

# Interaction of Actinide Cations with Heteropolyoxotungstate Ions $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ and $[\text{SiW}_{12}\text{O}_{40}]^{4-}$

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*New actinide polyoxometalates have been synthesized by conventional method under controlled conditions of pH and temperature. The synthesized compounds were characterized by FT-IR spectroscopy, UV-Vis spectrophotometry and scanning electronic microscopy (SEM) with electron diffraction X-ray (EDX) detection.*

*Keywords: polyoxometalate, polyoxotungstate, thorium, uranyl*

Polyoxometalates (POMs), inorganic metal-oxygen cluster compounds, [1] have received increasing interest owing to their applications in various fields, in particular in catalysis. Some of them, and especially the familiar Keggin-type POMs, have been widely used as acid, oxidation as well as bifunctional catalysts [2-4] and were also employed as effective photocatalysts in the oxidation of organics in recent years [5, 6]. Many polyoxometalates may act also as polydentate ligands that bond to a central ionic metal [7, 8].

In recent years the heteropolyoxometalates (HPOMs) chemistry attracted much attention especially for the immobilisation of radioactive ionic metals [9]. Polyoxometalates present a great potential to be used in the treatment of radioactive residual water systems as the newly formed polyoxometalate-radioactive ionic metal complex is characterized by thermo stability and insensitivity toward radioactive interaction [10].

Whenever intended to be used as ligand, a polyoxometalate has some remarkable properties namely: it is fully oxidized and therefore can easily accommodate the heteroatoms in high oxidation states; it is a "strong" sigma donor via the oxygen atoms, but can also act as a pi acceptor as a result of the availability of appropriate vacant d-orbitals of the adjacent metal atoms, [11] it has high thermal stability, and the polyoxometalate framework has stability to ionizing radiation. The capacity of heavy metal atoms to fill the gaps from the polyoxometalates structure has wide applications in the storage of radioactive waste [12-15].

Polyoxotungstates with actinide ions and the investigation of this field are still under development stage.

We report in this paper the synthesis and chemical characterization of new polyoxometalate complexes obtained from uranyl and thorium cations and monolacunary polyoxotungstate anions. The chemical characterization of the newly synthesised units has been done by the mean of state of the art technique as Fourier Transformed Infrared Spectroscopy (FTIR), UV-vis spectrophotometry, and scanning electronic microscopy (SEM) with electron diffraction X-ray (EDX) detection.

## Experimental part

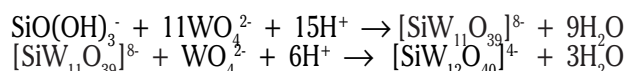
All chemicals were reagent grade and used as purchased from Sigma-Aldrich without any further purification.

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## Syntheses

The mono-lacunary structure anions were synthesized and characterized according to literature methods [16, 17]. In the following paragraphs we shall describe only the general points for the synthesis of the  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  anion. For the  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  units more details could be found elsewhere [18].

From the literature data  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  anion is regarded as an important intermediate product in the formation of  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  and the reaction proceeds as in the following routes [19]:



On the other hand,  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  anion can be regarded as a hydrolytic degradation product of  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  anion as is presented by the following reaction:



From the present work, at a  $\text{pH} < 3$ , a formation yield of about 80% has been obtained in  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ . The newly synthesized complexes of polyoxometalates with  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  were obtained by direct reactions of the monolacunary  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  ion with thorium nitrate and uranyl nitrate solution, under very well controlled hydrothermal conditions.

At a temperature of about 50°C, under continuous stirring, occurs dissolution of the  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  ion into 0.1 M NaCl solution. Further reaction of the dissolved ion, in the presence of uranyl nitrate (and thorium nitrate), yields a yellowish (and white) precipitate. After 48 h of equilibration the newly obtained precipitate will easily be separated from the solution leading to pale yellow crystals in the uranyl complex and white crystals for thorium complex. The formation yield of the newly synthesized product has been estimated at about 75% for uranyl complex and about 70% for thorium complex.

## Instrumentation

New obtained heteropolyoxotungstates have been characterized by spectral techniques (FT-IR spectroscopy, UV-Vis spectrophotometry) and scanning electronic microscopy (SEM) coupled with EDX detection. A Bruker Alpha spectrophotometer has been used for the FT-IR

**Table 1**  
ABBREVIATIONS USED FOR THE COMPOUNDS

Polyoxoanion	Uranyl complex	Thorium complex
$L_1: Na_8[SiW_{11}O_{39}]$	$C_{1U}: UO_2^{2+} - [SiW_{11}O_{39}]^{8-}$	$C_{1T}: Th^{4+} - [SiW_{11}O_{39}]^{8-}$
$L_2: Na_4[SiW_{12}O_{40}]$	$C_{2U}: UO_2^{2+} - [SiW_{12}O_{40}]^{4-}$	$C_{2T}: Th^{4+} - [SiW_{12}O_{40}]^{4-}$

spectra which were recorded in a KBr thin disk. All the FT-IR spectra were recorded with a spectral resolution better than  $2\text{ cm}^{-1}$ , with wavenumber accuracy of  $0.01\text{ cm}^{-1}$ . A RockSolid interferometer was permanently aligned with and DTGS detector. All optics is gold coated. A CINTRA 10e UV-vis spectrophotometer has been used for the investigation of the electronic absorption spectra. The wavelength range of apparatus is 190 to 1200 nm with very low stray light and noise specifications. A slit width of 0.5 nm and a dual Littrow monochromator in a Czerny Turner arrangement are used in order to achieve the highest resolution with extremely low stray light. The SEM was performed by means of a SEM VEGA II LSH scanning electronic microscope manufactured by TESCAN Company, coupled with an EDX QUANTAX QX2 detector manufactured by ROENTEC Company. Quantax QX2 is an EDX detector used for qualitative and quantitative micro-analysis in industry, research and education, which performs quantitative measurements without using specific calibration standards. Quantax QX2 uses a 3<sup>rd</sup> generation Xflash detector, which does not require liquid nitrogen cooling and is about 10 times faster than the traditional Si(Li) detectors.

## Results and discussion

### Electronic UV spectra analysis

Figure 1 presents a typical UV electronic spectra for  $Na_8[SiW_{11}O_{39}]$  ( $L_1$ ),  $UO_2^{2+} - [SiW_{11}O_{39}]^{8-}$  ( $C_{1U}$ ). As can be easily observed from figure 1 the UV electronic spectra have two characteristic bands which occur at  $\sim 205\text{ nm}$  and  $\sim 260\text{ nm}$ . These observations are in complete agreement with literature data [20, 21].

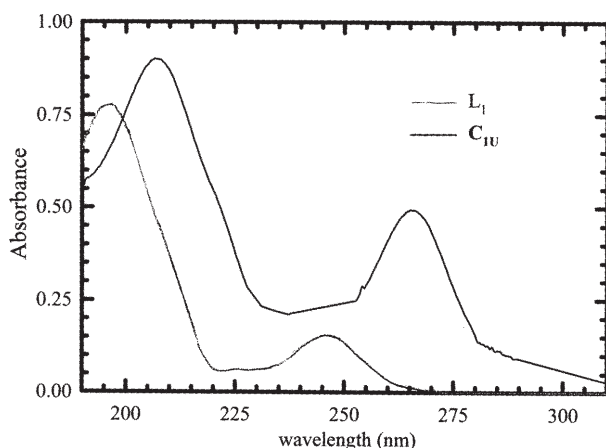


Fig. 1 UV spectra of  $L_1(1)$  and  $C_{1U}(2)$

The absorption band from  $\sim 205\text{ nm}$  can be attributed to an electronic transition  $d\pi \rightarrow p\pi$  type of  $W=O$  double bond and the absorption from  $\sim 260\text{ nm}$  to an electronic transition  $d\pi \rightarrow p\pi \rightarrow d\pi$  type of the tricentric  $W-O-W$  bond.

In the uranium complex (fig. 1, line 2) these bands are much more intense compared with the ligand due to the actinide cation coordination. Table 2 presents the UV spectral features of selected complexes and their corresponding ligands.

### FT-IR spectra analysis

Among all investigated structures, as an example, in figure 2 are presented the FT-IR spectra of the  $C_{2T}$  complex ( $Th^{4+} - [SiW_{12}O_{40}]^{4-}$ ) and its precursor  $L_2$  ( $Na_4[SiW_{12}O_{40}]$ ) in the main region ( $2000-400\text{ cm}^{-1}$ ). IR spectra of the uranyl and thorium complexes contain additional bands of spectrum ligand, which can be considered as an evidence of thorium and uranium ions coordination with oxygen atoms in the mono-lacunary structure of anions units. This coordination influences the position and form of the following frequency bands corresponding to asymmetric vibration:  $\nu_{as(W-W-Oa)}$ ,  $\nu_{as(W-Ob-W)}$ ,  $\nu_{as(W-Oc)}$

**Table 2**  
UV SPECTRAL FEATURES OF SELECTED COMPLEXES AND THEIR CORRESPONDING LIGANDS

Compound	Maximum absorption bands (nm) UV range	
	$p\pi \rightarrow d\pi$	$d\pi \rightarrow p\pi \rightarrow d\pi$
$L_1$	$\sim 200$	250
$L_2$	$\sim 200$	250
$C_{1U}$	$\sim 210$	260
$C_{2U}$	$\sim 210$	260
$C_{1T}$	210	260
$C_{2T}$	210	260

Frequencies corresponding to asymmetric vibration band  $\nu_{as(W-W-Oa)}$  from FT-IR spectra of the complex moves to lower values and the corresponding band  $\nu_{as(W-Ob-W)}$  is moving toward higher values compared with those from FT-IR spectra of the ligands (fig. 2). The change in the  $\nu_{as}$  frequency band ( $W-O_b-W$ ) is due to a decrease in the distance between atoms of tungsten bound of the octahedral edges of crystal structure. With regard to the  $W-W-Oa$  the change in the frequency band  $\nu_{as}$  is due to increasing distance between the tungsten atoms bound in the octahedral corners of the crystal structure [19]. These frequencies movements indicate that for each uranium or thorium ion occurs coordination with terminal oxygen atoms on the octahedral edges crystal structure. Stretching vibrations that involves centred heteroatom of polioxometalates units are masked in both cases. The transmittance bands in the range of  $807 - 878\text{ cm}^{-1}$  indicate the presence of radioactive ions polyoxotungstates.

### SEM-EDX analysis

Figures 3a,b present the SEM image for the  $L_1$  and  $C_{1U}$  structures while figures 3c,d present the same images for the  $L_2$  and  $C_{2T}$  unit. All images show clear differences in the morphology of the interest unit after their reaction with the uranyl and thorium cations. Figures 4a, b show associated EDX spectra of the  $L_1$  and  $C_{1U}$  compounds while figures 4c, d present EDX spectra for the  $L_2$  and  $C_{2T}$  compounds. Data from SEM-EDX (fig. 4) were also helpful in obtaining appropriate chemical compositions of the newly synthesized compounds. Thus, for  $C_{1U}$  new complex chemical composition is: K 2.81% (calculated 2.36 %), U 7.95 % (calculated 7.22 %), Si 1.09 % (calculated 0.84), W 33.85 (calculated 33.49 %),  $H_2O$  2.78 % (calculated 2.18 %) 7.24% (calculated 7.74%),  $\bar{U}$  7.95% (calculated 8.01%),

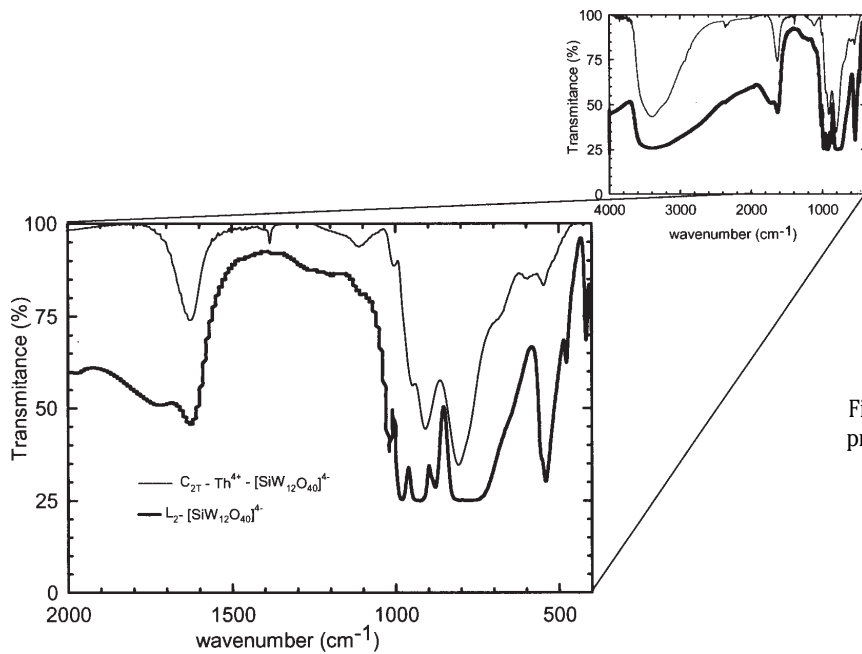


Fig. 2 FT-IR spectra of the  $C_{2T}$  complex and its precursor  $L_2$  in the main region ( $2000-400\text{ cm}^{-1}$ )

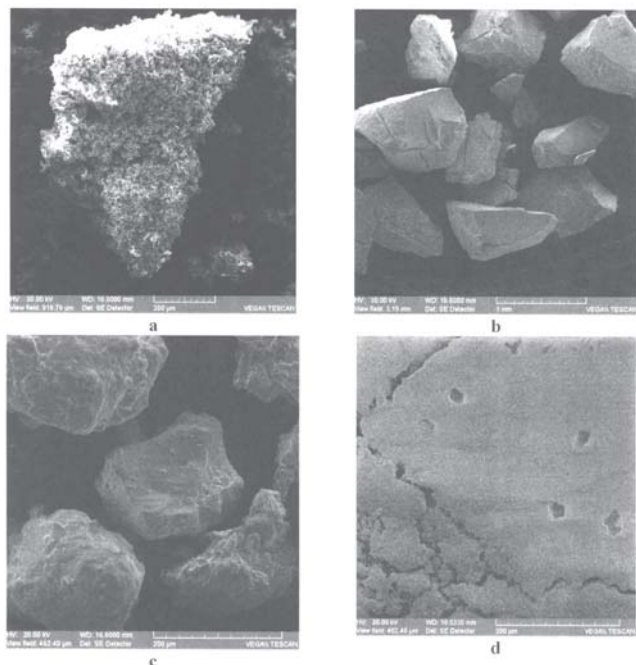


Fig.3. The SEM image of the  $L_1$ (a),  $C_{10}$ (b),  $L_2$ (c),  $C_{2T}$ (d)

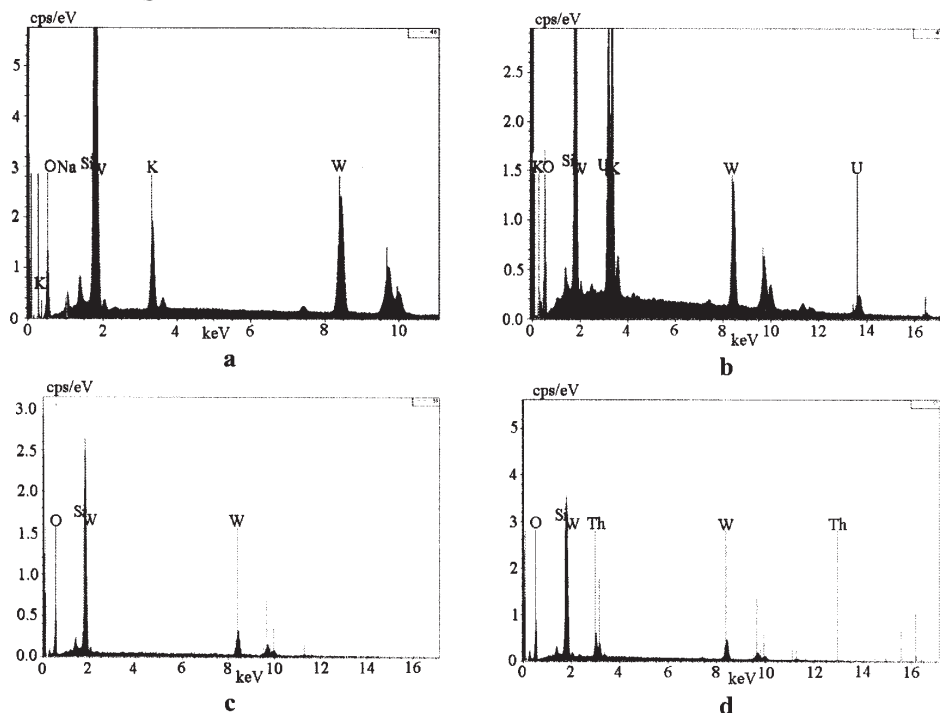


Fig. 4. The EDX chemical composition spectra of  $L_1$  (a),  $C_{10}$ (b),  $L_2$ (c),  $C_{2T}$ (d) units

Mo 45.43% (calculated 45.20%) and H<sub>2</sub>O 12.05% (calculated 12.11%) and for C2T: K 2.38% (calculated 2.44%), Th 3.7% (calculated 3.62%), Si 1.02% (calculated 0.87%), W 35.1 (calculated 34.54%), H<sub>2</sub>O 4.52% (calculated 3.94%) From the data presented above it can be easily observed that theoretical chemical composition is pretty well correlated with that prefigured from the experimental data.

## Conclusions

New heteropolyoxotungstates units with UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> ions have been synthesized and characterized in terms of chemical composition. Characterization of new synthesized units has been carried out by using spectroscopic techniques namely FT-IR, UV-Vis and SEM-EDX. Because of rapid and high efficiency formation of the new complexes in aqueous solution it can be suggested that could be a possible route for sequestration of the studied actinide cations. Moreover, the efficiency in the separation step under the synthesis condition can suggest that the present procedure can be for uranium, thorium and other actinide cations a very good tool for their retention from aqueous samples.

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