

## Structural study of selective complexation of Sr(II) by XAFS method

Kazuhiro Akutsu<sup>1,\*</sup>, Hiroki Iwase<sup>1</sup>, Shiho Yada<sup>2</sup>, and Tomokazu Yoshimura<sup>2</sup>

<sup>1</sup> Comprehensive Research Organization for Science and Society (CROSS), 162-1 Shirakata, Tokai, Ibaraki, 319-1106, Japan

<sup>2</sup> Research Group of Chemistry, Division of Natural Sciences, Nara Women's University, Kitauoya-higashimachi, Nara, 630-8506, Japan

### 1 Introduction

Strontium-90 (<sup>90</sup>Sr) having long radiological half-life is radioactive in nature and it falls under the category of most hazardous of radioactive fallout [1]. Investigation of the effects of <sup>90</sup>Sr on environment and human body are one of the most important issues for the management of radioactive elements. Fluorescent probes are sufficiently sensitive to detect a tiny amount of metal ions such as strontium ion (Sr(II)) because of its exquisite sensitivity and selectivity. Therefore, many kinds of fluorescent probes for Sr(II) detection have been developed [2, 3].

Recently, we synthesized a Sr(II) selective fluorescent probe, *N*-(2-hydroxy-3-(1*H*-benzimidazol-2-yl)-phenyl methyl)-1-aza-18-crown-6-ether (Hbice), and studied its fluorescence properties and complexation behavior with Sr(II). In present study, the local structure of the Sr(II)-Hbice complex in DMSO is determined using EXAFS analyses to reveal the species of Sr(II) complex which formed in DMSO solution.

### 2 Experiment

Hbice was synthesized according to a procedure described previously [4]. An aqueous solution of SrCl<sub>2</sub> (1.0 M), 18-crown-6 ether (0.02 M), and a DMSO solution of Hbice (0.02 M) were prepared. 0.01 M of SrCl<sub>2</sub>, Sr(18-crown-6 ether) complex, and Sr(Hbice) complex solutions were prepared by adding 20  $\mu$ l of SrCl<sub>2</sub> solution, 500  $\mu$ l of ligand solution, and appropriate amount of water or DMSO in a cell. All of XAFS spectra were measured in fluorescence mode at the BL-27B station in the KEK-PF. The Sr *K*-edge XAFS spectra were recorded within 15.77 – 17.05 keV. Each sample was measured for 1 h. The EXAFS spectra were analyzed using the WinXAS 3.1 program [5]. Theoretical phase shifts and backscattering amplitude functions were generated using the FEFF8.00 code. The amplitude of the reduction factor,  $S_0^2$ , was fixed at 1.0. All of XAFS measurements were performed at room temperature.

### 3 Results and Discussion

We measured the XAFS spectra of SrCl<sub>2</sub> and Sr(18-crown-6 ether) complex as a standard sample for the XAFS analysis. Fig. 1 shows the  $k^3$ -weighted Sr *K*-edge EXAFS oscillation of Sr(II) complexes in solution, and the corresponding magnitude of the Fourier-transformed data. Because O/N and Cl can behave as ligands for Sr(II) in this system, both Sr-O/N and Sr-Cl models were used to fit the EXAFS data. The Fourier-transformed spectra

exhibited two peaks at 2.0 and 3.0 Å in the data of Sr(18-crown-6 ether) and Sr(Hbice) complex. The larger peak at 2.0 Å can be clearly assigned to a Sr-O/N interaction [6].

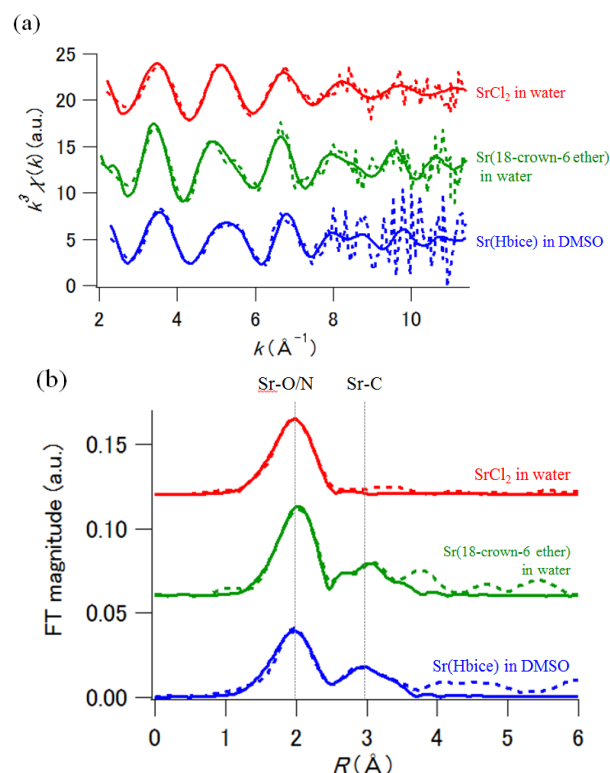


Fig. 1: (a)  $k^3$ -weighted Sr *K*-edge EXAFS oscillation of Sr(II) complexes in solution, and (b) the corresponding magnitude of the Fourier-transformed data. Solid lines and dashed lines indicate the experimental data and theoretical fit, respectively. The phase shift in the Fourier-transformed data was not corrected.

Table 1: EXAFS structural parameters obtained by curve fitting for Sr(II) complexes.

Sample	Interaction	<i>R</i>	CN	$\sigma^2$
SrCl <sub>2</sub>	Sr–O	2.56	7.7	0.013
	Sr–Cl	3.54	9.4	0.003
Sr(18-crown-6 ether)	Sr–O	2.61	7.0	0.011
	Sr–C	3.54	9.4	0.003
Sr(Hbice)	Sr–O/N	2.54	6.9	0.014
	Sr–C	3.66	9.2	0.005

*R*(Å): bond distance; CN: coordination number;  $\sigma^2$ (Å<sup>2</sup>): Debye-Waller factor squared.

In addition, other peak at 3.0 Å can also be clearly assigned to a Sr-C interaction [6, 7], which strongly proposed that carbon atoms of these ligands are in the second coordination sphere of Sr(II). Therefore, it can be suggested that both 18-crown-6 ether and Hbice directly interact with Sr(II), and Cl is not in the first coordination sphere of Sr(II) complexes. Table 1 shows the EXAFS structural parameters obtained from this analysis. The fitting results showed that the local structure of Sr(Hbice) complex is similar with that of Sr(18-crown-6 ether) complex. This result suggested that the primary coordination sphere of Sr(II) consists only of O/N atoms of Hbice, that is, the Sr(II):Hbice = 1:1 complex is formed in this system. Since the Hbice molecule is monovalent anion, [Sr(Hbice)]Cl species would be formed in DMSO solution in this system. To understand Sr(II) recognition mechanism in detail, more study is in progress.

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#### References

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\* k\_akutsu@cross.or.jp