

New isopolyoxomolybdates derived from heptamolybdate with UO_2^{2+} and Th^{4+} ions

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Abstract. Uranyl (UO_2^{2+}) and thorium (Th^{4+}) polyoxomolybdates, containing strictly $[\text{Mo}_7\text{O}_{24}]^{6-}$ entity, have been synthesized by self-assembly from raw materials as $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, uranyl acetate and thorium nitrate in acidic media under controlled conditions of temperature and pH. Although some polyoxometalates derived from heptamolybdate ($[\text{Mo}_7\text{O}_{24}]^{6-}$) presently are known, the novelty of this work derives from the fact that for the newly synthesized units accomplishments for their chemical characterization was foreseen through the data obtained by the mean of state of art technique as Fourier Transformed Infrared Spectroscopy (FTIR), UV-vis spectrophotometry, scanning electronic microscopy (SEM) with electron diffraction X-ray (EDX) detection, and thermogravimetric analysis. Our work reveals that all the polyoxomolybdates containing the $[\text{Mo}_7\text{O}_{24}]^{6-}$ unit might have reduced retaining properties when compared with the polyoxomolybdate including in its structure the $[\text{Mo}_4\text{O}_{13}]^{2-}$ unit. The polyoxomolybdate containing the $[\text{Mo}_7\text{O}_{24}]^{6-}$ entity can be used in the synthesis process of raw materials with direct application in the concentration/preconcentration of radioactive cations including UO_2^{2+} and Th^{4+} from aqueous solution.

Keywords: isopolyoxomolybdates uranyl, thorium, synthesis, characterization.

1. Introduction

(Iso)polyoxometalates represent a wide class of molecular clusters with an almost unmatched range of physical properties and ability to form structures that can bridge several length scales [1].

Polyoxometalates (POMs) present a great ability to be used in the treatment of radioactive wastewaters. Isopolyoxomolibdates are chemical coordinative compounds of much current interest due to their special properties [2-5].

In recent years the polyoxometalates chemistry attracted much attention especially for the immobilization of radioactive ionic metals [6]. The high thermal stability and radiation-resistant nature of (iso)polyoxomolybdates attract attention to the use of these species for the separation and sequestration of radioactive species. Radioactive species sequestration by POMs affects their stability and the structures

move towards ionizing radiation which is greater than that of organic sequestrants [7].

2. Experimental

All chemicals were reagent grade and used as purchased from Aldrich-Sigma without any further purification. The newly synthesized (iso)polyoxometalates derivative complexes were characterized by the mean of several state of art analytical techniques including Fourier Transformed Infrared Spectroscopy (FTIR), UV-vis spectrophotometry, scanning electronic microscopy (SEM) with electron diffraction X-ray (EDX) detection, and thermogravimetric analysis. Previous work report only potentiometric and conductometric methods for the characterisation of some molybdates with uranyl and thorium ions [8-9].

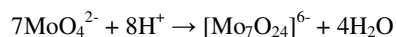
A BRUKER ALPHA spectrophotometer has been used for the FT-IR spectra recording in a KBr thin disk. A CINTRA 10e UV-vis spectrophotometer has been

used for the investigation of the electronic absorption spectra.

The scanning electronic microscopy was performed by means of a SEM VEGA II LSH, TESCAN, coupled with an EDX QUANTAX QX2. The microscope is entirely operated by computer and contains an electron gun with tungsten filament that may achieve a 3 nm resolution at 30 KV, with a magnifying power between 13 and 1,000,000 X in the resolution mode, a gun potential between 200 V and 30 kV, a scanning speed between 200 ns and 10 ms pixel⁻¹. The working pressure is lower than 1×10⁻² Pa. Quantax QX2 is an EDX detector used for qualitative and quantitative micro-analysis which can perform quantitative measurements without using specific calibration standards. It has an active area of 10 mm², and it can analyze all items heavier than carbon, smooth or rough samples, thin coatings or particles, with a resolution below 1.33 eV. Quantax QX2 uses a X-flash detector, which does not require liquid nitrogen cooling and is about 10 times faster than the traditional Si(Li) detectors.

The thermo-gravimetric analysis has been performed by using a Perkin Elmer-Diamond TG/DTA system equipped with platinum made crucible. For the thermogravimetric analysis the experiments have been conducted in the temperature range from 35 – 900 °C, with a 10 °C min⁻¹ heating rate and at a nitrogen flow of 110 mL min⁻¹.

For the synthesis of the polyoxomolybdates containing the heptamolybdate ([Mo₇O₂₄]⁶⁻) unit, a method reported in the literature [10] has been used. Although the method seems to be similar with that leading to metamolybdate ([Mo₄O₁₃]²⁻), a polyoxomolybdate reported elsewhere [10], the heptamolybdate can be obtained when the working conditions are as follows: analyt concentrations higher than 10⁻³ M and pH strictly controlled between 3÷5.5. The synthesis takes place according with the next chemical reaction sequence:



In order to obtain the complex compounds, aqueous solutions of sodium

isopolyoxomolybdate were prepared and treated with UO₂(NO₃)₂ and Th(NO₃)₄ respectively, at temperature of 40 °C under continuous stirring at pH = 4.5 for the uranyl compounds, and 5.5 for the thorium compounds, respectively.

The obtained compounds were collected on a medium glass frit, dried under suction for about 4 h, washed with saturated NaCl solution and dried overnight under suction. The formation yields were about 89.76 % for uranyl complex and about 85 % for the thorium complex.

As the aim of the present work is to bring into attention the characteristics of the newly synthesised uranyl (UO₂²⁺) and thorium (Th⁴⁺) polyoxomolybdates containing [Mo₇O₂₄]⁶⁻ entity, and to discuss these in comparison with those specific for a polyoxometalate containing metamolybdate ([Mo₄O₁₃]²⁻) [10], Table 1 gives the annotations available for the various structures described herein. These are also available within the Results and Discussions chapter.

Table 1. Annotations available for the various structures described in the paper

Ligand	Complex with uranyl	Complex with thorium
L ₁ * - [Mo ₄ O ₁₃] ²⁻	C _{1U} - UO ₂ L ₁ *	C _{1T} - ThL ₁ *
L ₂ - [Mo ₇ O ₂₄] ⁶⁻	C _{2U} - UO ₂ L ₂	C _{2T} - ThL ₂

* [10]

3. Results and Discussions

SEM-EDX analysis

Figure 1 presents SEM images for the interest compounds, in the form of specific systems containing metamolybdate [10] and heptamolybdate (this work) ions. From Figure 1 some clear differences can be observed between the morphology of the interest unit after the formation of new complexes of uranyl and thorium ions with the POMs taken into discussion.

Data from SEM-EDX (Figure 2) were also helpful in obtaining appropriate chemical compositions of the newly synthesized compounds. Thus, for C_{2U} new complex chemical composition is Na 7.24% (calculated 7.74%), U 7.95% (calculated 8.01%), Mo 45.43% (calculated 45.20%) and H₂O 12.05% (calculated 12.11%) and for C_{1T} new complex Na 8.92 % (calculated 8.66%), Th 4.24% (calculated 4.36%), Mo 50.43% (calculated 50.58%) and H₂O 7.39% (calculated 7.45%). 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. Based on these data the following formulas for the newly obtained isopolyoxomolybdates with uranyl and thorium cations, have been proposed: $\text{Na}_{10}[\text{UO}_2(\text{Mo}_7\text{O}_{24})_2 \cdot 4\text{H}_2\text{O}] \cdot 16\text{H}_2\text{O}$ and $\text{Na}_{20}[\text{Th}(\text{Mo}_7\text{O}_{24})_4 \cdot 4\text{H}_2\text{O}] \cdot 18\text{H}_2\text{O}$, respectively.

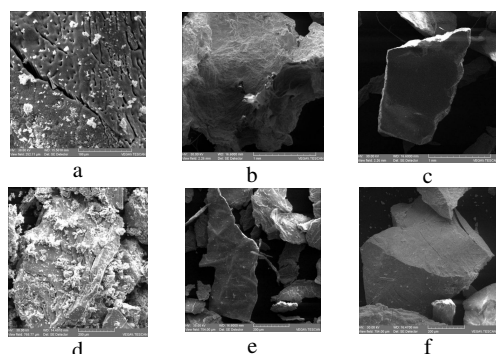


Fig. 1 The SEM image of the system containing the $[\text{Mo}_4\text{O}_{13}]^{2-}$ unit with a- Na^+ , b- UO_2^{2+} , c- Th^{4+} [10] and for that containing the $[\text{Mo}_7\text{O}_{24}]^{6-}$ ligand with d- Na^+ , e- UO_2^{2+} , f- Th^{4+} (present work).

Electronic UV-vis spectra analysis

Figure 3 presents the UV spectra of the ligands L_1 and, respectively, L_2 , and of the formed complexes with uranyl ($\text{C}_{2\text{U}}$) and thorium ($\text{C}_{2\text{T}}$) ions. The data in Figure 3a [10] are herein presented mainly for comparison purposes.

From figure 3 it can be observed that the UV electronic spectra have two characteristic bands with maxima at about 210 nm and about 235 nm for the (iso)polyoxomolybdate anions [11]. However, from the spectra in Figure 3a,b it can be easily observed that the polyoxomolybdate containing the L_2 ligand might have different properties when compared with that containing the L_1 structure.

The absorption bands with maxima at about 210 nm could be assigned to $d\pi \rightarrow p\pi$ electronic transition in the $(\text{M}=\text{O})$ bonds and those with maxima at approximately 230 nm could be assigned to $d\pi \rightarrow p\pi \rightarrow d\pi$ electronic transition in tricentric M-O-M bonds, conform to similar studies presented in the literature [12].

In complexes, the above mentioned bands are shifted when compared with the ligand bands,

especially due to the coordination of the metallic cations.

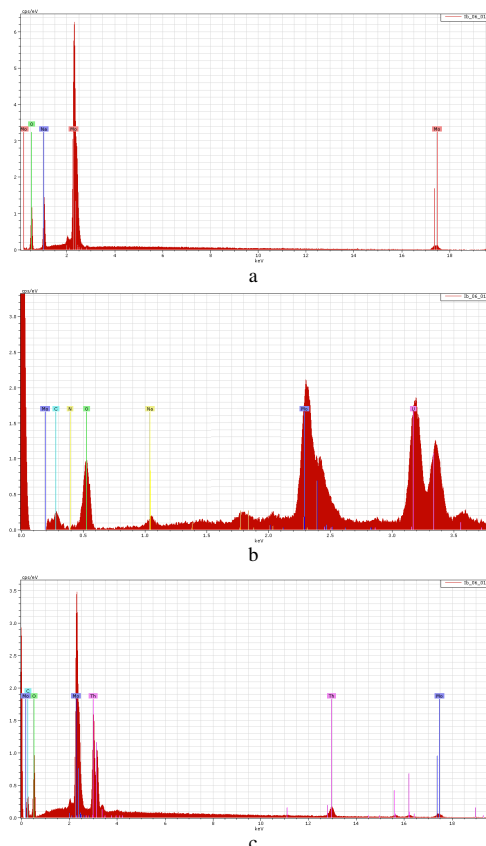


Fig.2. The EDX chemical composition spectra of L_2 (a), $\text{C}_{2\text{U}}$ (b), $\text{C}_{2\text{T}}$ (c) systems.

FTIR analysis

All investigated compounds showed characteristic IR bands for the (iso)polyoxometalates in the range of $400\text{-}2000\text{ cm}^{-1}$. Maxima of the characteristic bands of the systems related with $\text{Na}_2[\text{Mo}_4\text{O}_{13}]$ [10] and $\text{Na}_6[\text{Mo}_7\text{O}_{24}]$ systems are presented in Table 2.

The observed bands in the IR spectra of the complexes are shifted by comparison with those associated to (iso)polyoxomolybdate ligands, especially because of the structural changes caused by coordination of both uranyl and thorium cations.

Additional bands corresponding to vibrations $\nu_{(\text{UO})/(\text{ThO})}$ indicates the coordination of uranium and thorium with the ligands. Vibration bands of

polyoxometalate are displaced in the complex spectrum to spectrum ligand, due to coordination of the radioactive cations to oxygen atoms.

Table 2. Maxima of FTIR vibration bands (in cm^{-1}) of the $\text{Na}_2[\text{Mo}_4\text{O}_{13}]$ [10] and $\text{Na}_6[\text{Mo}_7\text{O}_{24}]$ systems and of the complexes with uranyl and thorium.

Assignment	$\text{Na}_2[\text{Mo}_4\text{O}_{13}]$	$\text{C}_{1\text{U}}$	$\text{C}_{1\text{T}}$
$\nu_{\text{as.s}}(\text{H}_2\text{O})$	3400	3400	3400
$\delta(\text{H}_2\text{O})$	1630	1619	1620
$\delta(\text{OH})$	1350		
M-O	-	1018	976
$\nu_{\text{as}}(\text{M}=\text{O})$	885	1125	998
$\nu_{\text{as}}(\text{M}-\text{O}-\text{M})$	738	730	735
Assignment	$\text{Na}_6[\text{Mo}_7\text{O}_{24}]$	$\text{C}_{2\text{U}}$	$\text{C}_{2\text{T}}$
$\nu_{\text{as.s}}(\text{H}_2\text{O})$	3459	3435	3420
$\delta(\text{H}_2\text{O})$	1648	1632	1620
$\delta(\text{OH})$	1370	-	-
U-O/(Th-O)	-	936	984
$\nu_{\text{as}}(\text{M}=\text{O})$	955	969	1010
$\nu_{\text{as}}(\text{M}-\text{O}-\text{M})$	880	885	995

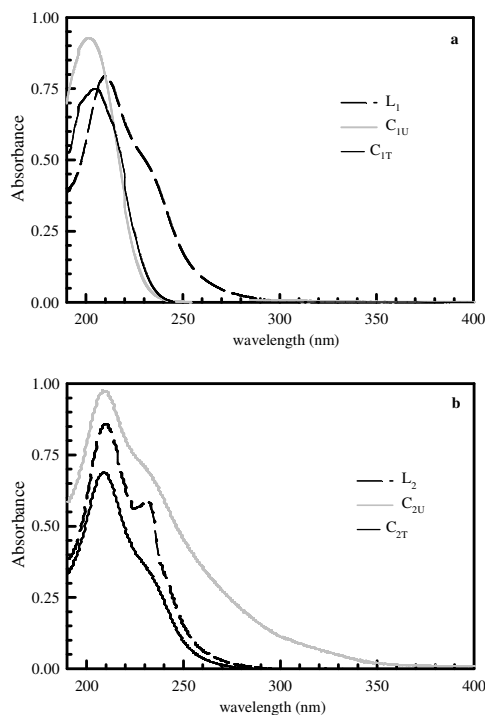


Fig. 3 UV spectra for the systems containing the $[\text{Mo}_4\text{O}_{13}]^{2-}$ unit [10] and for those containing the $[\text{Mo}_7\text{O}_{24}]^{6-}$ ligand (present work).

Thermogravimetric analysis

For the newly synthesised isopolyoxomolybdates a thermo-differential and thermogravimetric analysis has been undertaken in order to obtain information on the dehydration and transformation processes induced by the temperature. The analysis is useful especially in order to obtain information on the crystallisation water both zheolytic and non-zheolytic in nature.

Figure 4 presents the thermo-differential curves (derivative weight, mg min^{-1}) for the interest compounds. It contains information regarding the behaviour of the compounds $\text{C}_{2\text{U}}$ and $\text{C}_{2\text{T}}$ (this work, Figure 4b) in comparison with former analyzed compounds ($\text{C}_{1\text{U}}$ and $\text{C}_{1\text{T}}$ presented in Figure 4a) [10].

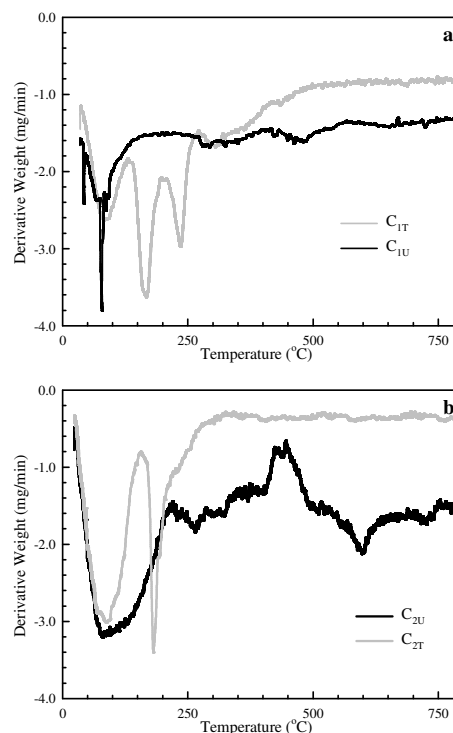


Fig. 4. Thermo-differential data plots from the thermo analysis of the compounds. (a)- $\text{C}_{1\text{U}}$, $\text{C}_{1\text{T}}$ [10] and (b)- $\text{C}_{2\text{U}}$, $\text{C}_{2\text{T}}$.

The distribution presented in Figure 4b shows that for the newly synthesised structures the dehydration process occurring between 35 and 200 °C (endothermic in nature which corresponds with desorption of the physically bound water) follows a more latent dynamic in comparison with that characteristic for the $\text{C}_{1\text{U}}$ and

C_{1T} units. Such behaviour suggests actually different organisational structures of the C_{2U} and C_{2T} units.

The DTG profiles for the C_{2U} and C_{2T} units (although not presented here) reveal the presence of some minor endothermic effects at temperatures in the 250 - 300 °C. However, at this stage is really difficult to make a clear attribution of their importance and further experiments should be performed in order to elucidate this aspect. The thermogravimetric analysis for the present work could be affected by some limitation induced by the small amount (weight mass less than 5 mg) of the investigated complexes used during analyses. In the 250 - 300 °C the C_{1U} and C_{1T} units [10] reveal more important exothermic processes and however, the above mentioned units are better characterised in this regard. Apart minor problems induced by the weight mass used in thermogravimetric analysis of the C_{2U} and C_{2T} units, our study suggest that significant structural and conformational differences may exist between them and the C_{1U} and C_{1T} units.

4. Conclusions

Under specific controlled conditions of temperature and pH, new polyoxomolybdates derived from [Mo₇O₂₄]⁶⁻ entity, containing uranyl (UO₂²⁺) and thorium (Th⁴⁺) radioactive ions, have been synthesized in aqueous solution. Accomplishments for the chemical characterization of the newly synthesized units was foreseen through the data obtained by the mean of state of art technique as Fourier Transformed Infrared Spectroscopy (FTIR), UV-vis spectrophotometry, scanning electronic microscopy (SEM) with electron diffraction X-ray (EDX) detection, and thermogravimetric analysis.

The rapid and efficient formation of these complexes in aqueous solution has been suggested as a possible route for separation of the actinyl cations. From the obtained data it can be suggested that the present newly synthesised complexes have high M:Mo (M = U or Th) ratios. Although the behaviour of the synthesised (iso)polyoxomolybdates suggest some possible application of the [Mo₇O₂₄]⁶⁻ unit in the

sequestration process of specific radioactive cations, the observed behaviour and the identified chemical composition infer some practical limitations when compared with the [Mo₄O₁₃]²⁻ unit. The (iso)polyoxomolybdates derived from heptamolybdate will possess reduced capacities of uranyl and thorium incorporation in their structure when compared with metamolybdate.

5. Acknowledgments

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6. References

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