New Heteropolyoxotungstates and Heteropolyoxomolybdates Containing Radioactive Ions (uranyl and thorium) in their Structure

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New heteropolyoxotungstate and heteropolyoxomolybdate complexes containing uranyl (UO_2^{2+}) and thorium (Th^{4+}) radioactive ions have been synthesized in aqueous solution under controlled conditions of temperature and pH. The synthesised compounds were unambiguous characterized by means of elemental analysis, Fourier Transformed Infrared Spectroscopy (FTIR), UV-vis spectrophotometry, scanning electronic microscopy (SEM) with electron diffraction X-ray (EDX) detection and thermogravimetric analysis. The reported structures of the newly synthesised units correspond to formulas as it follows: $K_{12}[(UO_2)_2(SiW_{11}O_{39})_2(H_2O)]\cdot 23H_2O$/ $Na_{12}[Na_2(UO_2)_2(PW_9O_{34})_2]\cdot 26H_2O$/$Na_5[Th(PW_9O_{34})(H_2O)_8]\cdot 18H_2O$/$(NH_4)_4[UO_2(PMo_{12}O_{40})_2]\cdot 14H_2O$/ $Na_4[UO_2(P_2W_{18}O_{62})(H_2O)_4]\cdot 24H_2O$/$Na_2[Th(P_2W_{18}O_{62})(H_2O)_4]\cdot 24H_2O$ and $K_2[UO_2(Cr_2Mo_{12}O_{39})_2(H_2O)_4]\cdot 23H_2O$.

Keywords: Heteropolyoxometalates, polyoxotungstate, polyoxomolybdate, uranyl, thorium

Polyoxometalates are chemical coordinative compounds of much current interest due to their special properties [1-2]. Many polyoxometalates may act as polydentate ligands that bond to a central ionic metal [3-4]. In recent years the heteropolyoxometalates (HPOMs) chemistry attracted much attention especially for the immobilisation of radioactive ionic metals [2]. 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 radiative interaction [5].

The structures of the polyoxometalates are mainly described by the Keggin anions which derive from a saturated or "complete" system $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ from where one or three adjacent octahedral groups are removed, resulting in the formation of mono-lacunary $[X^{n+}M_{11}O_{39}]^{(12-n)-}$ or three-lacunary $[X^{n+}M_9O_{34}]^{(14-n)-}$ units [6]. The first report about complexes between mono-lacunary anions of Keggin and Dawson type ($(SiW_{11}O_{39})^{8-}$, $(PW_{11}O_{39})^{7-}$ and $(P_2W_{17}O_{61})^{10-}$), and various lanthanides was made in 1971 [7] and the interaction between various polioxometales and uranium ion (IV) is also extensively described in the literature [6, 8-10].

We report in this paper the synthesis and chemical characterization of new heteropolyoxometalates obtained between uranyl and thorium cations and large polyoxotungstate and polyoxomolybdate anions. Accomplishments for the chemical characterization of the newly synthesised units is 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.

Experimental Part

Chemicals and instrumentation

All chemicals were reagent grade and used as purchased from Sigma-Aldrich without any further purification. The newly synthesized heteropolyoxometalates were characterized by means of spectroscopic (Fourier Transform Infrared Spectroscopy, FT-IR, and UV-vis spectrophotometry), scanning electronic microscopy (SEM) coupled with EDX detection method and thermogravimetric analysis. A JASCO FTIR 600 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 SEM analysis and photographs have been recorded by using a TESCAN model unit. The thermo-gravimetric analysis has been performed by means of a Perkin Elmer-Diamond TG/DTA system equipped with a crucible made of platinum. 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}.

Syntheses

New heteropolyoxometalates have been obtained from the treatment of various lacunary (defect) and plenary (complete) anion structures and uranyl and thorium cationic units. In the synthesis, as anions with high capacity to coordinate with UO_2^{2+} and Th^{4+}, were used mono-lacunary ($[SiW_{11}O_{39}]^{8-}$) and three-lacunary ($[PW_9O_{34}]^{9-}$) Keggin anions, complete Keggin units ($[PMo_{12}O_{40}]^{3-}$) and anions with complete Dawson-Wells structure ($[P_2W_{18}O_{62}]^{6-}$). For the synthesis the method reported by Rocchiecioli-Dettcheff et al. [11] has been applied and for convenience the annotation given in table 1 is also available within the Results and Discussions chapter.

Polyoxotungstosilicate - uranyl complex

The mono-lacunary structure $[SiW_{11}O_{39}]^{8-}$ has been synthesized in acidic solution of SiO_3^{2-} and WO_4^{2-} at a ratio of 1:1. A formation yield of about 85% has been estimated for $[SiW_{11}O_{39}]^{8-}$, a chemical compound characterized by a distortional Keggin lacunary structure [12]. At a

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Table 1
ANNOTATIONS AVAILABLE FOR THE VAROIUS STRUCTURES DESCRIBED IN THE PAPER

Anion type	Lacunary structure	Uranyl complex	Thorium complex
defect Keggin	L_1: $Na_8[SiW_{11}O_{39}]$	C_{1U}: UO_2^{2+} - $[SiW_{11}O_{39}]^{8-}$	-
defect Keggin	L_2: $K_9[PW_9O_{34}]$	*C_{2U}: UO_2^{2+} - $[PW_9O_{34}]^{9-}$	C_{2T}: Th^{4+} - $[PW_9O_{34}]^{9-}$
complete Keggin	L_3: $(NH_4)_3[PMo_{12}O_{40}]$	C_{3U}: UO_2^{2+} - $[PMo_{12}O_{40}]^{3-}$	-
complete Dawson-Wells	L_4: $(NH_4)_6[P_2W_{18}O_{62}]$	C_{4U}: UO_2^{2+} - $[P_2W_{18}O_{62}]^{6-}$	C_{4T}: Th^{4+} - $[P_2W_{18}O_{62}]^{6-}$
Not attributed yet	L_5: $(NH_4)_2[Cr_2Mo_{12}O_{42}]$	C_{5U}: UO_2^{2+}- $[Cr_2Mo_{12}O_{42}]^{2-}$	-

*The complex is referred also in the literature [2].

temperature of 50°C under continuous stirring, the $[SiW_{11}O_{39}]^{8-}$ ion led in the presence of uranyl nitrate in NaCl 0.1 M to a yellowish precipitate which after adequate treatment separated pale yellow crystals. The formation yield of the newly synthesized product with the uranyl cation was estimated at 75%.

Polyoxotungstophosphate - uranyl or thorium complex

The formation of $[PW_9O_{34}]^{9-}$ occurred in acidic solution (H_3PO_4, 85%) and the crystallisation process was favoured in the presence of acetic acid at *p*H=5.5. The structure $[PW_9O_{34}]^{9-}$ was obtained with a formation yield of 87.5%. The reaction between the three-lacunary anion and uranyl or thorium cations was favoured at temperature of 50°C under continuous stirring. The complex form between $[PW_9O_{34}]^{9-}$ and uranyl or thorium ions were obtained with formation yields of about 80%.

Other polyoxotungstates and polyoxomolybdates

The synthesis of the $[PMo_{12}O_{40}]^{3-}$ is based on the following reaction

$$2[5(NH_4)_2O \cdot 12MoO_3] + Na_2HPO_4 + 18HNO_3 = 2(NH_4)_3[PO_4(Mo_3O_9)_4] + 14NH_4NO_3 + 4NaNO_3 \quad (1)$$

which results in the production of $[PMo_{12}O_{40}]^{3-}$ with a formation yield of 90%. The uranyl complex was obtained under similar conditions as described above. The structures $[P_2W_{18}O_{62}]^{6-}$ [13] and $[Cr_2Mo_{12}O_{42}]^{2-}$ were synthesized on the base of the following reaction:

$$18[WO_4]^{2-} + 32H_3PO_4 + 6K^+ = = K_6[P_2W_{18}O_{62}] + 30[H_2PO_4]^- + 18H_2O \quad (2)$$

$$5(NH_4)_2O \cdot 12MoO_{3(aq)} + 2KCr(SO_4)_2 + H_2O = 3(NH_4)_2O \cdot Cr_2O_3 \cdot 12MoO_3 + 2KHSO_4 + 2(NH_4)_2SO_4 \quad (3)$$

The estimated formation yields of the $[P_2W_{18}O_{62}]^{6-}$ and $[Cr_2Mo_{12}O_{42}]^{2-}$ units were of 93% and, 87.5%, respectively.

Results and Discussions

SEM-EDX analysis

Figures 1a,b present the SEM image for the L_2 and C_{2T} structures while figures 1c,d present the same images for the L_3 and C_{3U} unit. Both figures 1b and 1d show clear differences in the morphology of the interest unit after their reaction with the thorium and uranyl cations. Figures 2a,b present the associated EDX spectra of the L_2 and C_{2T} structures. Both the data from SEM combined with the thermogravimetric analyses helped to infer the chemical compositions of the newly synthesised structures. In table 2 are presented the obtained data for selected synthesized structures. The data presented in table 2 proves the existence of an excellent agreement between the

Table 2
CHARACTERISATION OF THE CHEMICAL COMPOSITION

Code	Chemical compound	Molecular mass	Analysis	Contribution %				
C_{1U}	$K_{12}U_2Si_2W_{22}O_{106}H_{48}$	6792	Element	K	U	Si	W	H_2O
			Calculated	6.89	7.00	0.82	59.59	6.36
			Found	7.04	6.85	0.76	59.74	6.58
	$K_{12}[(UO_2)_2(SiW_{11}O_{39})_2(H_2O)]\cdot 23H_2O$		(proposed formulae)					
C_{2U}	$Na_{14}U_2P_2W_{18}O_{98}H_{52}$	5792	Element	Na	U	P	W	H_2O
			Calculated	5.55	8.21	1.07	57.18	8.08
			Found	5.52	8.05	0.93	57.49	8.42
	$Na_{12}[Na_2(UO_2)_2(PW_9O_{34})_2]\cdot 26H_2O$		(proposed formulae)*					
C_{2T}	$Na_5ThPW_9O_{60}H_{56}$	2994	Element	Na	Th	P	W	H_2O
			Calculated	3.84	7.74	1.03	55.31	13.89
			Found	3.95	7.56	1.15	55.45	13.56
	$Na_5[Th(PW_9O_{34})(H_2O)_8]\cdot 18H_2O$		(proposed formulae)					
C_{3U}	$UP_2Mo_{24}N_4O_{100}H_{32}$	4312	Element	U	P	Mo		H_2O
			Calculated	5.51	1.43	53.43		7.51
			Found	5.69	1.65	53.75		7.85
	$(NH_4)_4[UO_2(PMo_{12}O_{40})_2]\cdot 14H_2O$		(proposed formulae)					
C_{4U}	$Na_4UP_2W_{18}O_{94}H_{60}$	5268	Element	Na	U	P	W	H_2O
			Calculated	1.74	4.51	1.17	62.87	10.25
			Found	1.75	4.64	1.3	62.35	10.54
	$Na_4[UO_2(P_2W_{18}O_{62})(H_2O)_4]\cdot 24H_2O$		(proposed formulae)					
C_{4T}	$Na_2ThP_2W_{18}O_{90}H_{52}$	5148	Element	Na	Th	P	W	H_2O
			Calculated	0.89	4.50	1.20	64.33	9.79
			Found	1.0	4.72	1.42	64.76	9.65
	$Na_2[Th(P_2W_{18}O_{62})(H_2O)_4]\cdot 24H_2O$		(proposed formulae)					
C_{5U}	$K_2UCr_4Mo_{24}O_{107}H_{46}$	4594	Element	K	U	Cr	Mo	H_2O
			Calculated	1.69	5.18	4.52	50.15	10.57
			Found	1.75	5.15	4.73	50.35	10.25
	$K_2[UO_2(Cr_2Mo_{12}O_{39})_2(H_2O)_4]\cdot 23H_2O$		(proposed formulae)					

*in agreement with [2].

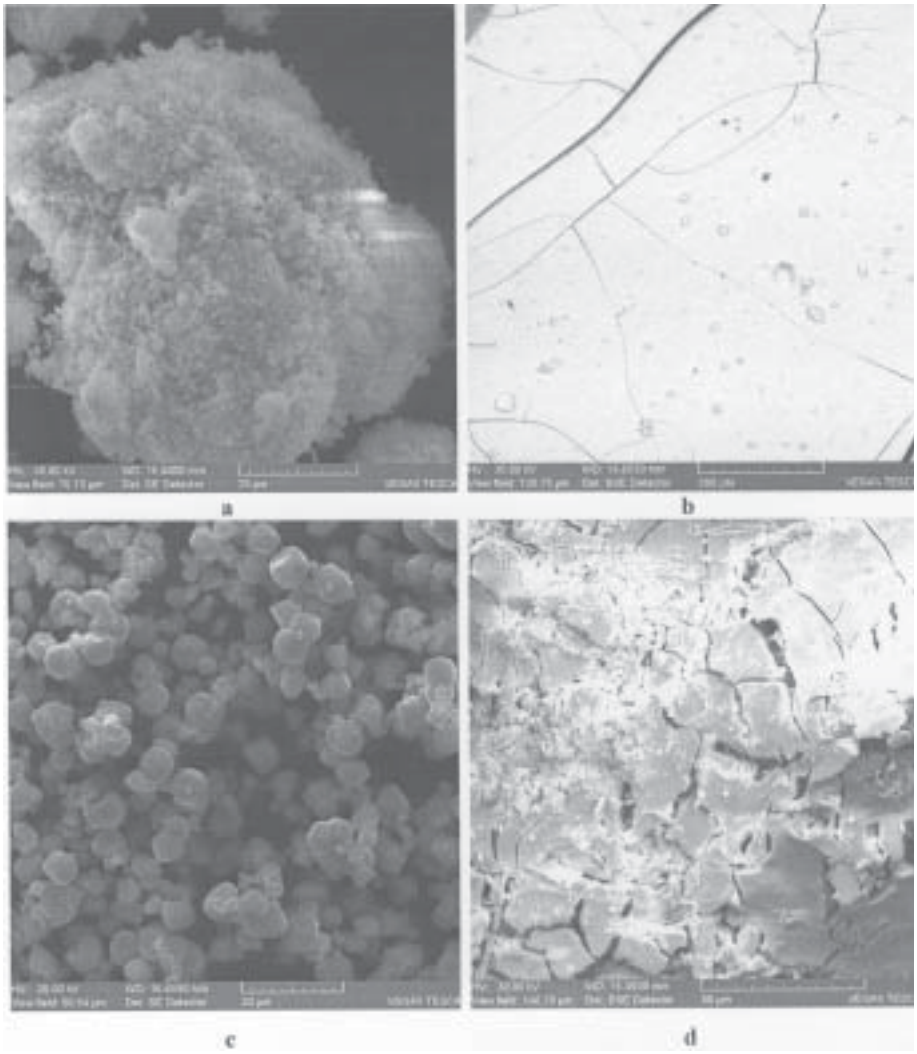


Fig. 1a,b,c,d. The SEM image of the L_2 (a), C_{2T} (b), L_3 (c), C_{3U} (d) structures

calculated composition and the data obtained by the performed elemental analysis.

FT-IR analysis on the synthesised heteropolioxometalates

Information about the interaction between the cations of interest and the lacunary and plenary anions were obtained by comparing the FTIR spectra of the metallic complexes with their corresponding ligands. The characteristic bands of the ligands and their complexes with uranyl and thorium ions are presented in table 3. The data were interpreted taking into account the fact that the vibration absorption band due to the M-O bond will appear in the radiation frequency range 1100 – 400 cm^{-1}. The same region (both for the asymmetric stretching vibration (ν_{as}) and bending vibration (δ)) is expected for the X-O bond. It is worthy to mention however that in most of the situations the IR spectra of the newly synthesized polyoxometalate complexes showed a frequency shift of the stretching vibrations toward higher wavelengths compared with their precursor ligands.

Among all investigated structures, as an example, in figure 3 are presented the FTIR spectra of the C_{2U} complex and its precursor L_2 in the main region (2000-400 cm^{-1}). The insets in figure 3 are presenting the spectra over the entire range of investigation (4000-400 cm^{-1}), right side, upper part, and that corresponding to the 1100-400 cm^{-1} range, right side, lower part. Figure 3 shows that owing to the structural modifications there is a clear change over the entire investigated range.

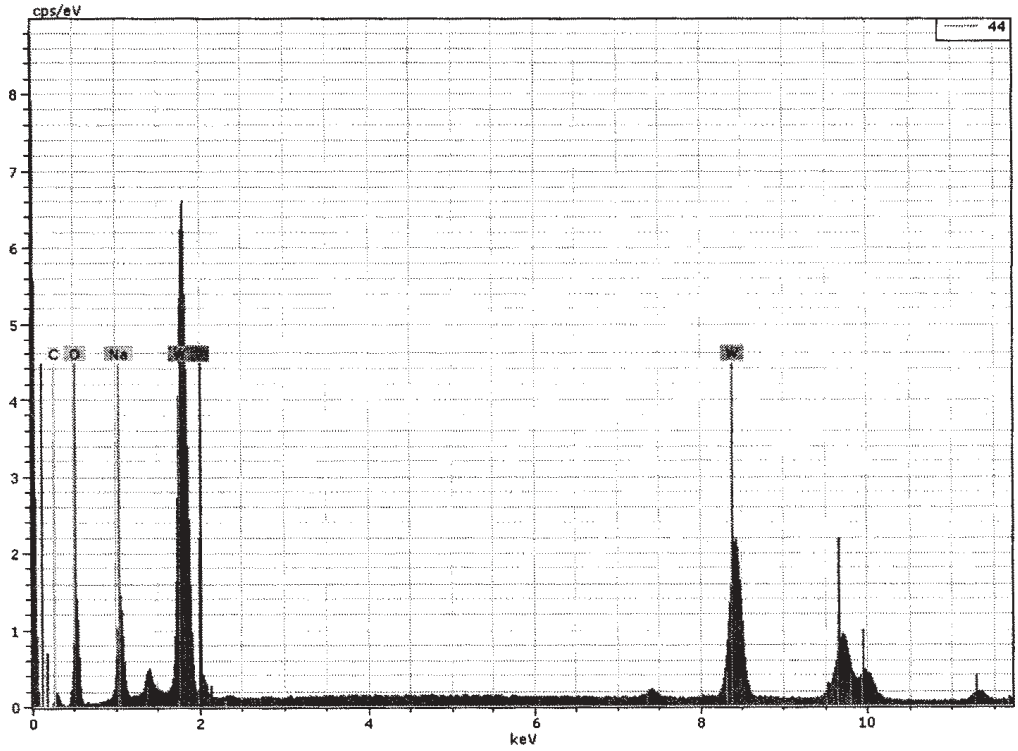
In the 1100 - 1000 cm^{-1} range the asymmetric stretch vibration specific for the X-O bond appears and, the region is characterised by a band splitting for the ligand which is diminished upon uranyl coordination. The above presented observation implies an increase in the symmetry of P-O bond upon vacancy completion an observation in agreement with other studies [14].

In the 1000 – 700 cm^{-1} range other characteristic bands were observed which could be assigned to the asymmetric stretching vibrations of the bridges (M-O_b-M) and the terminal bonds (M-O_t). The bands appearing in the region assigned to the stretching vibrations of the internal bonds (M-O_i-M), which is in the 600 – 500 cm^{-1} range, are not significantly influenced upon uranyl coordination.

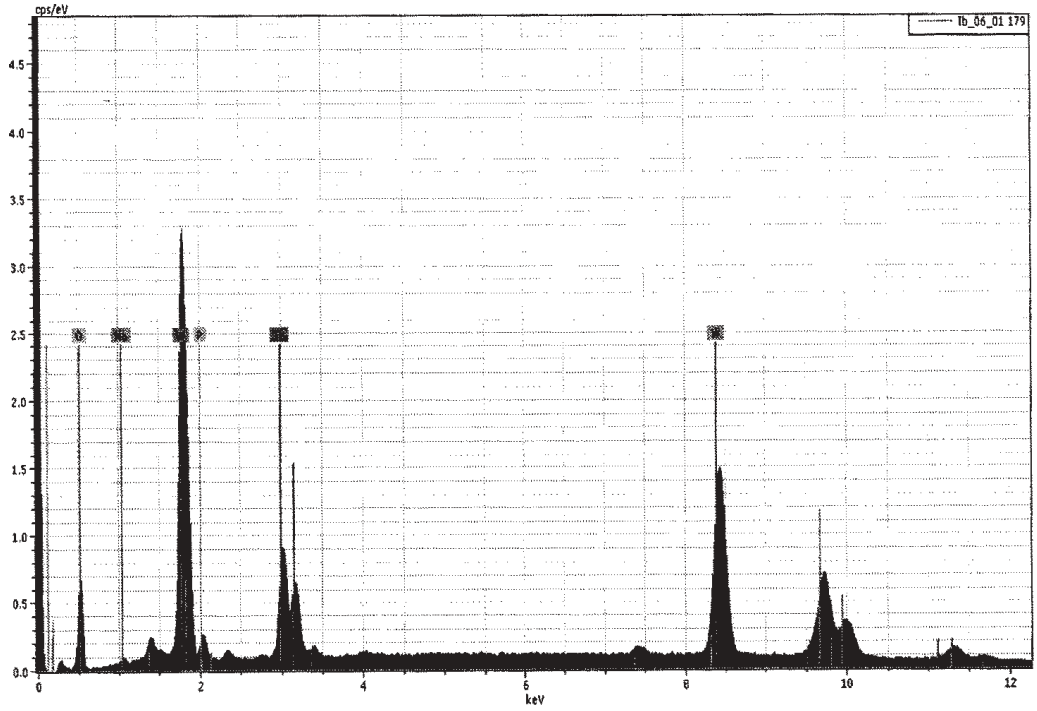
The data presented in table 3 proves that in the case of heteropolyoxomolybdates, their less stability as compared with the heteropolyoxotungstates will determine the band characteristic for the X-O bond to be shifted towards smaller wave numbers, an observation in agreement with other studies [6].

Electronic UV-vis spectra analysis

Table 4 presents the UV-vis spectral features of selected complexes and their corresponding ligands. In figures 4a,b are given spectra in the UV (a) and vis (b) range for selected analysed matrices with interesting behaviour. The synthesised heteropolyoxometalates, including either Keggin or Dawson-Wells units, present two characteristic charge transfer bands in agreement with the selection spin and Laporte rule. In all situations the maxima of the bands attributed to $p_\pi - d_\pi$ transitions, characteristic for the $M=O_t$ bond, were observed around 200 nm, while the bands maxima attributed to the electronic transitions between the energy levels of the M-O_b-M ($d_\pi -> p_\pi -> d_\pi$) tricentric



a



b

Fig. 2. EDX spectra for the L_2(a) and C_{2T}(b) units

Compound	ν_{as}(OH)	$\delta_{(HOH)}$	$\delta_{(OH)}$	U-O (Th-O)	ν_{as}(M=O)	ν_{as}(MOM)	ν_{X-O}
	cm^{-1}						
L_1	3400	1626	-	-	1020	725 / 796 / 898	1120
L_2	3450	1576 1632	1416	-	960	-	1040 / 1085
L_3	3459	1612	1406	-	963	789 / 864	1013
L_4	3440	1604	1401	-	960	775 / 912	1020 / 1090
L_5	3420	1635	1420	-	985	850 / 920	1015 / 1020
C_{1U}	3400	1621	1443	951	1020	611	1020
C_{2U}	3420	1621	-	1050	960	720 / 790 / 800	1010 / 1075
C_{3U}	3450	1640	1472	936	989	796 / 894	1054
C_{4U}	3430	1636	1432	973	944	894 / 938	1040 / 1115
C_{5U}	3490	1620	1430	1120	995	970 / 1050	1020 / 1050
C_{2T}	3425	1626	1440	980	895	730 / 780 / 820	1050 / 1100
C_{4T}	3465	1623	1450	1038	952	801 / 960	1025 / 1100

Table 3
FTIR CHARACTERIZATION OF THE LIGANDS AND COMPLEXES WITH URANYL AND THORIUM IONS

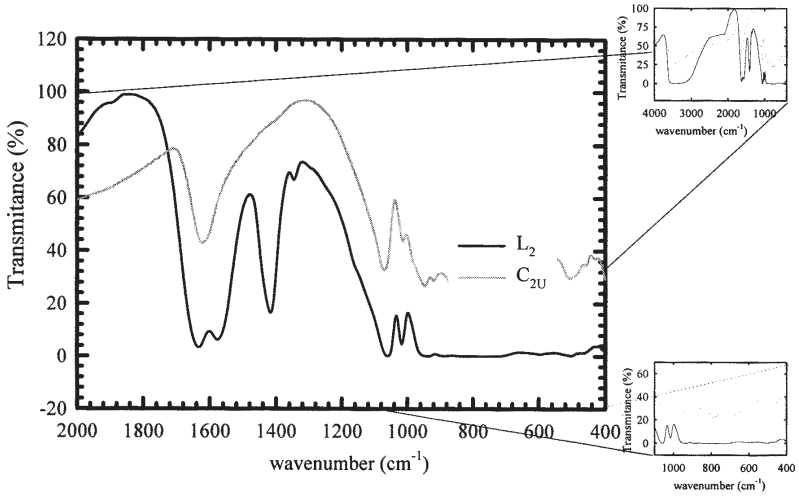


Fig. 3. FTIR spectra of the ligand L_2 and associated complex C_{2U}. The entire range of investigation (4000-400 cm^{-1}) is presented in the inset figure, right side, upper part, and that corresponding to the 1100-400 cm^{-1} range, in the inset located right side, lower part

Table 4
UV-VIS SPECTRAL FEATURES OF SELECTED COMPLEXES AND THEIR CORRESPONDING LIGANDS

Compound	Maximum absorption bands (nm)		
	UV range		vis range
	p_π–>d_π	d_π–>p_π–>d_π	Internal electronic transition
L_1	~200	250	-
L_2	~200	250	-
L_3*	207	230	-
L_4	~200	254/300	-
C_{1U}**	-	-	-
C_{2U}	~200	254	433 with a shoulder at 474
C_{3U}***	-	-	-
C_{4U}****	~200	260/300	416 / 427 / 440 / 454 / 472 / 485
C_{2T}	204	Totally attenuated	Tailed band in the 400 – 650 nm range
C_{4T}	206	256 (attenuated)	Tailed band in the 400 – 650 nm range

*It confirms the information from the literature regarding a Dawson-Wells unit characterised by a large band with shoulders in the 200-300 nm range [8].
**Insoluble compound in inorganic and organic reagents.
*** Insoluble compound in inorganic and organic reagents.
****Large band in vis range with similar shoulders as observed in [5] for $[As_2W_{18}U_3O_{74}]^{12-}$ and $[As_2W_{18}U_2O_{73}]^{12-}$ units.

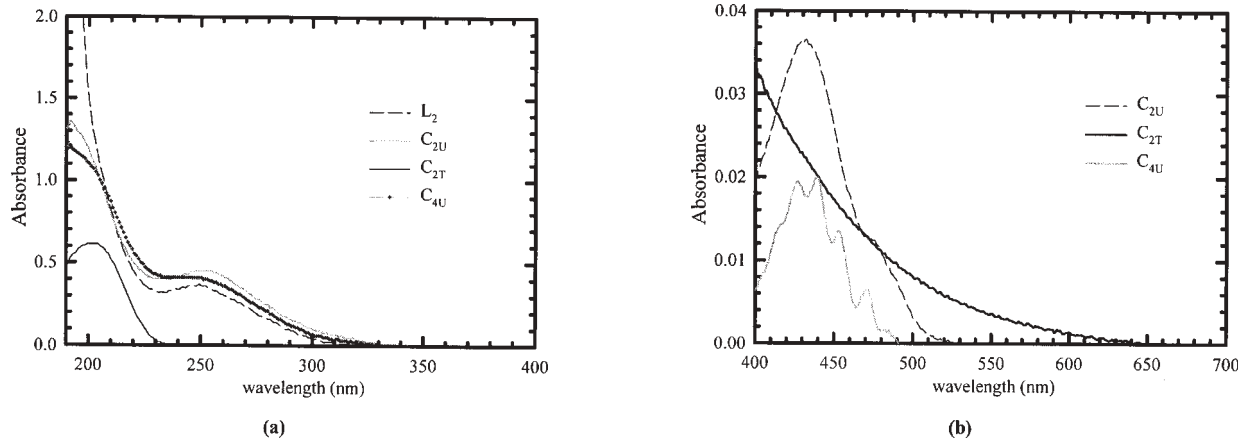
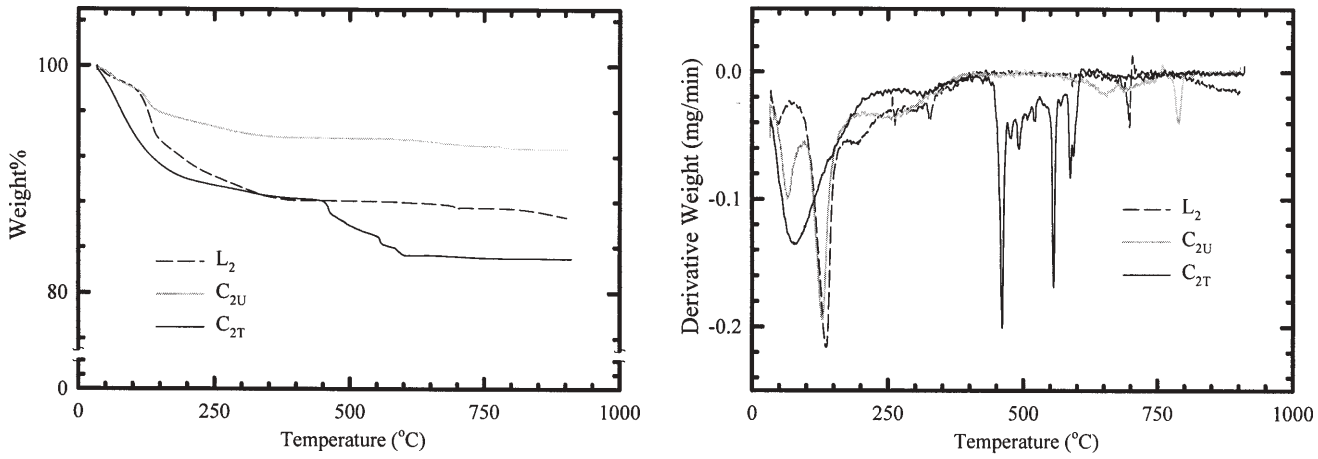


Fig. 4a,b. Spectra in the UV (a) and vis (b) range for selected analysed matrices with interesting behaviour

bonds were observed at about 250 nm and 300 nm, respectively. In the spectra of the newly synthesised complexes the band with maximum at 250 nm is red shifted when compared to the corresponding bands of their ligands precursors. It is worthy to mention however that the maxima of the absorption bands are relatively little influenced by the nature of the principal heteroatom (P, Si) or adenz (Mo, W) atoms.

Thermogravimetric analysis

Information on the dehydratation and transformation processes induced by the temperature on the synthesised hetero-polyatomic units was obtained by mean of the thermogravimetric and thermodifferential analyses. Such analysis gives information on the crystallisation water both zheolytic and non-zheolytic in nature. Examples of thermogravimetric (% weight loss) and thermodifferential curves (derivative weight, mg min^{-1}) for the L_2, C_{2U} and C_{2T} are presented in figures 5a,b. From figures 5a,b it s obvious that the C_{2T} unit behaves apart in the 450 – 610 °C range, an observation which implies strong modifications in its polymorphic structure. However, the analyses performed on the newly synthesised structures revealed that in all situations the units were characterised by a dehydration process which occurred between 35 and 200°C (endothermic in nature which corresponds with the desorption of water physically bound). All the ligands were characterised by large exothermic effects which were observed at temperatures of about 500°C which are mainly



(a) **(b)**

Fig. 5a,b. Thermogravimetric (a) and thermodifferential (b) curves of the L_2, C_{2U}, and C_{2T} analysed structures

attributed to the decomposition process of the interest units (L_1 with maximum at 480°C, L_2 with maximum at 440°C, L_3 with maximum at 500°C, and L_4 with maximum at 590°C). The exothermic effect in the 500°C range was much diminished in all investigated complexes. At temperatures above 650°C few minor thermo effects have been observed which would suggest actually modifications in the polymorphic structure of the investigated units (especially C_{2U} and C_{2T}), changes which may occur in the structures of the investigated units due to melting and/or sublimation processes of the resulting oxides.

Conclusions

New polyoxotungstates and polyoxomolybdates including UO_2^{2+} and Th^{4+} ions in the form: $K_{12}[(UO_2)_2(SiW_{11}O_{39})_2(H_2O)]\cdot 23H_2O$ / $Na_{12}[Na_2(UO_2)_2(PW_9O_{34})_2]\cdot 26H_2O$ / $Na_5[Th(PW_9O_{34})(H_2O)_8]\cdot 18H_2O$ / $(NH_4)_4[UO_2(PMo_{12}O_{40})_2]\cdot 14H_2O$/$Na_4[UO_2(P_2W_{18}O_{62})(H_2O)_4]\cdot 24H_2O$/$Na_2[Th(P_2W_{18}O_{62})(H_2O)_4]\cdot 24H_2O$ and $K_2[UO_2(Cr_2Mo_{12}O_{39})_2(H_2O)_4]\cdot 23H_2O$ were synthesised and chemically characterised. The chemical proportions obtained by the mean of SEM-EDX and thermogravimetric analyses were in excellent agreement with the calculated composition. The performed UV-vis and FTIR analyses revealed that upon cation coordination important modifications occurred in the structure of the complexes as compared with their ligand precursors. The UV spectra show an increase in the stability of the Keggin and Dawson-Wells units after their complexation with radioactive cations. This observation might imply a wide range of applications of lacunary and plenary Keggin and Dawson-Wells units in the decontamination of radioactive residual waters.

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