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Structural investigations on Uranium(VI) and Thorium(IV) complexation with TBP and DHOA: A spectroscopic study

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Electronic Supporting information

INSTRUMENTATION

Details of EXAFS measurements

The scanning EXAFS beamline (BL-09) of the INDUS-2 Synchrotron Source (2.5 GeV, 125 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India operates in the energy range of 4 to 25 KeV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror followed by a Si(111) (2d = 6.2709 Å) based double crystal monochromator. The second crystal of DCM is a sagittal cylindrical crystal used for horizontal focusing. Three ionization chambers (300 mm length each) have been used for data collection in case of measurements in transmission mode, one ionization chamber for measuring incident flux (I_0), second one for measuring transmitted flux (I_t) and the third ionization chamber for measuring spectrum of standard reference on-line. Appropriate gas mixtures have been chosen to maintain 10-20% absorption in first ionization chamber and 70-90% absorption in second ionization chamber to improve signal to noise ratio. The absorption coefficient μ is obtained using the relation:

$$I_T = I_0 e^{-\mu x} \qquad (1)$$

Where, x is the thickness of the absorber. Liquid samples, as detailed in **Table S1**, of appropriate amount, have been taken to obtain a reasonable edge jump in EXAFS measurements. U_3O_8 and ThO_2 powder pallets are used for energy calibration at the third ionization chamber. In order to take care of the oscillations in the absorption spectra $\mu(E)$ has been converted to absorption function $\chi(E)$ defined as follows: [31]

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)} \tag{2}$$

Where E_0 absorption edge energy, $\mu_0(E_0)$ is the bare atom background and $\Delta\mu_0(E_0)$ is the step in $\mu(E)$ value at the absorption edge. The energy dependent absorption coefficient $\chi(E)$ has been converted to the wave number dependent absorption coefficient $\chi(k)$ using relation,

$$K = \sqrt{\frac{2m(E - E_0)}{\mathrm{h}^2}} \tag{3}$$

Where m is the electron mass. $\chi(k)$ is weighted by k^2 to amplify the oscillation at high k and the $\chi(k)k^2$ functions are Fourier transformed in R space to generate the $\chi(R)$ versus R spectra in terms of the real distances from the center of the absorbing atom. The set of EXAFS data analysis available within IFEFFIT software package have been used for EXAFS data analysis. This includes background reduction and Fourier transform to derive the $\chi(R)$ versus R spectra from the absorption spectra (using ATHENA software), generation of the theoretical EXAFS spectra starting from an assumed crystallographic structure and finally fitting of experimental data with the theoretical spectra using ARTEMIS software.

UV-Vis and FTIR spectroscopy measurements

The UV-Vis spectra of all the samples were recorded against suitable blank in quartz cuvette. The raw data used was processed (such as base line correction, normalization) and plotted with the help of Origin 6.0. The FTIR spectra of all the samples were recorded in ATR mode. At least thirty scanned were taken for each sample. About 100 µl of the sample (organic extract or aqueous phase) was directly smeared onto the diamond crystal to make a thin layer and the scans were recorded in transmission mode. The spectra were processed with the help of Origin 6.0.

Karl Fisher Titration

Single component reagent from Merck (Germany) was used for the KF titration. The active concentration (mg of water/ml)) of the reagent was measured just before the titration of ACN and methanol (to determine the water content). The functioning of the instrument was futher verified with water as a standard. All the measurements were taken in triplicate.

SAMPLE PREPARATION

The organic extract used in the present studies were made using liquid-liquid extraction keeping organic phase at 30% extractant (TBP/DHOA) in *n*-hexane and aqueous phase as ~1M uranium nitrate in 3M HNO3. The 5 ml of organic phase was shaked with 5 ml of organic phase (O/A:1) for 4 hrs. The two phases were separated by centrifugation at 5000 rpm for 5 min. The organic phase was transferred to 10 ml beaker and kept overnight to remove the *n*-hexane at room temperature. The viscous complex (U(VI)-L (L:TBP/DHOA)) was obtained. About 50 µl of this viscous complex was added to 500 µl different media and the different measurements were made. For EXAFS studies sample preparation was given in **Table S1** of the manuscript. For luminescence studies 25 µl of complex was dissolved in to 1.5 ml of respective media and the spectra were recorded at room temperature.

Table S1: Details of samples used for EXAFS studies

S. No.	**Details**
1	U(VI) (0.084 M) equilibrated with 3 M Nitric Acid
2	U(VI) -equilibrated with 1.1 M TBP in *n*-dodecane
3	U(VI) -equilibrated with 1.1 M DHOA in *n*-dodecane
4	Th(IV) (0.086 M) equilibrated with 3 M Nitric Acid
5	Th(IV)-TBP (1.1 M in *n*-dd) Th(IV) -equilibrated with 1.1 M TBP in *n*-dodecane
6	Th(IV) -equilibrated with 1.1 M DHOA in *n*-dodecane

Figures

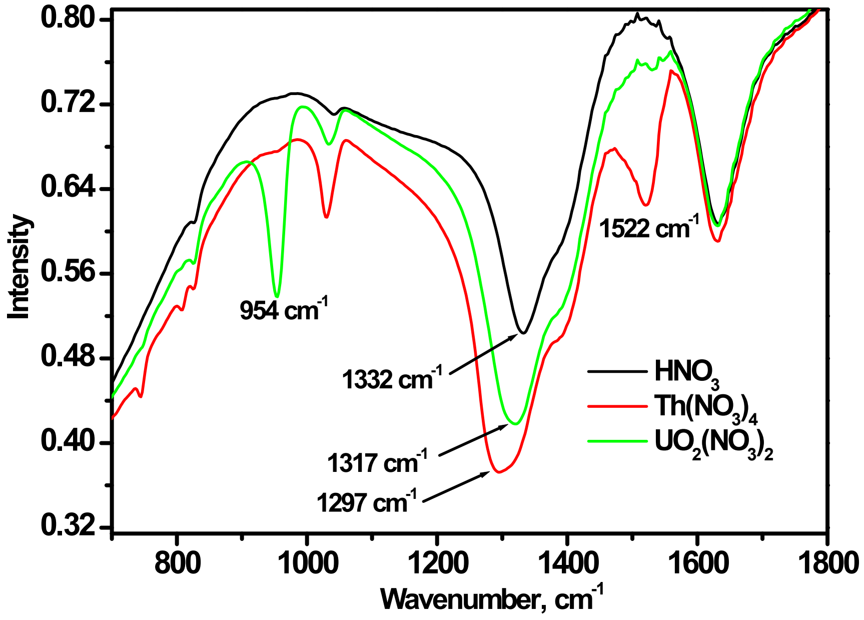

Fig.S1: FTIR spectra of HNO_3 (3M), $Th(NO_3)_4$ and $UO_2(NO_3)_2$ in 3M Nitric acid ; T : 298 K

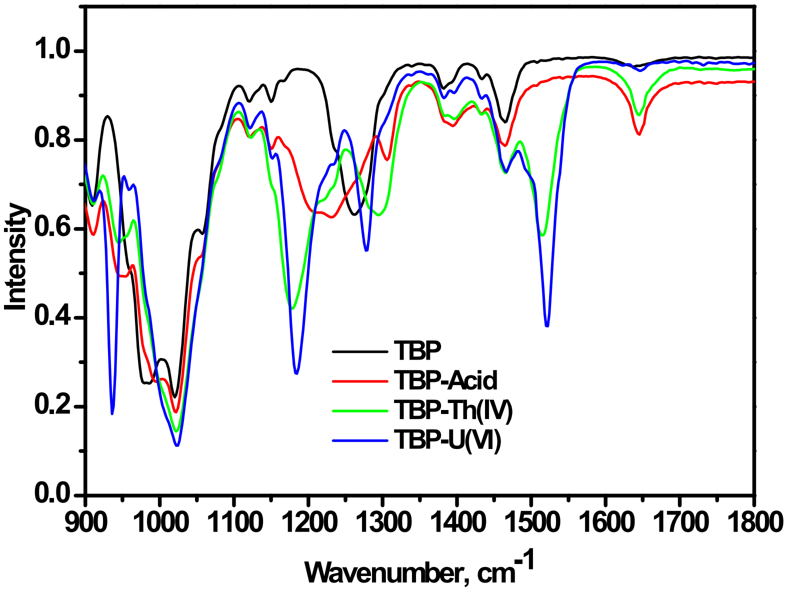

Fig.S2: FTIR spectra of pure TBP, organic phase of 3M Nitric acid equilibrated TBP (TBP-Acid), TBP-Th(IV) and TBP-U(VI) extracts in organic phase from 3M HNO_3 ; T : 298 K

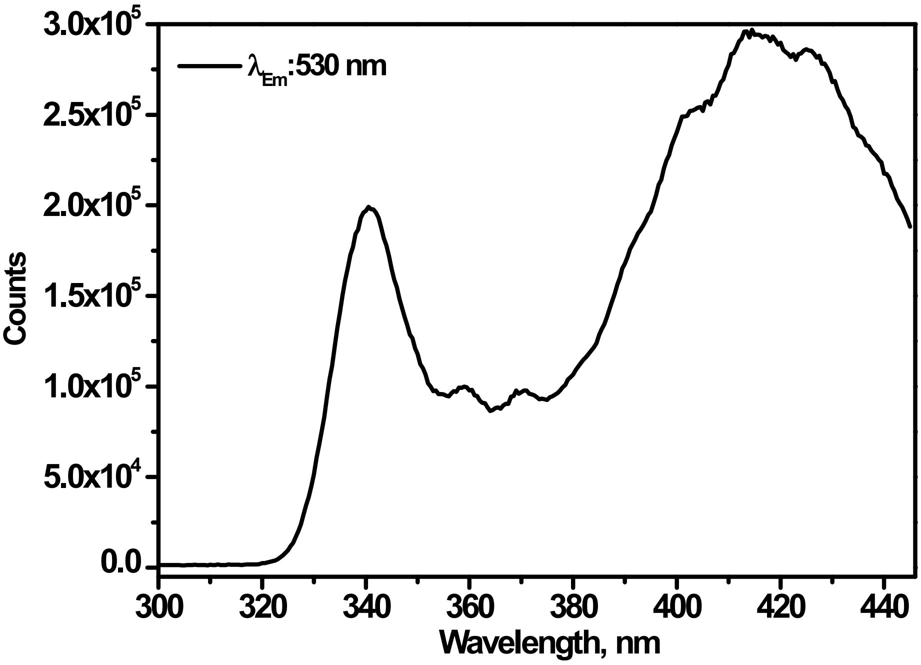

Fig.S3: Excitation spectra of $UO_2(NO_3)_2$ in 3M Nitric acid; T:278 K

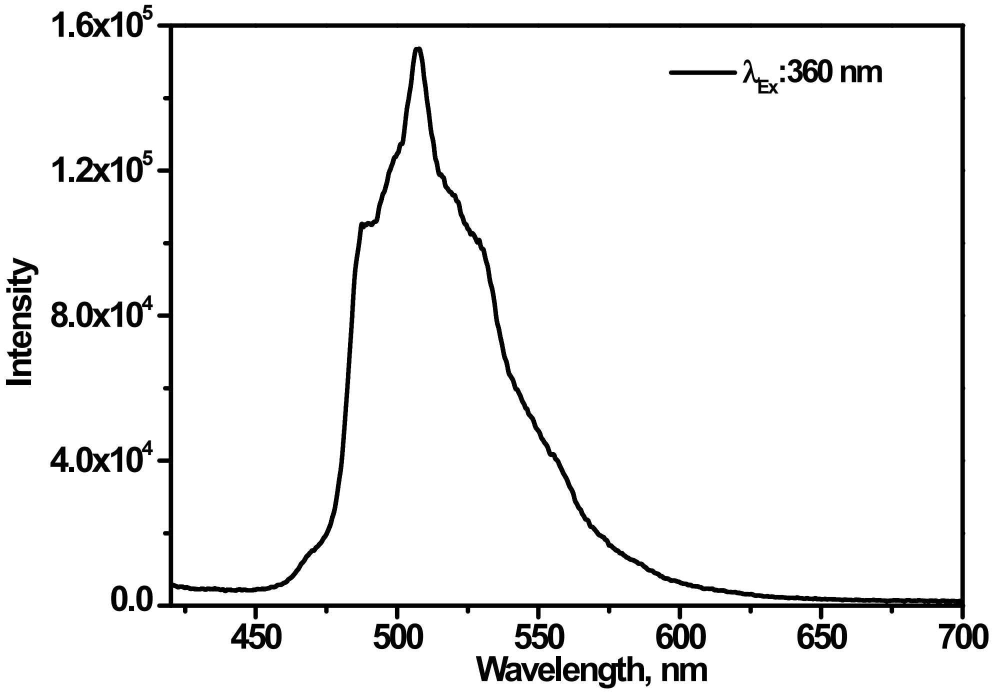

Fig.S4: Emission spectra of $UO_2(NO_3)_2$ in 3M Nitric acid; T:278 K

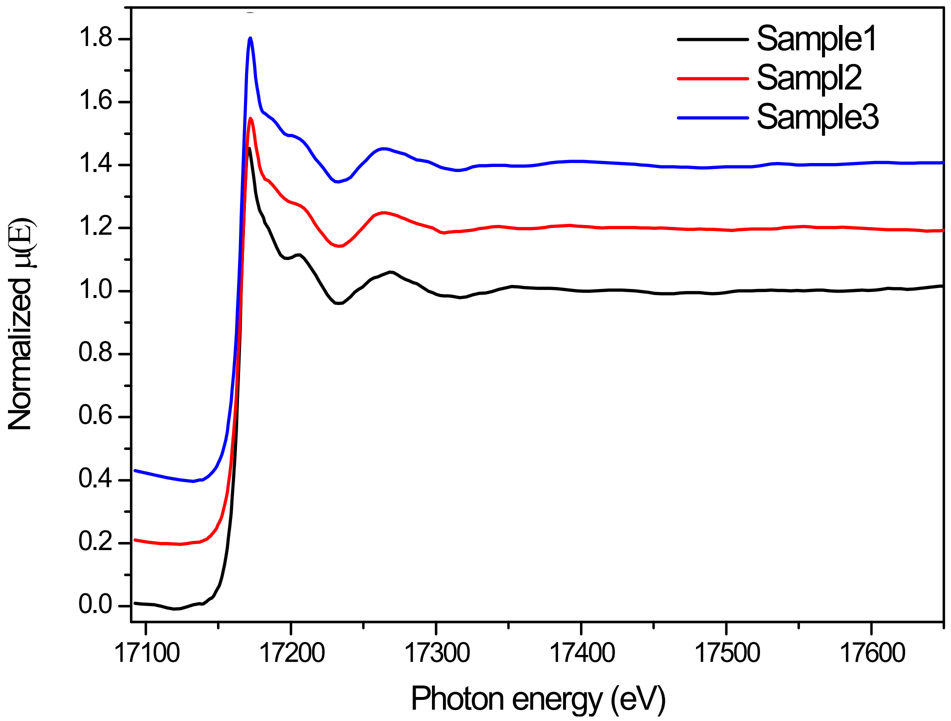

Fig.S5 : Normalised EXAFS spectra for sample1, sample 2 and sample 3 (see Table S1) at U L3 edge. Plots are presented with constant offset of 0.2 units.

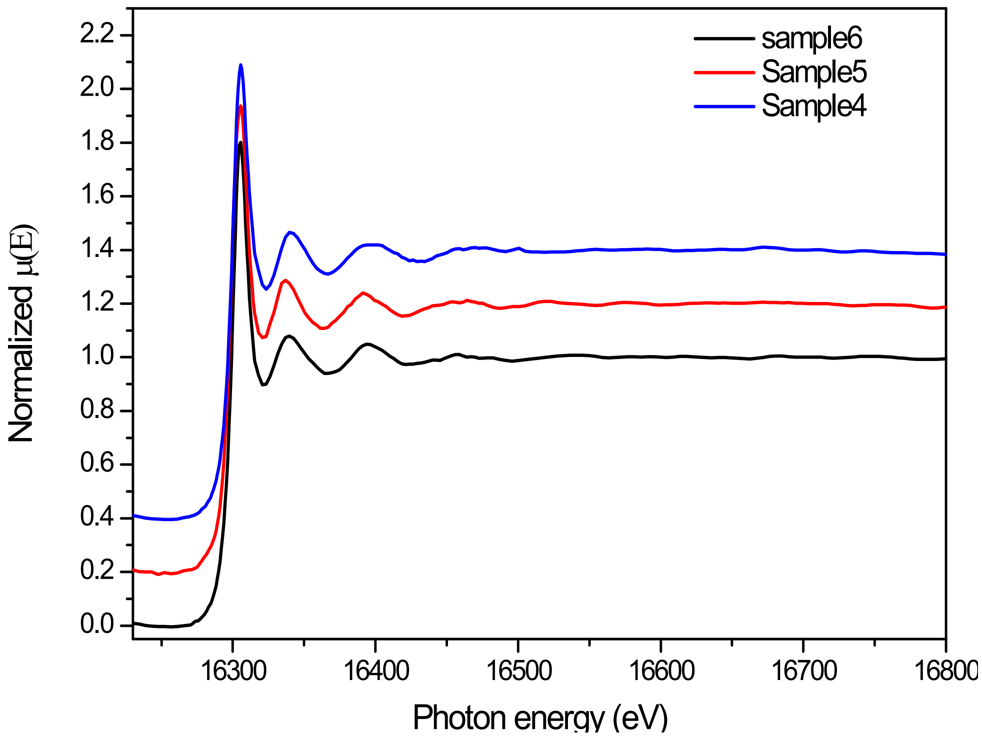

Fig. S6 : Normalised EXAFS spectra for sample 4, sample 5 and sample 6 (see Table S1) at Th L3 edge. Plots are presented with constant offset of 0.2 units.