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Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

SYNTHESIS AND SPECTROSCOPIC INVESTIGATIONS OF NEW UO_2^{2+}– POLYOXOMETALATE COMPLEXES

DAN RUSU[a], OANA BABAN[b], SIMINA DREVE[c], MIRCEA PUIA[d], MARIANA RUSU[b]

ABSTRACT. The $Na_{10}[(UO_2)_2(H_2O)_2X_2W_{20}O_{70}]\cdot nH_2O$ heteropolyoxo-metalates ($Na_{10}1$: X =Sb^{III}, n = 28; $Na_{10}2$: X =Bi^{III}, n = 34) were synthesized and investigated by chemical and thermal analysis, FT- IR, Raman, UV-Vis and fluorescence emission spectroscopies for determining subsequently the behavior of the encapsulated uranyl cations, their coordination by the tungstoantimonate(**III**) or tungstobismutate(**III**) fragments, and the corresponding pentagonal-bipyramidal local symmetry. Polyoxoanions $[(UO_2)_2(H_2O)_2X_2W_{20}O_{70}]^{10-}$ are structural similarly and consist from two β-B-$[XW_9O_{33}]^{9-}$ (X= Sb^{III}, Bi^{III}) framework which are linked by an equatorial belt of two $UO_2(H_2O)_2^{2+}$ units and two WO_2 groups.

Keywords: *Uranium (VI); Heteropolyoxotungstates; IR, Raman, UV, Vis and fluorescence emission spectroscopies.*

INTRODUCTION

The current research in polyoxometallate (POM) chemistry is characterized by the perception and the achievement of their applications in different areas, especially in the field of nanomaterials, catalysis, image reactive, as potential agents for nuclear waste sequestration and storage, magnetic chemistry and medicine [1]. At the same time, it must be pointed out that the polyoxometallate chemistry has a tradition in studying the formation and stability of heteropolyoxotungstates containing heteroatoms of lanthanides and actinides [2-15]. The structure of these polyoxotungstate species was first reported by Weakley [16], and it can be described as a 1:2 sandwich type structure of $Ln^{3+/4+}$ or An^{4+} ions with monolacunary polyoxoanions

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[a] *Universitatea de Medicină şi Farmacie Iuliu Haţieganu, Facultatea de Farmacie, Str. E. Isac Nr. 13, RO-400023, Cluj-Napoca, Romania*

[b] *Universitatea Babeş-Bolyai, Facultatea de Chimie şi Inginerie Chimică, Str. M. Kogalniceanu Nr. 1, RO-400084 Cluj-Napoca, Romania, mrusu@chem.ubbcluj.ro*

[c] *Institutul Naţional pentru Izotopi şi Tehnologie Moleculară, Str. Donath Nr. 63, RO-400293 Cluj-Napoca, Romania*

[d] *Universitatea Babeş Bolyai, Facultatea de Fizică, Str. M. Kogalniceanu Nr. 1, RO-400084 Cluj-Napoca, Romania*

“ligands”, such as $[Ln^{III}(PW_{11}O_{39})_2]^{11-}$, in which the metallic cations occupy a anti-phrysmatic coordinative position. Sometimes, although U^{IV} can be stabilized in these complexes, the chemistry of the aqueous solutions of the first actinides is dominated by trans-dioxin cations, from which the most familiar is UO_2^{2+}. Pope [17] reports the example of the heteropolyoxotungstate which incorporates the UO_2^{2+}, linear steric, as expected. Subsequently, other uranyl polyoxometallate complexes were reported. [18-27]

Since 1970 [28-30], a number of articles have been published regarding the $\{XW_{11}\}$, with ($X=Sb^{III}$, Bi^{III}), type of monolacunary polyoxocations and their complexes with a ratio of 1:1 with the di- and trivalent cations of transitional metals. Recently, these species have been revealed as dimmers on the basis of the structure determined on the Krebs salts $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$, $[Sb_2W_{20}Fe^{III}{}_2O_{70}(H_2O)_6]^{8-}$, $[Sb_2W_{20}Co^{II}{}_2O_{70}(H_2O)_6]^{10-}$ and $[Bi_2W_{20}Fe^{III}{}_2O_{70}(H_2O)_6]^{6-}$ [31, 32]. The polyoxotungstate anion structure consists of two trilacunary groups $\{B\text{-}\beta\text{-}XW_9\}$, bonded by two additional tungsten atoms and other two additional tungsten centers with a weaker bond, which can be replaced with $M^{II/III}$ cations in the substituted polyoxoanions.

The Krebs $[X_2W_{22}O_{74}(OH))_2]^{12-}$ polyoxoanion type belongs to the clusters that incorporate different lacunary trivacante polyoxometallic fragments with the formula B-β $[XW_9O_{33}]^{9-}$ where X = Sb^{III}, Bi^{III}.

The aim of the present paper is to report the new natrium salts of the di-substituted Krebs tungstoantimonate and tungstobismutate $[(UO_2)_2(H_2O)_2X_2W_{20}O_{70}]^{10-}$, X = Sb^{III}, Bi^{III}. The 2:1 complexes corresponding to the formula $Na_{10}[(UO_2)_2(H_2O)_2X_2W_{20}O_{70}]$, X = Sb^{III}, Bi^{III} were obtained according to the following reaction:

$$2UO_2^{2+} + [X_2W_{22}O_{74}(OH)_2]^{12-} + 6H_2O \rightarrow [(UO_2)_2(H_2O)_4X_2W_{20}O_{70}]^{10-} + 2WO_4^{2-} + 6H^+ \quad (1)$$

In order to establish the behavior of UO_2^{2+} cations encapsulated in heteropolyoxometalates, the coordination pattern of the metallic ions to the Keggin fragments and the local symmetry around them, the new complexes were investigated by means of spectroscopic (FT-IR, Raman, UV, Vis and fluorescence emission) methods.

RESULTS AND DISCUSSIONS

Chemical and thermal analysis

The following abbreviations will be used: i) for the anions: $\mathbf{L_1}$ for $[[Sb_2W_{22}O_{74}(OH)_2]^{12-}$, **1** for $[(UO_2)_2(H_2O)_4Sb_2W_{20}O_{70}]^{10-}$, $\mathbf{L_2}$ for $[Bi_2W_{22}O_{74}(OH)_2]^{12-}$, **2** for $[(UO_2)_2(H_2O)_4Bi_2W_{20}O_{70}]^{10-}$ ii) for the salts: $Na_{12}\mathbf{L_1}$ for $Na_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 42H_2O$, $Na_{10}\mathbf{1}$ for $Na_{10}[(UO_2)_2(H_2O)_4Sb_2W_{20}O_{70}]\cdot 28H_2O$, $Na_{12}[Bi_2W_{22}O_{74}(OH)_2]\cdot 44H_2O$, $Na_{10}\mathbf{2}$ for : $Na_{10}[(UO_2)_2(H_2O)_4Bi_2W_{20}O_{70}]\cdot 34H_2O$.

The chemical reaction of UO_2^{2+} with $[X_2W_{22}O_{74}(OH)_2]^{12-}$ (X=Sb^{III}, Bi^{III}) in water can be described by eqn. (1). The isolation of the final products as sodium salt, and their recrystallization from hot water, resulted in relatively good yields of the Na_{10}**1** and Na_{10}**2.** The analytical data are presented in table 1.

Table 1. Analytical data of the Na_{10}**1** and Na_{10}**2** polyoxometalate complexes

Complex	Yield (g / %)	Colour	Found (calc.) (%)				
			Na	X	W	U	H_2O
Na_{10}**1**	4.15 / 65	Yellow-Orange	3,72 (3,60)	3.86 (3.81)	57.70 (57.57)	7.48 (7.45)	8.98 (9.02)
Na_{10}**2**	4.73 / 71	Yellow-Orange	3.54 (3.45)	6.28 (6.27)	55.60 (55.15)	7.18 (7.14)	10.22 (10.26)

Due to the fact that the $[X_2W_{22}O_{74}(OH)_2]^{12-}$ species -where X= Sb^{III}, Bi^{III} - were not stable in aqueous solutions, the reaction was led by adding solid sodium salt of the ligands to the $UO_2(NO_3)_2$ aqueous solution. The polyoxoanion complexes obtained were stable only in the presence of an excess of sodium ions. The complexes were crystallized, with a good yield, after a few days, from solution kept at 5 °C.

The suggested formula for $Na_{10}[(UO_2)_2(H_2O)_4Sb_2W_{20}O_{70}].28H_2O$ and $Na_{10}[(UO_2)_2(H_2O)_4Bi_2W_{20}O_{70}]\cdot 34H_2O$ complexes are consistent with results of the analyses of the final products (Table 1).

The thermo-gravimetric analysis shows that between 35-325 ^{0}C the mass loss was 1.3491 mg (8.98 %) and 1.5039 mg (10.22 %) for (Na_{10}**1**) and (Na_{10}**2**) complexes respectively. The water loss process took place in two successive phases: the first between 35-120 ^{0}C which corresponds to 28 (Na_{10}**1**) and 34 (Na_{10}**2**) crystallization water molecules respectively, and the second between 120-325 ^{0}C, corresponding to 4 coordinating water molecules for both complexes.

The DTA curves indicate two endothermic and two exothermic effects. The endothermic effects with a maximum temperature of ≈ 120 °C and ≈ 325 ^{0}C corresponds to the water loss processes. The exothermic effect with a maximum at ≈ 430 °C correspond to the crystallization process of the oxides from the mixture, and the exothermic effect with a maximum temperature at ≈ 500 °C corresponds to the phase transformation from the oxides structures in the mixture [33].

Vibrational spectra

FT – IR spectra

By comparing the FT-IR spectra of the uranyl complexes with those for the corresponding ligands and their shifts toward higher or lower frequencies, we obtained information regarding the UO_2^{2+} ions coordination to the lacunary polyoxometallates units, the symmetry and the bond strength. The FT-IR spectra of the polyoxometallates generally exhibit contributions of the polyoxoanion frameworks. The characteristic IR vibration bands of $Na_{10}\mathbf{1}$ and $Na_{10}\mathbf{2}$ complexes, as compared to those of the $Na_{12}\mathbf{L_1}$ and $Na_{12}\mathbf{L_2}$ ligands, are shown in Table 2.

Table 2. Main vibration bands observed in the FT-IR spectra (cm^{-1})

Vibration	$Na_{12}\mathbf{L_1}$	$Na_{12}\mathbf{L_2}$	$Na_{10}\mathbf{1}$	$Na_{10}\mathbf{2}$
$\nu_{as}(W{=}O_t)$	939	948	940	948
$\nu_{as}(W–O_c–W)$	879	875	889 870	880 868
$W\text{-}O\text{-}UO_2^{2+}$			836	836
$\nu_{as}(W–O_e–W)$	798 762	790 735	775 720	795 720

In the 1000-700 cm^{-1} range, we observed characteristic bands, which we assigned to the asymmetric stretching vibrations of the bridges $W\text{-}O_{c,e}\text{-}W$, $W\text{-}O_i$ and of the terminal bonds $W{=}O_t$.

All anti-symmetric frequency bands involving tungsten ions are shifted towards higher or lower frequencies (by 1 – 39 cm^{-1}) in the complex spectra, compared to the ligands.

The tiny shift of the $\nu_{as}(W{=}O_t)$ vibration indicates that terminal O_t atoms are not involved in the coordination of UO_2^{2+} ions.

The $v_{as}(W–O_c–W)$ vibration band of the tricentric $W\text{-}O_c\text{-}W$ bond of the corner sharing WO_6 octahedra is split in both complexes, being shifted in the complexes spectra toward higher frequencies in comparison with the ligands. This is consistent with an increase in the anion cohesion, when the co-ordination of the uranyl ions in the polyoxometalates frameworks takes place.

The $v_{as}(W–O_e–W)$ vibration band of the tricentric $W–O_e–W$ bond of the edge sharing WO_6 octahedra is split in both complexes, being shifted in the complexes spectra toward lower frequencies for $Na_{10}\mathbf{1}$ or higher for $Na_{10}\mathbf{2}$ in comparison with the ligands. This is consistent with a decrease or increase of the anions cohesion, when coordination of the uranyl ions in the polyoxometalates frameworks takes place.

The shift of $\nu_{as}(W–O_{c,e}–W)$ vibration bands is due to the uranyl ions coordination with the lacunary polyoxometalate ligands by O_c and O_e atoms.

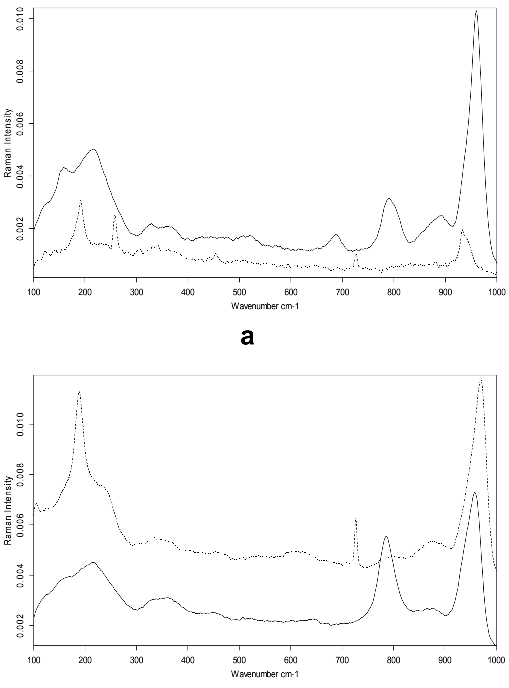
In addition, the IR spectra of the uranyl polyoxometalate complexes exhibit at ~ 836 cm^{-1} a band which is assigned to the stretching vibrations of the $\nu_{as}(UO_2^{2+})$.

The $v_{as}(UO_2^{2+})$ bands are shifted in polyoxotungstate complexes to lower frequencies, in comparison with the corresponding band from the

$UO_2(NO_3)_2 \cdot 4H_2O$ (965 cm^{-1}) [34], because the polyoxometalate ligands form strong bonds with uranium by lowering the order of the U=O band and consistently lowering the v_{as}(O=U=O) frequency.

Raman spectra

The Raman spectra of the complexes Na_{10}**1** and Na_{10}**2** (Figure 1) also show vibration bands which are characteristic to the polyoxometalate framework. The strongest bands occurring at 958 and 956 cm^{-1}, respectively, can be assigned to v_s(W-O_t) vibrations. The less intense bands appearing in the 900-700 cm^{-1} range are assigned to the stretching of the W-$O_{c,e}$-W bridges, and the band appearing at 214 cm^{-1} is assigned to v_s(W-O_i) vibration, where O_i is an internal oxygen atom which links Sb or Bi and W atoms. In comparison to the related lacunary ligands Na_{12}**L₁** and Na_{12}**L₂**, a shift of these bands towards higher or lower energies is observed, indicating an increase in stability for the Na_{12}**L₁** and a decrease in stability for the Na_{12}**L₂** complexes of the polyoxoanion framework, upon coordination of the uranyl ions [35].



a

b

Figure 1. Raman spectra of the polyoxometalate complexes (solid linie) a) Na_{10}**1** and b) Na_{10}**2,** and of the related ligands (dotted linie) a) Na_{12}**L₁** and b) Na_{12}**L₂**.

Electronic spectra

UV-spectra

The complexes' spectra are similar to the ones of the ligands. Each spectrum presents two bands assigned to the $p_\pi \rightarrow d_\pi$ ligand-to-metal charge transfer transition in the W=O$_t$ bonds and d_π–p_π–d_π electronic transitions between the energy levels of the W-O$_{c,e}$-W bonds (Table 3).

The higher energy band (ν_1), due to the d_π-p_π proper transitions from the W=O$_t$ bonds, with an absorption maximum at ~ 210 nm, are insignificantly shifted in the complexes compared to the ligands, which can been associated with the lack of involvement of the terminal oxygen atoms in the coordination of the cations of uranyl.

The lower energy band (ν_2) corresponding to the d_π-p_π-d_π electronic transitions from the tri-centric W-O$_{c,e}$-W bonds, displays an expected absorption maximum in the range of 250-300 nm, for all polyoxotungstate complexes, shifted towards lower energies compared to the ligands, which is associated with the involvement of the oxygen atoms of these bonds in the coordination of the uranyl cations [36, 37].

Table 3. Charge transfer bands observed in the UV absorption spectra (cm^{-1}/nm)

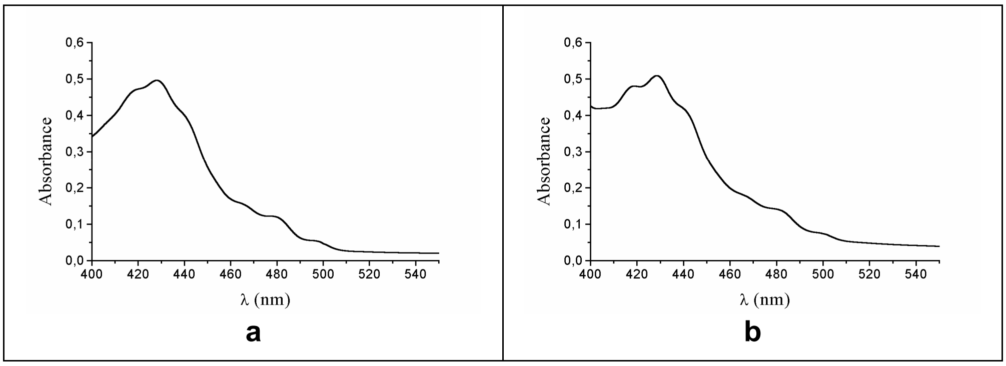
Bands	Na$_{12}$**L$_1$**	Na$_{12}$**L$_2$**	Na$_{10}$**1**	Na$_{10}$**2**
ν_2 : $d_\pi \rightarrow p_\pi \rightarrow d_\pi$ (W–O$_b$–W)	39682/252	39525/253	39215/255 36200/276	39062/256 35840/279
ν_1 : $p_\pi \rightarrow d_\pi$ (W=O$_t$)	47169/212	47169/212	46728/214	46728/214

Visible-spectra

Visible spectra of the Na$_{10}$**1 and** Na$_{10}$**2** complexes are similar and present six bands. The transition assignments were made in accordance with [18], and were presented in Figure 2.

The visible electronic spectra of uranyl complexes exhibit two charge transfer bands at ~ 420 nm and ~430 nm respectively, which can be attributed to internal O=U=O transitions and four charge transfer bands at ~440, ~468, ~480 and ~500 nm which can be assigned to ligand – uranyl electronic transitions [17-21].

As resulting from the specialty literature, as well as from the present report, when it comes to the polyoxometalate-uranyl complexes, we observe a trend, namely that the U(VI) always adopts its favored seven-coordinate pentagonal-bipyramidal geommetry but with a certain degree of distortion, in order to accommodate the positions of the unsaturated oxygen donor atoms of the polyoxoanion [20,21].



a

b

Figure 2. The electronic visible spectra of the polyoxometalate complexes: a) Na$_{10}$**1**; b) Na$_{10}$**2**.

Fluorescence emission spectra

The spectrofluorimetric analysis reveals a strong fluorescence emission in the range of 470–580 nm, corresponding to the excitation of the 300 nm band and a sharp emission at 824 nm for an excitation of the 550 nm band.

When comparing the values with some literature data, we can assume that the sharp emission band at 824 nm, presented in both uranyl systems, can be the fluorimetric signal of the uranyl ion in both systems [38-40].

The accuracy of the determinations and the shape of bands suggest that no important quenching phenomenon occurs, confirming the high purity of the Na$_{10}$**1**, and Na$_{10}$**2** complexes, respectively.

CONCLUSIONS

In this work, we have synthesized two new polyoxometalate complexes with uranyl ions of $[(UO_2)_2(H_2O)_4(X_2W_{20}O_{70})]^{10-}$, X = Sb^{III}, Bi^{III} type.

The UV and FT-IR spectra indicate the coordination of each uranyl ion to oxygen atoms from the corner-sharing and edge-sharing octahedra of the trilacunary Keggin anions.

Visible electronic spectra indicate the coordination of the uranyl cations in the $[(UO_2)_2(H_2O)_2(X_2W_{20}O_{70}]^{10-}$ complexes, too.

The fluorescence emission spectra reveal the presence of the uranyl ions in both studied compounds and suggest that no important quenching phenomenon occurs, confirming the high purity of Na$_{10}$**1** and Na$_{10}$**2** respectively.

According to our studies, we recommend for the uranyl polyoxometalate complexes a “sandwich” kind of structure, which consist of two B–β–XW_9O_{33} Keggin frameworks which are linked by two uranyl ions and two WO_2 fragments (Figure 3). Each uranium atom adopts the pentagonal- bi-pyramidal coordination, forming two equatorial bonds with the terminal oxygen atoms of one pair of two WO_6 octahedra bonded by common edges, which belong to one of the B–β–XW_9O_{33} fragments and a bond with the terminal oxygen of one of the WO_6 octahedra belonging to the other B–β–XW_9O_{33} fragment, the other two equatorial coordinating points of the uranyl cation being satisfied by two molecules of water.

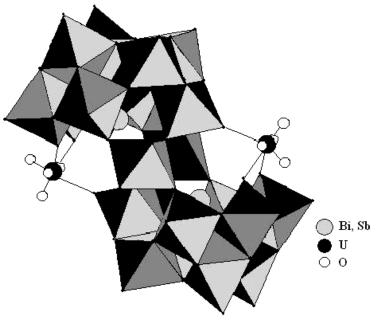


Figure 3. Proposed structure of the Na_{10}**1** and Na_{10}**2** polyoxometallate complexes.

EXPERIMENTAL SECTION

Materials

We have used reagent grade chemicals and all syntheses and studies were carried out in distilled water.

Both the sodium salt of the polyoxometallate ligand $Na_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 42H_2O$ ($Na_{12}\mathbf{L_1}$), and the sodium salt of the polyoxometalate ligand $Na_{12}[Bi_2W_{22}O_{74}(OH)_2]\cdot 44H_2O$ ($Na_{12}\mathbf{L_2}$) were prepared as previously reported [31] and [32] respectively.

Synthesis of $Na_{10}[(UO_2)_2(H_2O)_4Sb_2W_{20}O_{70}]\cdot 28H_2O$ (Na_{10}1) and $Na_{10}[(UO_2)_2(H_2O)_4Bi_2W_{20}O_{70}]\cdot 34H_2O$ (Na_{10}2) complexes

To a solution of $UO_2(NO_3)_2\cdot 4H_2O$ (0.47 g, 2 mmol) in distilled water (50 ml) we added solid sodium salts of the ligand $Na_{12}[X_2W_{22}O_{74}(OH)_2]$ ($X=Sb^{III}$, Bi^{III}) (6.27 g $Na_{12}\mathbf{L_1}$ or 6.75 g $Na_{12}\mathbf{L_2}$, respectively, 1 mmol). The slightly turbid yellow-orange final solution was strongly stirred at 70°C for 30 minutes, its pH was adjusted to the value of 4.5 with 1M HCl and filtered under suction. It was then cooled to room temperature and 10 g of NaCl was added. An orange-yellow precipitate appeared, which was recrystallized from hot water, having a pH value of 4.5. The orange translucent crystals of $Na_{10}[(UO_2)_2(H_2O)_4Sb_2W_{20}O_{70}]\cdot 28H_2O$ or $Na_{10}[(UO_2)_2(H_2O)_4Bi_2W_{20}O_{70}]\cdot 34H_2O$ respectively, were obtained within a few days from a solution kept at 5 °C. The yield was: 4.15 g (65%) and 4.73 g (71%), respectively.

Methods and instrumentation

We used inductively Coupled Plasma spectroscopy (I.C.P.) for the elemental analysis of uranium, antimonium, bismuth and tungsten and flamephotometry for sodium. The water content was thermogravimetrically determined, by means of a METTLER-TGA/SDTA 851^e device, with a balance sensibility of 1 mg, using a SOFT:STAR^e Software program. The working parameters are as follows: the working mass, m_{sample}=15.1280 mg for $Na_{10}[(UO_2)_2(H_2O)_4Sb_2W_{20}O_{70}]$ compound and m_{sample}=14.8256 mg for $Na_{10}[(UO_2)_2(H_2O)_4Bi_2W_{20}O_{70}]$ compound (temperature range, T=20-800 °C, the heating rate, dT/dt=10 °C, the balance sensibility, S=1 μg).

The FT-IR spectra were recorded with an Equinox 55 Bruker spectrophotometer on KBr pellets, in the 4000–400 cm^{-1} range. Raman spectra were recorded on solid powders, at room temperature, with a DILOR OMARS 89 Raman spectrophotometer. Electronic spectra were obtained in aqueous solutions within a range of λ =200-800 nm using a JASCO 530 spectrophotometer.

The fluorescence emission spectra were obtained using a ABLE& JASCO FP-6500 spectrofluorometer with 150W xenon lamp, solid sample sealed holder, with a PC acquisition system running on Microsoft Windows. The measurements were made by exposing the samples directly in the sealed solid holder, using an excitation degree of 300 nm and 550 nm respectively, at room temperature.

REFERENCES

1. M. T. Pope, A. Müller, "*Polyoxometalates. From Platonic Solids to Anti-Retroviral Activity",* Kluwer Academic Publishers, Dordrecht, The Netherlands, **1994**, pp.1.
2. B.H. Myasoedov, *Sov. Radiochem.,* **1990**, *32,* 361.
3. Gh. Marcu, M. Rusu, A.V. Botar, *Rev. Roum. Chim.,* **1974**, *19*, 827.
4. Gh. Marcu, M. Rusu, *Rev. Roum. Chim.,* **1976**, *21,* 385.
5. Gh. Marcu, M. Rusu, *Rev. Roum. Chim.*, **1977**, *22*, 227.
6. Gh. Marcu, M. Rusu, L. Ochesel, *Rev. Roum. Chim.,* **1977**, *22,* 849.
7. M. Rusu, Gh. Marcu, E. Perte, *Rev. Roum. Chim.,* **1978**, *23*, 1403.
8. M. Rusu, Gh. Marcu, *Rev. Roum. Chim.*, **1979**, *24,* 351.
9. Gh. Marcu, M. Rusu, E. Perțe, *Rev. Roum. Chim.,* **1979**, *24,* 159.
10. Gh. Marcu, A. Botar, M. Rusu, *Rev. Roum. Chim.*, **1979**, *24*, 1465.
11. M. Rusu, A. Curticăpean, A. V. Botar, *Rev. Roum. Chim.*, **1995**, *41*, 687.
12. M. Rusu, D. Rusu, Gh. Marcu, *J. Radioanalyt. Nucl. Chem.,* **1999**, *242*, 119.

13. M. Rusu, D. Rusu, C. Roşu, A.R. Tomşa, Gh. Marcu, *J. Radioanalyt. Nucl. Chem.,* **1999**, *242*, 467.
14. M. Rusu, *J. Radioanalyt. Nucl. Chem.*, **2000**, *245*, 353.
15. M. Rusu, D. Rusu, C. Roşu, C. Crăciun, L. David, A.R.Tomşa, Gh. Marcu, *J. Radioanalyt. Nucl. Chem.,* **2000**, *245/2*, 363.
16. R.D. Peacock, T.J.R. Weakley, *J. Chem. Soc. A.*, **1971**, 1836.
17. K.C. Kim, M. T. Pope, *J. Am. Chem. Soc.,* **1999***, 121,* 8512.
18. K.C. Kim, M. T. Pope, *J. Chem. Soc. Dalton Trans.*, **2001**, 986.
19. C. Rosu, M. Rusu, C. Ciocan, *Rev. Chim. (Bucuresti),* **2002**, *53*, 57.
20. K. C. Kim, A.J. Gaunt, M. T. Pope, *Journal of Cluster Science,* **2002***, 13,* 423.
21. A.J. Gaunt, I. May, R. Copping, I. Bhatt, D. Collison, O.D. Fox, K.T. Holman, M.T. Pope, *J. Chem. Soc. Dalton Trans.*, **2003**, 3009.
22. C. Craciun, D. Rusu, L. Pop-Fanea, M. Hossu, M. Rusu, L. David, *Journal of Radioanal. and Nucl. Chem,* **2005**, *264(3*), 589.
23. R. Khoshnavazi, H. Eshtiagh-hossieni, M.H. Alizadeh, M.T. Pope, *Polyhedron*, **2006**, *25*, 1921.
24. R. Copping, I. May, D. Collison, C.J. Jones, C.A. Sharrad, M.J. Sarsfield, *Royal Society of Chemistry*, **2006**, 305.
25. R. Tan, X. Wang, F. Chai, Y. Ian, Z. Su, *Inorg. Chem. Commun*., **2006**, 1331.
26. R. Khoshnavazi, H. Eshtiagh-hossieni, M.H. Alizadeh, M.T. Pope, *Inorg. Chim. Acta*, **2007**, *360*, 686.
27. M.H. Alizadeh, M. Mohadeszadeh, *Journal of Clust. Sci.,* **2008**, *19(2)*, 435.
28. P. Souchay, M. Leray, G. Hervè, *C. R. Acad. Sci. Ser. C,* **1970**, *271*, 1337.
29. M. Michelon, P. Souchay, R. Massart, G. Hervè, *C. R. Acad. Sci., Ser. C*, **1971**, *273*, 1117.
30. M. Michelon, G. Hervè, *C. R. Acad. Sci., Ser. C,* **1972**, *273*, 209.
31. M. Bösing, I. Loose, H. Pohlmann, B. Krebs, *Chem. Eur. J.*, **1997**, *3*, 1232.
32. I. Loose, E. Droste, M. Bosing, H. Pohlmann, M.H. Dickman, C. Rosu, M.T. Pope, B. Krebs, *Inorg. Chem*., **1999**, *38*, 2688.
33. M. Pospisil, *J. Thermal Analysis*, **1995**, *44*, 133.
34. W. M. Hosny, *Synth. React. Inorg. Met.-Org. Chem.*, **1998**, *28*, 1029.
35. F. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.,* **1983**, *22*, 46.
36. G. M. Varga, E. Papaconstantinou, M.T. Pope, *Inorg. Chem.*, **1970**, *9,* 662.
37. H. So, M.T. Pope, *Inorg. Chem.*, **1972**, *11,* 1441.
38. S. Amayri, T. Arnold, T. Reich, H. Foerstendorf, G. Geipel, G. Bernhard and A. Massanek, *Environ. Sci. Technol.,* **2004**, *38*, 6032.
39. C. Jacopin, M. Sawicki, G. Plancque, D. Doizi, F. Taran, E. Ansoborlo, B. Amekraz C. Moulin, *Inorg. Chem.* **2003**, *42*, 5015.
40. X. Kong, Y. Ren, L. Long, R. Huang, L. Zheng, *Inorg. Chem. Comm.,* **2007**, 894.