

## EXAFS studies of americium (III)-benzimidazole complex in ethanol

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The local structures of Am, Nd and Er-Benzimidazole (Biz) in solution were determined by EXAFS. The BIZ molecule coordinated to Am and Nd through two nitrogen atoms in a bidentate fashion. Two nitrogen atoms of BIZ ligated to Am and Nd with the bond distances  $R_{Am-N} = 2.63 \text{ \AA}$  and  $R_{Nd-N} = 2.65 \text{ \AA}$ , respectively. The total coordination number of the Am BIZ complexes (at a molar ratio of metal ion to ligand of 1:20) was  $\sim 10$  but that of Nd BIZ complex was  $\sim 9$ .

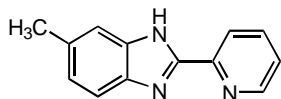
**Key words:** americium, benzimidazole, EXAFS; ethanol; neodymium; structure.

### 1. Introduction

A central process in the recovery of actinides from high level radioactive wastes is separation of trace amounts of the minor actinides, Am and Cm, from macro amounts of light lanthanides of the fission products. However, the specific separation of the trivalent actinides from lanthanides is difficult because the chemical behavior of these ions is similar. From recent studies, it was found that the required separation can be attained utilizing neutral soft donor extractants (Kolarik et al, 1997; P.Y. Cordier et al., 1998). In this study, we used one of the ideal ligands: benzimidazole (BIZ) developed by Kolarik et al., which is easily synthesized, and has a good ability to separate trivalent Am and Cm from the light lanthanides trivalent ions. Kolarik et al have systematically studied the extraction of Am and Eu with BIZ, and concluded that the An/Ln separation was related to the solvation number of BIZ from their results on the coordination behavior of BIZ and the counter ion. Therefore, structural studies on these compounds are very important in order to explain these mechanisms. Understanding the separation mechanism by determining the molecular structure between the metal ions and BIZ will be very useful for the molecular design of the new reagents. In this study, we measured the EXAFS of Am and Nd ions with the BIZ complexes in solution. Nd(III) was the light lanthanide ion chosen to model the separation from Am(III).

### 2. Ligand

The ligand used in this study is 6-methyl-2-(2-pyridyl) benzimidazole: BIZ, and is shown in Fig.1. The synthesis of BIZ and its use in the separation of Am(III)/Eu(III) were reported by Kolarik et al, 1997. This ligand is a neutral compound, forming  $MA_3 \cdot nBIZ$  ( $n=1\sim 3$ ; M: trivalent lanthanides and actinides; A:  $SCN^-$ ,  $NO_3^-$ ,  $Cl^-$ ).



**Figure 1**  
Chemical structure of 6-methyl-2-(2-pyridyl) benzimidazole

### 3. Sample preparation

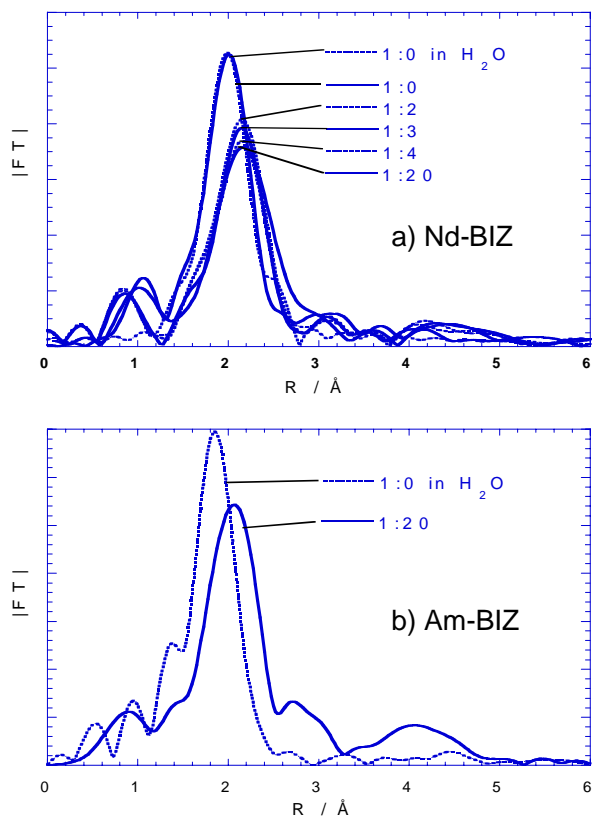
Hydrated lanthanide chlorides:  $NdCl_3 \cdot 6H_2O$  were dissolved in the ethanol solutions which contained BIZ at a concentration equivalent to the mole ratios M:BIZ=1:0, 1:2, 1:3, 1:4, and 1:20. The concentrations of the metal ions were 0.1 mol/L for the 1:0 - 1:4 samples, and 0.005 mol/L for the 1:20 samples. The solution used for dissolving the salts was an ethanol solution of about 96 wt%. Americium-243 in hydrochloric acid solution was evaporated almost to dryness. This residue was dissolved in about 96 wt% of ethanol solution that contained BIZ. The preparation of americium solutions was handled in the glove box at LBNL. Additionally, aqueous solutions of Am and the lanthanide ions were prepared for comparison with the above ethanol solution systems. Anhydrous lanthanide chlorides did not dissolve in 100% ethanol solution but could be dissolved easily by adding a small quantity of water. Therefore, ethanol solutions of lanthanide ions were prepared mixed with a small amount of water.

### 4. Exafs measurement

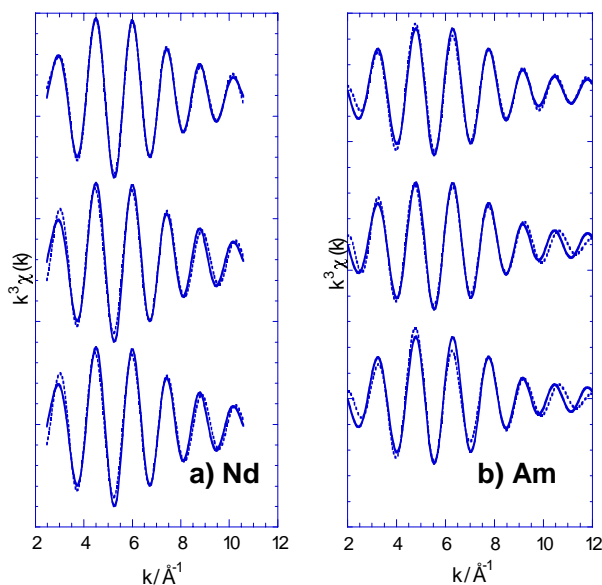
The EXAFS spectra at the  $L_{III}$ -edge of Nd and Am solutions were measured in transmission and fluorescence modes at the BL-27B of Photon Factory (PF), KEK, Japan, and the BL 4-1 of SSRL, SLAC, USA. The synchrotron radiation was monochromatized with double crystal Si(111) at PF and Si(220) at SSRL. Solution samples were sealed in a polyethylene bag with a Teflon spacer for the lanthanides, and in polyethylene tubes for americium. EXAFS reduction and curve fitting were carried out by XAS data analysis package WinXAS ver.2.0 (Ressler, 1997). The theoretical phases and amplitude were calculated by FEFF8 (Zabinsky et al, 1995).

### 5. Results and discussion

Figures 2a,b show the radial structural function (RSF) about the Nd and Am ions in ethanol solutions which contained benzimidazole (BIZ). The RSF of  $NdCl_3$  in 96% ethanol solutions are the same as those in water, indicating that only water coordinates to Nd in these solution. For the solutions that contain BIZ, the coordinated water about the metal ion was replaced by the BIZ ligand gradually as the concentration of the BIZ ligand increased in the solutions. BIZ preferentially ligated to Nd and Am, suggesting that BIZ is a strong ligand toward the trivalent lanthanide and the actinide ions in comparison with alcohol and water. The local structure about the Nd ion in the Nd-Biz system didn't change greatly as the mole ratio of Nd: BIZ was raised from 1:2 to 1:20. As for the Am-BIZ system, the coordination of BIZ to Am was clearly observed in the 1:20 sample similar to the Nd samples. The structure apparent in the RSF's shown in Figures 2a,b arise from the coordination of the O from water and from the N atoms in the BIZ ligands with the metal ions. Consequently, we have only to take the coordination of the oxygen atoms of water and the nitrogen of BIZ into consideration to analyze the structures of the nearest neighbors of the metals. BIZ is expected to coordinate through two N atoms (one N atom from the six-membered ring and one N atom from the five-membered ring shown in Figure 1 and retain its planar structure. Piguet et al. (1996) reported that BIZ retains its planar structure in various crystal structures. The multi-dentate heteronuclear ligands: terpyridine, and bipyridine-pyrazine derivatives also have the same planar structure in complexes as BIZ (M.G.B. Drew et al., 2000). The input for FEFF8 calculations, therefore, were based on these crystal structures. As mentioned previously, the nearest neighbor atoms to the metal ions consist of oxygen atoms from water and/or nitrogen atoms from BIZ. Therefore, the following models were considered as shown in Fig.3a,b: 1) oxygen atoms 1 shell model; 2) nitrogen atoms 1 shell model; 3) oxygen atoms and nitrogen atoms 2 shell mode, for fitting to the back Fourier-transformed 1<sup>st</sup> shell of the



**Figure 2 a), b)**  
 Radial structural functions of a) Nd-, and 2) Am-BIZ complexes in ethanol.  
 \*1:N=[M<sup>3+</sup>]:[BIZ]; N=0,2,3,4,20; M=Nd and Am.  
 \*\*1:0 in H<sub>2</sub>O denotes MCl<sub>3</sub> in water; M=Nd and Am.  
 \*\*\*FT range: a) k=1.85-10.92 Å<sup>-1</sup> for Nd-BIZ system;  
 b) k=1.4-12.04 Å<sup>-1</sup> for Am-BIZ



**Figure 3a), b)**  
 EXAFS oscillations of a) Nd- and b) Am-BIZ complexes in ethanol.  
 \*The solid line and the dotted line denote the raw and theoretical data.  
 \*\* Back FT range: a) R=1.2-2.5 Å for Nd in H<sub>2</sub>O, and 1.5-2.8 Å for Nd-BIZ in ethanol system; b) R=1.1-2.5 Å for Am in H<sub>2</sub>O, and 1.2-2.6 Å for Am-BIZ in ethanol system.

**Table 1** The fitting results of the EXAFS oscillations for back fourier-transformed radial structural function of Am and Nd-Benzimidazole ([M<sup>3+</sup>]:[BIZ]=1:20) complexes in ethanol.

Ion	Fit model	atom	N	R/ Å	σ <sup>2</sup> /Å <sup>2</sup>	ΔE	S <sub>0</sub> <sup>2</sup>	r%
Am	O 1 shell	O	9.5	2.55	0.010	9.6	0.9	25
	N 1 shell	N	10	2.56	0.011	11	0.9	20
	O,N 2 shell	O	6.0	2.48 <sup>a)</sup>	0.009	7.4	0.9	10
	N	4.0	2.63	0.004	12			
Nd	O 1shell	O	9.3	2.57	0.011	7.9	0.8	20
	N 1 shell	N	9.2	2.57	0.011	9.0	0.8	20
	O,N 2shell	O	5.3	2.51 <sup>b)</sup>	0.009	4.6	0.8	7
	N	3.8	2.65	0.006	14			

N: coordination number; R: bond distance σ<sup>2</sup>: Debye-waller factor squared; ΔE: energy shift; S<sub>0</sub><sup>2</sup>: amplitude reduction factor;  
 r: residual={Σ|y<sub>exp(i)</sub>-y<sub>theo(i)</sub>|/Σ|y<sub>exp(i)</sub>|} x 100 (%) \*y denote experimental and theoretical data points.  
 \*\* a) and b) were fixed parameters and referred from a)Allen et al., 2000; b) Yaita et al., 1999 and Yamaguchi et al, 1998.

RSF. We assumed the distances of the of the oxygen atoms to the metal ion for coordinated water in the BIZ sample solutions were the same as those found in the pure water samples except for the fitting to one shell of oxygen atoms only (Fig. 3a,b). It is clear from Figure 3a,b that the best fit is obtained with the two shell model for Am and Nd. The results for each of the above models for the sample with a metal:BIZ ratio of 1:20 are summarized in Table 1. The nitrogen atoms of BIZ coordinated to of BIZ and Am, and Nd would be almost ionic. Kolarik et al, 1997 reported that the separation factors for Am/Eu solutions ranged from 10 to 100, and concluded that the separation factor depended on the number of BIZ molecules in the extracted metal complex. In this study, however, no difference was found in the number of BIZ molecules in the 1st coordination sphere for the Am and Nd complexes at the metal:ligand ratio of 1:20. Many researcher proposed covalent interaction between actinide and soft donor ligand gives good separation between trivalent-lanthanide and actinide in extraction process. However, the chemical bond properties between the nitrogen of BIZ and Am can be estimated to be very similar to the bond in Nd complex from the results of the bond distances. The BIZ ligand appears to be bonded to americium and neodymium by a weaker interaction than the water oxygen atoms. Consequently, the contribution of the covalent bond to chemical bonds between nitrogen of BIZ and americium in the complex would be small.

**6. Summary and conclusion**

The structural parameters of Nd (III) and Am (III)-BIZ complexes in ethanol were determined by EXAFS.

The BIZ molecule coordinated to the metal ions through the nitrogen atoms in a bidentate mode. The bond distances between Nd, Am and the nitrogen atoms of BIZ are longer than the metal ion-O atoms from water.

The number of BIZ ligands in the first coordination sphere of the Nd and Am ions was ~2. The bond nature between nitrogen of BIZ and Am was regarded to be similar to that in Nd complexes.

This work was supported in part by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences under U. S. Department of Energy Contract No. DE-AC03-76F00098 at LBNL. This work was performed in part at SSRL that is operated by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences under U. S. Department of Energy Contract No. DE-AC03-76F00515.

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