ROBL-CRG	**Experiment title:** Structural investigation of complex of TcO_4^- and ReO_4^- with MIDOA by EXAFS spectroscopy	**Experiment number**: 20-01-703
Beamline: BM 20	**Date of experiment**: from: 16/9/2010 to: 18/9/2010	**Date of report**:
Shifts: 3	**Local contact(s)**: Dipanjan Banerjee	*Received at ROBL:*
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Report:

Introduction Recently, a new extractant, 2,2'-(methylimino) bis(N,N-dioctyl-acetamide) (MIDOA; Fig. 1) was synthesized by researchers of Japan Atomic Energy Agency [1]. The MIDOA extractant has high extraction ability for oxyanions, such as MO_4^- (M=Tc and Re), in liquid-liquid extraction, although the mechanism remains unresolved. To understand the mechanisms of liquid-liquid extraction by MIDOA, the structure of the MO_4^-–MIDOA complex was investigated. We observed infrared spectra of the complex by ATR FT-IR spectroscopy and analyzed them based on calculated structures and frequencies by density functional theory (DFT). As a result, the conformation shown in Fig. 2 was suggested as the most stable structure of MO_4^-–MIDOA, assuming that oxidation state of MO_4^- is kept constant during the extraction process. However, this assumption has not been assured. In this work we tried to get information about the oxidation state in the extraction and geometrical parameters of the MO_4^-–MIDOA complex by extended X-ray absorption fine structure (EXAFS) spectroscopy, in order to confirm the structure determined by IR spectroscopy and DFT calculation.

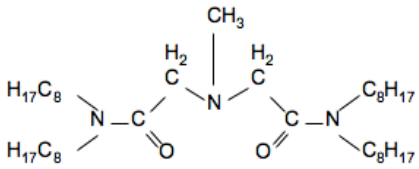

Figure 1: Structural formula of MIDOA

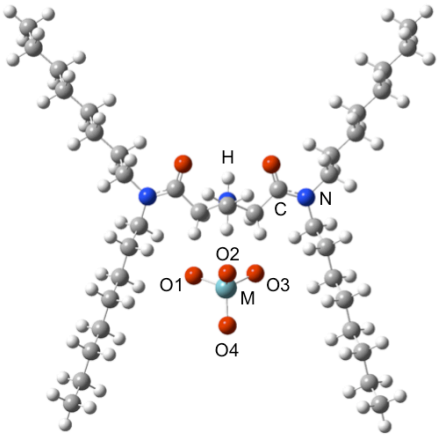

Figure 2: Suggested structure of the MO_4^-–MIDOA complex

Table 1: Geometrical parameters of MO_4^-–MIDOA at B3LYP/cc-pVDZ

Bond length (Å)	Tc	Re
M–O1	1.723	1.737
M–O2	1.735	1.748
M–O3	1.725	1.739
M–O4	1.704	1.721

Experimental The EXAFS samples, dodecane (DD) solution of the MO_4^-–MIDOA complex, were prepared by liquid-liquid extraction. At first, the DD solution of 100mM MIDOA (organic phase) was mixed with aqueous solution of 200mM HCl and

5–10mM KMO_4 (M=Tc and Re) (aqueous phase). The solution composed of organic and aqueous phases was shaken for 3 hours at room temperature. After 10-min centrifugation, the organic phase was separated and used as the sample. The EXAFS measurements were performed by using absorption edges of 21.05 keV for Tc(K) and of 10.53 keV for Re(LIII). The spectra were energy calibrated using Mo-K edge (20 004 eV).

Results The EXAFS measurement was performed for the DD solutions of the 5-mM MO_4^-– MIDOA complex (M-1), 10-mM MO_4^-–MIDOA complex (M-2) and the 200-mM HCl solutions of 5-mM MO_4^- (M-3), where M indicates ^{99}Tc and Re. Fig. 3 shows the Fourier transform magnitude (FTM) of the Tc and Re samples. Both FTM spectra of Tc and Re are dominated by the Tc–O and Re–O coordination shell. Two small peaks at 2.1 and 2.7 Å in Tc are 3-legged and 4-legged multiple scattering contributions from the Tc-O shell, respectively The coordination number (CN), radial distance (R) and Debye-Waller factor (σ^2), which were obtained by analysis of Fig. 3, are listed in Table 2. The uncertainty of these values is ±0.5 for CN, ±0.005Å for R and ±0.0005Å^2 for σ^2. Table 2 suggests that the CN values of all samples are 4 (within its uncertainty limit). It agrees with the fact that the Tc and Re metals are dissolved in the HCl solution as TcO_4^- and ReO_4^-, and indicates that their oxidation states are kept constant in the organic phase. The radial distance slightly increases from the Tc samples (1.72–1.73Å) to the Re samples (1.73–1.74Å). In both Tc and Re samples the radial distance hardly change by formation of the complex between MO_4^- and MIDOA. The calculated geometrical parameters of the MO_4^-–MIDOA complex are shown in Table 1, which suggest that the average bond length of M–O is 1.722Å and 1.736Å for Tc and Re, respectively. The calculated bond lengths are in good agreement with the R values by EXAFS. From Table 1 standard deviation of M–O is calculated to be 0.0129Å and 0.0112Å for Tc and Re, respectively. This results is also consistent with small Debye-Waller factors in Table 1, which are 0.0009–0.0014Å^2 for Tc and 0.0025–0.0031Å^2 for Re. Thus, we confirmed that the MO_4^-–MIDOA complex has the structure shown in Fig. 2.

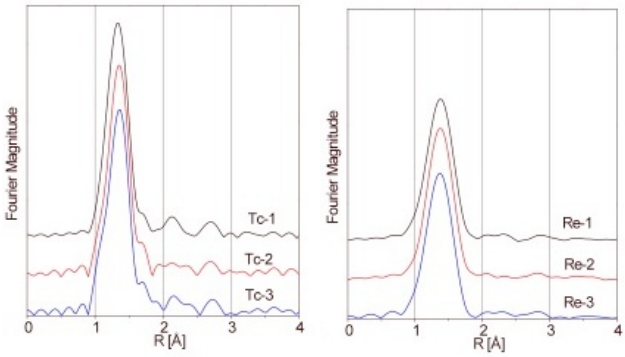

Figure 3: The FTM spectra of the Tc and Re complex

Table 2: Tc-K and Re-LIII edges EXAFS shell fit results.

Samples	CN	R	σ2
Tc-1	4.0	1.72	0.0014
Tc-2	3.5	1.72	0.0009
Tc-3	3.8	1.73	0.0013
Re-1	4.2	1.74	0.0031
Re-2	4.0	1.74	0.0025
Re-3	4.4	1.73	0.0034

Acknowledgements We are grateful to Dr. D. Banerjee and Dr. A. C. Scheinost for their experimental support.

Reference

[1] Y. Sasaki, Y. Kitatsuji and T. Kimura, Chemistry Letter, Vol.36, 2007, p1394-1395.