission of electron density from phenyl groups into the Ln (or Ac)–DPDO complex's basic rings. Therefore, TTMDPDO, having 4 phenyl groups, would coordinate more strongly to lanthanides and actinides than the other ligands, regardless of basicity. Actually, the distribution ratio of trivalent lanthanide and actinide with TTMDPDO is higher than that with TOMDPDO. In this study, the difference in the

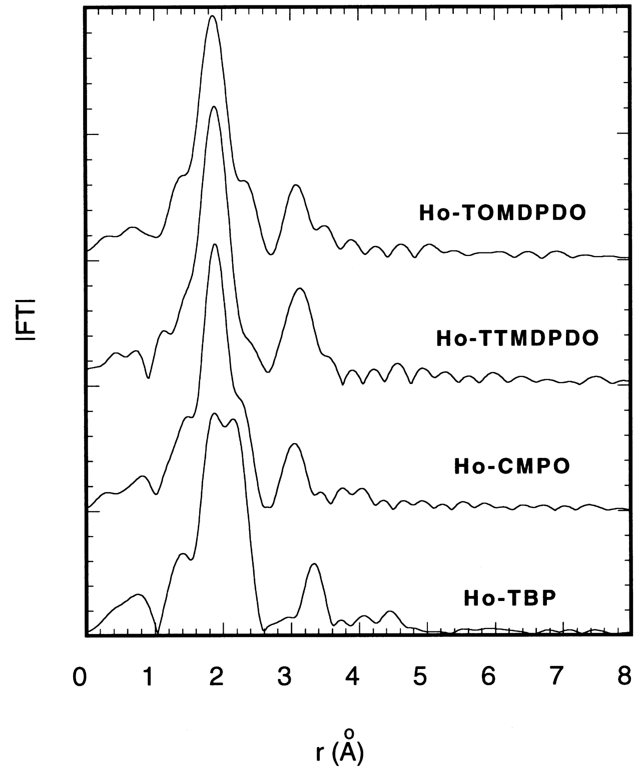


Fig. 1. Radial structural functions for Ho-ligand complexes in ethanol. * The phase shifts were not corrected.

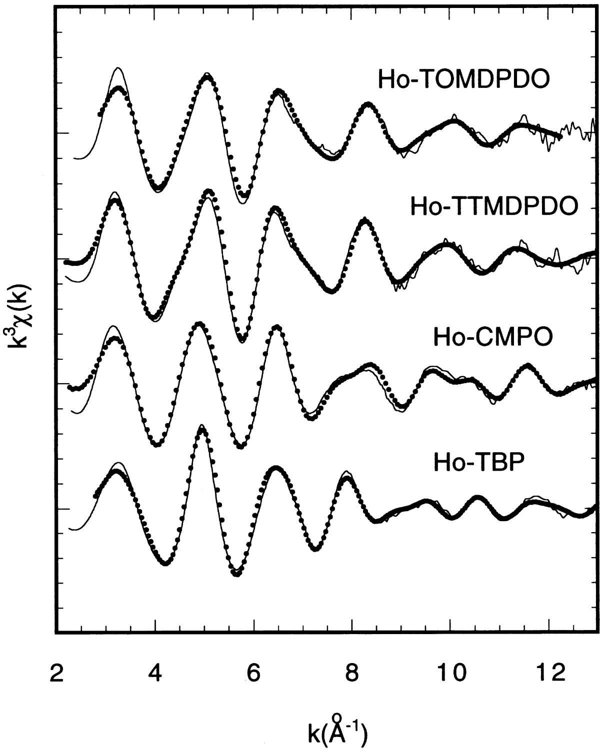


Fig. 2. Raw Ho L$_{III}$-edge k^3-weighted EXAFS data for Ho-ligand complexes in ethanol. The solid lines are the experimental data, and the dotted lines are the best theoretical fits of data.

interatomic distances and coordination numbers is a noteworthy result and regarded as a important factor for the explanation for the AAS effect, since the coordination number of the ligand closely relates to the hydrophobicity of the extraction complex. Accordingly, distribution ratios of lanthanide and actinide with TOMDPDO, in spite of showing stronger interaction with these elements, are lower than that with TTMDPDO.

As mentioned above, the RSF pattern for CMPO is similar to that for DPDOs. However, the EXAFS oscillation for CMPO complex, especially in the region above 7 $Å^{-1}$, is different from that for DPDO complex and shows the intermediate pattern between DPDO and TBP. From the fitting results, the phosphoryl group of TBP, as compared with the DPDOs and CMPO, is located at the longer position; the Ho-O_1 and Ho-P are 2.55 Å and 3.8 Å, respectively. Additionally, the carbonyl group for CMPO is also at the longer position; Ho-O_1 and Ho-C are 2.51 Å and 3.7 Å, respectively. As a result, CMPO coordinates to holmium with asymmetric bidentate mode. The previous single crystal result for CMP complexes [11] reported that the two CMP molecules coordinate to Sm with symmetrical bidentate mode, and in contrast, to Er with asymmetric bidentate mode through water. Horwitz et al. [13] have investigated extraction chemistry of carbamylmethylenephosphonate (DHDECMP) with lanthanides and actinides. They suggested that monodentate tris-chelates are formed in the organic phase. In this study, however, CMPO's carbonyl oxygen possibly coordinates directly to holmium from the standpoint of the bond distance.

3.2. Uranium complexes

Fig. 3 shows the RSFs for the uranium (VI)—DH3EHA complex in dodecane and the uranium (VI) in aqueous nitrate solutions. The RSF's phase shifts were not corrected. Fig. 4 shows that the raw EXAFS signals weighted with k^3 and the fitting results for the uranium complexes. For both the samples, assignments of shells were performed by taking a hexagonal bipyramidal coordination of the UO_2^{2+} ion into account. Fitting results are listed in Table 2. For the uranium (VI) in aqueous nitrate solutions, the first shell, at 1.75 Å, corresponds to two axial oxygen of UO_2, while the second shell, at 2.40 Å, arises from two oxygen atoms of waters in the equatorial plane. The third shell, at 2.50 Å, is due to four oxygen atoms of nitrate ions. These fits were performed on the basis of the single crystal structure result [14]. On the other hand, the DH3EHA, according to the previous solvent extraction studies [15], forms a bis complex: $UO_2(NO_3)_2\cdot$2DH3EHA. Thus, the structure of this complex would be estimated by replacing two water molecules with two DH3EHA molecules. Fits were based on a 5-shell cluster with 12 atoms having a 4.0-Å radius. As a result, the bond distance between uranium and oxygen atoms of DH3EHA is 2.39 Å, which is approximately equal to the bond

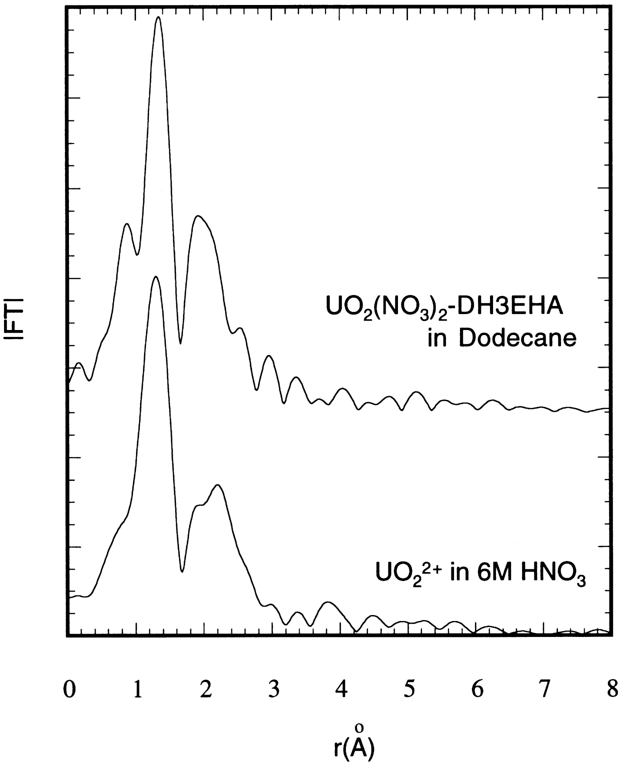


Fig. 3. Radial structural functions for uranium complexes. * The phase shifts were not corrected.

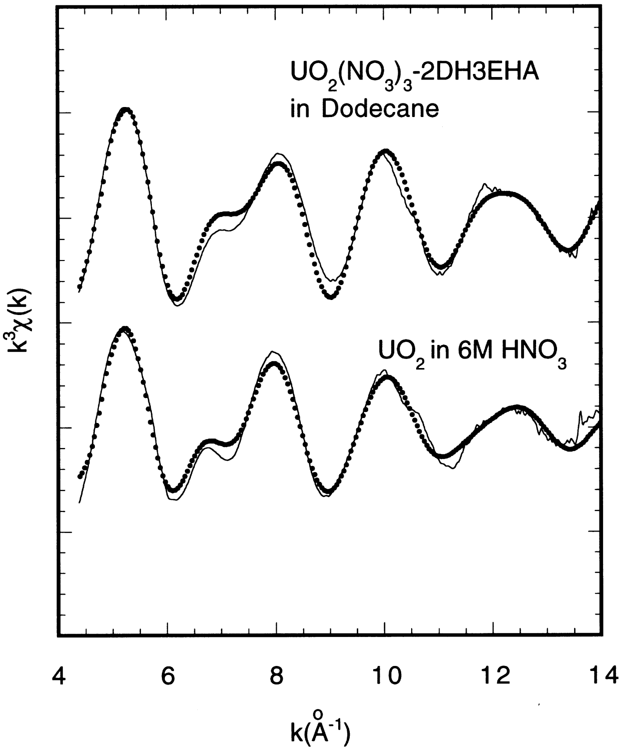
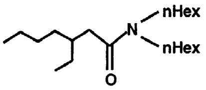


Fig. 4. Raw L_{III}-edge k^3-weighted EXAFS data for the uranium complexes in the solutions. The solid lines are the experimental data, and the dotted lines are the best theoretical fits of data.

Table 2
EXAFS structural parameters for uranium–DH3EHA complex in dodecane and uranium nitrate in aqueous 6 M HNO_3 solution

Complex / Distance	$UO_2(NO_3)_2 \cdot 2H_2O$			 $UO_2(NO_3)_2 \cdot 2\underline{DH3EHA}$		
	r / Å	N	σ^2	r / Å	N	σ^2
U-O_{ax} ($U\underline{O}_2$)	1.75	2	0.004	1.75	2	0.003
U-Oeq_1 ($\underline{O}H_2^{1)}$, $\underline{O}$=$C^{2)}$)	$2.40^{1)}$	$2^{1)}$	$0.01^{1)}$	$2.39^{2)}$	$2^{2)}$	$0.01^{2)}$
U-Oeq_2 ($\underline{O}_2NO$)	2.51	4	0.008	2.50	4	0.008
U--C ($\underline{C}$=O)				3.60	2	0.008
U--N($O_2\underline{N}O$)	2.95	2	0.005	2.95	2	0.005

r: Bond distance, N: Coordination number, σ: Debye-Waller Factor
1) Oxygen atoms of water
2) Oxygen atoms of carbonyl group

distance between uranium and the oxygen atoms of water. The shell, at 1.75 Å, corresponds to axial oxygen of uranyl ion. The nitrate ions are located at approximately the same position as in the uranyl nitrate results. The carbon of carbonyl group is at approximately 3.6 Å. This distance is less accurate, since this position includes an O=U=O multi-scattering shell [16,17]. A comparison ofthe uranyl nitrate and DH3EHA complex shows that most of the positions of coordinated atoms of DH3EHA complex are very similar to uranyl nitrate.

References

[1] W.W. Schultz, E.P. Horwitz, Sep. Sci. Technol. 23 (1987) 1191.
[2] T. Yaita, S. Tachimori, Radiochim. Acta 73 (1996) 27.
[3] E.P. Horwitz, K.A. Martin, H. Diamond, L. Kaplan, Solv. Extr. Ion Exch. 4 (1980) 449.
[4] B.F. Myasoedov, M.K. Chmutova, N.E. Kochetkova, O.E. Koiro, G.A. Pribylova, N.P. Nesterova, M.I.T.Ya. Kabuchnik, Solv. Extr. Ion Exch. 4 (1986) 61.
[5] E.P. Horwitz, H. Diamond, K.A. Martin, Solv. Extr. Ion Exch. 5 (1987) 447.
[6] T.H. Siddall, J. Inorg. Nucl. Chem. 25 (1963) 883.
[7] T.H. Siddall, J. Inorg. Nucl. Chem. 26 (1964) 1991.
[8] W.E. Stewart, T.H. Siddall, J. Inorg. Nucl. Chem. 32 (1970) 3599.
[9] A.G. MaKale, B.W. Veal, A.P. Paulikas, S.-K. Chan, G.S. Kanpp, J. Am. Chem. Soc. 110 (1988) 3763.
[10] J.J. Rehr, R.C. ALbers, S.I. Zabinsky, Phys. Rev. Lett. 69 (1992) 3397.
[11] S.M. Bowen, E.N. Duesler, R.T. Paine, Inorg. Chim. Acta 61 (1982) 155.
[12] A.M. Rozen, Z.A. Berkman, Radiokhimiya 18 (1976) 493.
[13] E.P. Horwitz, A.C. Muscatello, D.G. Kalina, L. Kaplan, Sep. Sci. Technol 16 (1981) 417.
[14] U. Bauder, E. Henrich, R. Stahl, KfK-Report, KfK-4476, 1988, pp. 255.
[15] S. Suziki, K. Tamura, S. Tachimori, Y. Usui, Proceeding of Fall meeting of the Atomic Energy Society of Japan, K24, 1996, pp. 606.
[16] E.A. Hudson, P.G. Allen, L.J. Terminello, M.A. Denecke, T. Reich, Phys. Rev. B 54(1) (1996) 156.
[17] M.A. Denecke, T. Reich, S. Pompe, M. Bubner, K.H. Heise, H. Nitche, J.J. Bucher, N.M. Edelstein, D.K. Shuh, J. Phys. IV France 7 (1997) 637.