

RESEARCH ARTICLE

The UV and IR Comparative Spectrophotometric Study of Some Saturated and Lacunary Polyoxometalates

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Objectives: The polyoxometalates are a class of inorganic compounds with controllable shapes and sizes, and with excellent properties that make them attractive for various applications. This study is aimed at the comparative UV and IR spectra of Keggin type polyoxometalates.

Methods: Compounds under (UV and IR) investigations were divided into several groups to highlight similarities between compounds or classes of compounds for the same category. There are four types of saturated Keggin structures and six lacunar compounds included in this study. The study begins with the UV investigations on aqueous solutions with 10^{-5} M concentration for these compounds. IR spectra were recorded as KBr pressed pellets.

Results: The UV spectras presents large strong peaks between 185–195 nm corresponding to W = Od bonds, between 251–268 nm for W-O-W bridge bonds, depending on heteroatom types (As, Sb). The unsaturated cryptand ligand having Co^{2+} coordinated presents the most intense peak, due to the involvement of oxygen atoms from terminal W = Od coordinative bonds with high electronic densities in coordination of W-O-Co bond. The IR spectra present many peaks that are associated as follows: for terminal bonds W = Od, 955–970 cm^{-1} ; for W-O-W bridging bonds, 790–910 cm^{-1} ; for W-O-As/Sb bonds to heteroatom, 690–760 cm^{-1} . Vibrations of the bonds between heteroatoms and oxygen (As/Sb-O) appear around 620–660 cm^{-1} .

Conclusions: Similarities appear from the recorded spectra, between compounds of the same class, by category association. Very fine displacements of peaks that occur explain the influence of heteroatoms, addenda atoms or coordinated cations.

Keywords: polyoxometalates, spectroscopy, bonds association

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Introduction

The polyoxometalates, as transitional metal-oxygen clusters, are a class of inorganic compounds with controllable shapes and sizes, and with excellent properties that make them attractive for various applications [1,2]. This study follows the comparative UV and IR spectra of Keggin type polyoxometalates. Electronic loads of Keggin type anion are a very important factor influencing the structure of polyoxometalates [3].

The saturated or lacunar Keggin structures contain one tetrahedral coordinated heteroatom XO_4 surrounded by twelve octahedral MO_6 arranged in four groups of three octahedra linked by common edges and vertices of the tetrahedron central (XM_{12}) (X = heteroatom, M = addenda). Oxygen atoms delimit the structure [4]. The MO_6 octahedra take shape because of the hexacoordination of addenda atoms (W, Mo in this case). Assemblies are due to the possibilities of condensation of these elements around the coordination of the polyhedra of heteroatoms (As, Sb in this case) [5,6].

These structures present five isomers α , β , γ , δ , and ϵ obtained by turning each 60° of one, two or three triples

against α -isomer. As a result of chemical reaction, usually alkaline degradation, octahedral removal of one or more of the basic structure of polyoxometalates occurs to give unsaturated mono- or multi-lacunary with special properties (XM_{11} , XM_{10} , XM_9) [5,6].

Sidgwick describes four types of addendum-oxygen connections in polyoxometalate molecules [7] that are responsible for the appearance of peaks:

- O_a – oxygen atoms connecting bridge between the heteroatom X and Addendum M (common both octahedron coordination of the Addendum and heteroatom X polyhedron);
- O_b – oxygen atoms connecting bridge between two metal addenda atoms M located in two different sets of triplets M_3O_{13} ;
- O_c – oxygen atoms connecting bridge between two addenda atoms in the same group M_3O_{13} ;

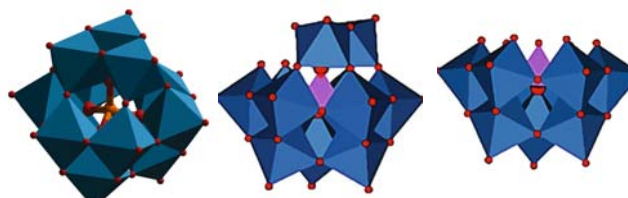


Fig. 1. Keggin structures

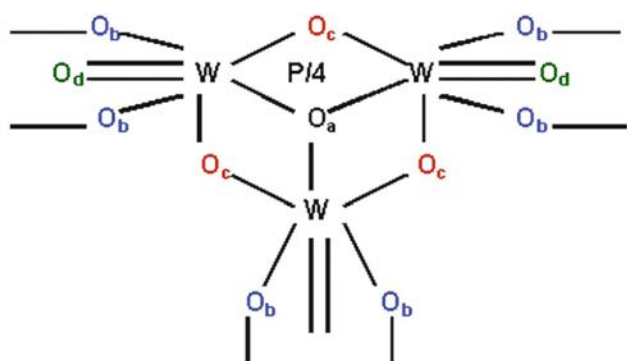


Fig. 2. Types of addendum-oxygen connections in polyoxometalates by Sidgwick [7]

– O_d – terminal oxygen atoms belonging to the MO_6 octahedron.

Materials and methods

Compounds under (UV and IR) investigations were divided into several groups to highlight similarities between compounds or classes of compounds for the same category. Some of the compounds were commercially purchased and used without further purification. Others were prepared according to the published methods [8,9,10,11].

The studied compounds are:

a) Saturated compounds:

- $H_3[P(Mo_{12}O_{40})] \cdot xH_2O$
- $H_3[P(W_{12}O_{40})] \cdot xH_2O$
- $H_4[Si(W_{12}O_{40})] \cdot xH_2O$
- $Na_3[P(W_{12}O_{40})] \cdot xH_2O$

b) Lacunary compounds:

- $K_7[AsW_{11}O_{39}] \cdot xH_2O$
- $Na_8[HASW_9O_{33}] \cdot xH_2O$
- $Na_8[HSbW_9O_{33}] \cdot xH_2O$
- $K_{27}[KAs_4W_{40}O_{140}] \cdot xH_2O$
- $Na_{27}[NaAs_4W_{40}O_{140}] \cdot xH_2O$
- $K_{23}[KAs_4W_{40}O_{140}Co^{(2+)}] \cdot 40H_2O$

UV measurements were made using a UV-VIS spectrophotometer AnalytikJena SPECORD 210 at $\lambda = 190$ – 400 nm in 1 cm quartz cuvettes. The aliquots for the aqueous solutions had concentration of 10^{-5} M.

IR determinations were performed using Thermo Nicolet380 FTIR spectrophotometer and KBr pressed pellets, using a hydraulic press, were made for each compound.

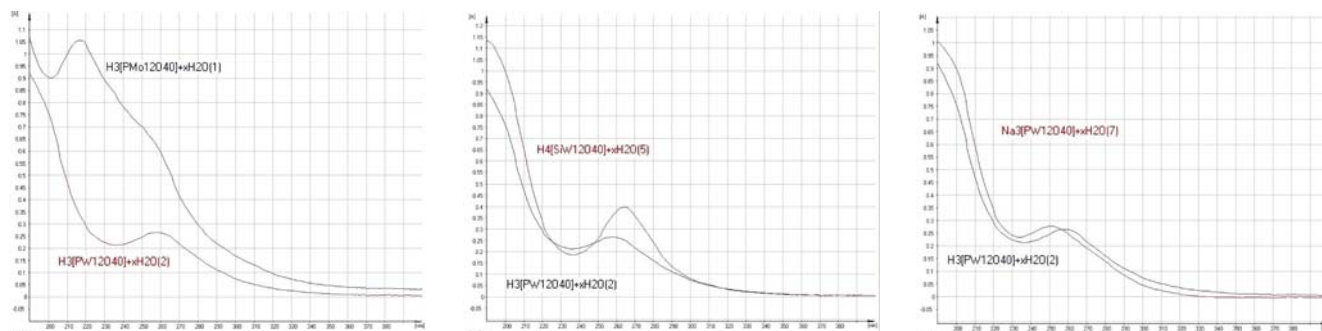


Fig. 3. UV spectra of the saturated compounds

Results

a) UV determinations

The study begins with the UV investigations on saturated compounds marketed: $H_3[P(Mo_{12}O_{40})] \cdot xH_2O$ / $H_3[P(W_{12}O_{40})] \cdot xH_2O$, $H_3[P(W_{12}O_{40})] \cdot xH_2O$ / $H_4[Si(W_{12}O_{40})] \cdot xH_2O$, $H_3[P(W_{12}O_{40})] \cdot xH_2O$ / $Na_3[P(W_{12}O_{40})] \cdot xH_2O$ Figure 3.

Then, the determinations were made for:

- The monolacunary compounds: $K_7[AsW_{11}O_{39}] \cdot xH_2O$ – structure α / β Figure 4.
- The trilacunary compounds: $Na_8[HASW_9O_{33}] \cdot xH_2O$ / $Na_8[HSbW_9O_{33}] \cdot xH_2O$ Figure 5.

For the clusters $K_{27}[KAs_4W_{40}O_{140}] \cdot xH_2O$ / $Na_{27}[NaAs_4W_{40}O_{140}] \cdot xH_2O$, $K_{27}[KAs_4W_{40}O_{140}] \cdot xH_2O$ / $K_{23}[KAs_4W_{40}O_{140}Co^{(2+)}] \cdot 40H_2O$ the UV spectra are shown in Figure 6.

b) IR investigations

The IR investigations were made on the same compounds and they are presented in the same order.

In Figure 7 are presented the IR spectra of the saturated compounds: $H_3[P(Mo_{12}O_{40})] \cdot xH_2O$ / $H_3[P(W_{12}O_{40})] \cdot xH_2O$, $H_3[P(W_{12}O_{40})] \cdot xH_2O$ / $H_4[Si(W_{12}O_{40})] \cdot xH_2O$, $H_3[P(W_{12}O_{40})] \cdot xH_2O$ / $Na_3[P(W_{12}O_{40})] \cdot xH_2O$.

In Figure 8 is presented the spectra of monolacunary $K_7[AsW_{11}O_{39}] \cdot xH_2O$ (structure α / β) compounds.

After that, determinations were made for:

- Trilacunary compounds $Na_8[HASW_9O_{33}] \cdot xH_2O$ / $Na_8[HSbW_9O_{33}] \cdot xH_2O$ in Figure 9
- Clusters in Figure 10, $K_{27}[KAs_4W_{40}O_{140}] \cdot xH_2O$ / $Na_{27}[NaAs_4W_{40}O_{140}] \cdot xH_2O$, $K_{27}[KAs_4W_{40}O_{140}] \cdot xH_2O$ / $K_{23}[KAs_4W_{40}O_{140}Co^{(2+)}] \cdot 40H_2O$.

Discussions

Polyoxometalate class sizes characteristic vibration absorption for M–O bonds appear in the specific frequency range of 190–400 nm for UV radiation and 400–2000 cm^{-1} for IR [12–18].

a) UV determinations

UV spectra show bands associated with terminal $W = O_d$

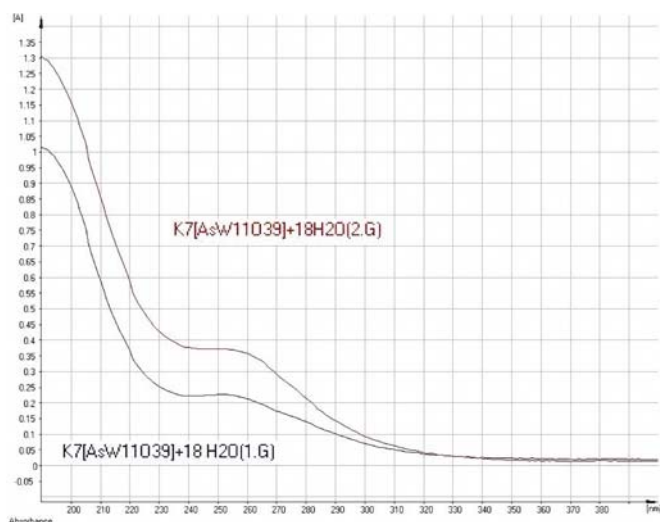


Fig. 4. Mono-lacunary $K_7[AsW_{11}O_{39}] \cdot xH_2O$ (structure α/β) UV spectra

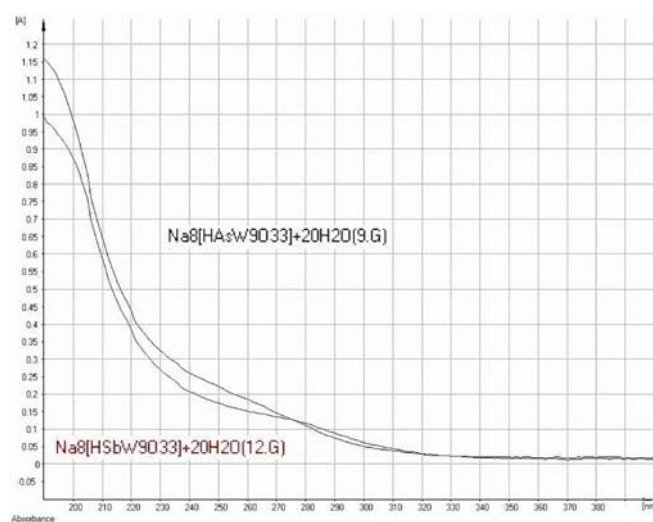


Fig. 5. UV spectra for trilacunary compounds

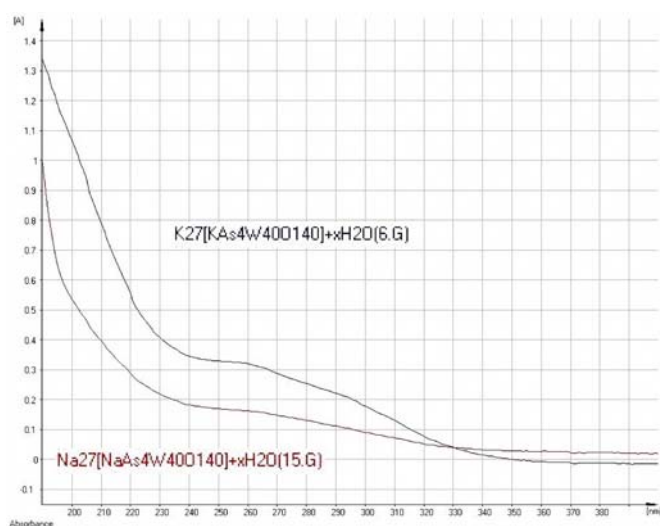
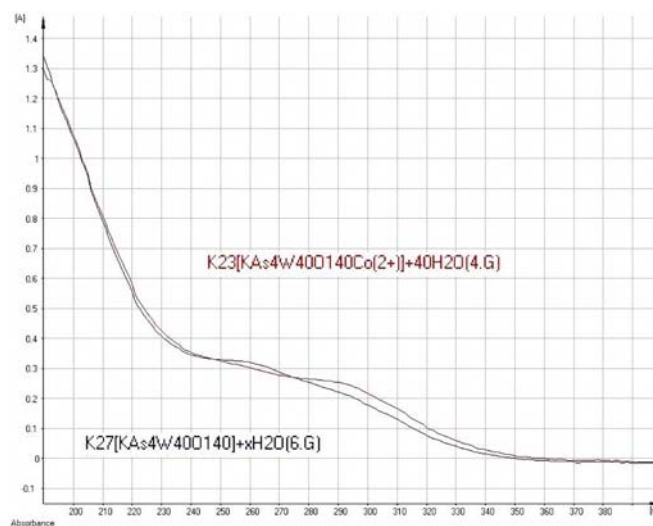


Fig. 6. UV spectra for clusters



links for $\pi p-d$ electronic transitions, and W-O-W characteristic tricentric links with oxygen atom bridged between two addenda atoms. Values in the spectra correspond to those found in the literature [12–14].

According to literature data, in order to link $W = Od$ a peak occurs at 185–195 nm. UV determinations were made in the range 190–400 nm. Only the peak tail corresponding to $W = Od$ appears in the spectrum, but we noticed that the peak was very intense, which corresponds to higher binding energies.

The UV spectra of saturated compounds $H_3[P(Mo_{12}O_{40})] \cdot xH_2O/H_3[P(W_{12}O_{40})] \cdot xH_2O$, $H_3[P(W_{12}O_{40})] \cdot xH_2O/H_4[Si(W_{12}O_{40})] \cdot xH_2O$, $H_3[P(W_{12}O_{40})] \cdot xH_2O/Na_3[P(W_{12}O_{40})] \cdot xH_2O$ (Figure 3) present a second peak that is characteristic for W-O-W bounds. Values are between 255–265 nm. The most intense peak occurs for silicotungstic acid and is weakest for phosphomolybdic acid, which demonstrates the influence that both the heteroatoms and the addendum have on the structure. For sodium phosphotungstate the peak shifts

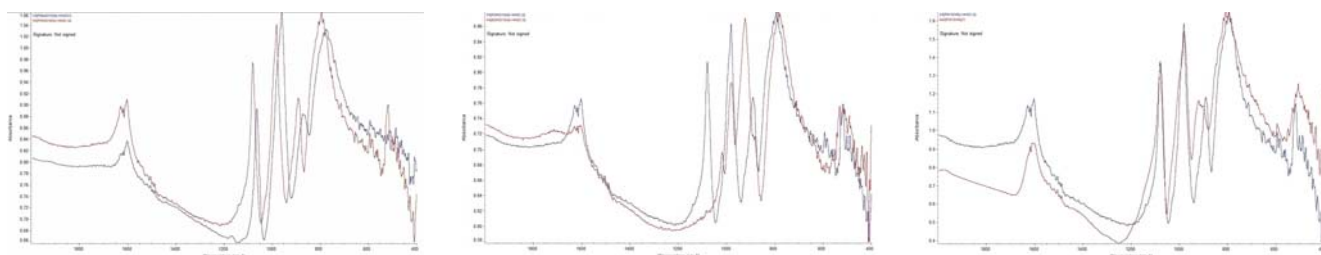


Fig. 7. IR spectra for saturated compounds

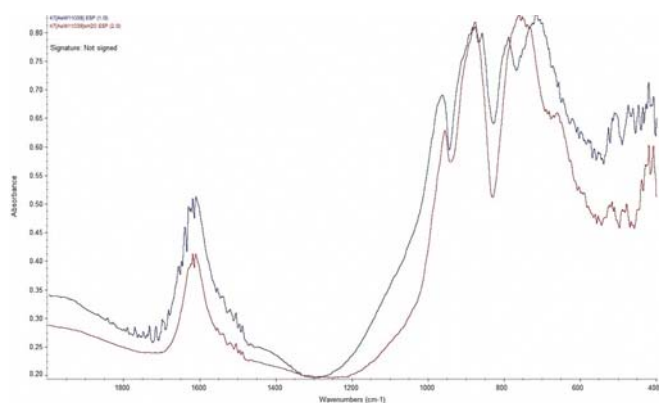


Fig. 8. IR spectra for monolacunary compounds

towards lower values of the wavelength so the structure is stabilizing.

The molar extinction for these compounds are: for $H_3[P(W_{12}O_{40})] \cdot xH_2O$ at the 258 nm, absorbance is 0.2650 and the molar extinction is $0.37 \cdot 10^5$ ($cm^{-1}M^{-1}$); for $H_3[Si(W_{12}O_{40})] \cdot xH_2O$ at the 264 nm, absorbance is 0.3984 and the molar extinction is $0.5 \cdot 10^5$ ($cm^{-1}M^{-1}$); for $Na_3[P(W_{12}O_{40})] \cdot xH_2O$ at the 251 nm, absorbance is 0.2774 and the molar extinction is $0.34 \cdot 10^5$ ($cm^{-1}M^{-1}$).

The spectra of monolacunary compounds (Figure 4) do not show much difference between the two α and β forms of the $K_7[AsW_{11}O_{39}] \cdot xH_2O$ compound: one shows a maximum at 251 nm and the other at 252 nm.

Trilacunary compounds are both sodium salts: $Na_8[HASbW_9O_{33}] \cdot xH_2O$ / $Na_8[HSbW_9O_{33}] \cdot xH_2O$ and their spectra are presented in Figure 5. Compounds have the same W addenda and different heteroatoms As/Sb. For Sb compound, the peak appears at 268 nm and is more intense than the one for As compound (255 nm).

The molar extinction for these compounds are: for $Na_8[HASbW_9O_{33}] \cdot xH_2O$ at the 255 nm, absorbance is 0.2010 and the molar extinction is $0.25 \cdot 10^5$ ($cm^{-1}M^{-1}$); for $Na_8[HSbW_9O_{33}] \cdot xH_2O$ at the 268 nm, absorbance is 0.1376 and the molar extinction is $0.18 \cdot 10^5$ ($cm^{-1}M^{-1}$).

The Clusters spectra are presented in Figure 6. For the K salt of the arsenotungstate cluster the peak occurs at 261 nm and for the Na salt at 253 nm. This difference is due to the influence of various internal cations (Na, K).

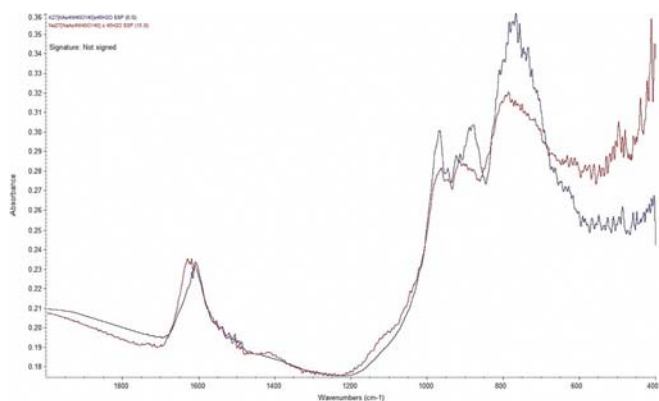


Fig. 10. IR spectra for clusters

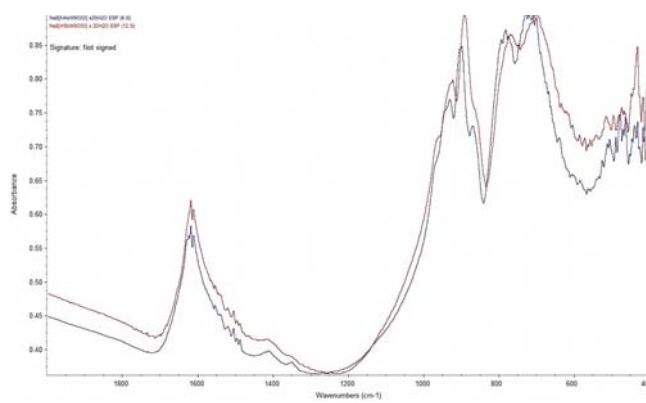


Fig. 9. IR spectra for trilacunary compounds

The molar extinction for these compounds are: for $K_{27}[KAs_4W_{40}O_{140}] \cdot xH_2O$ at the 253 nm, absorbance is 0.3269 and the molar extinction is $1.93 \cdot 10^5$ ($cm^{-1}M^{-1}$); for $Na_{27}[NaAs_4W_{40}O_{140}] \cdot xH_2O$ at the 261 nm, absorbance is 0.1609 and the molar extinction is $1.05 \cdot 10^5$ ($cm^{-1}M^{-1}$); for $K_{23}[KAs_4W_{40}O_{140}Co^{(2+)}] \cdot 40H_2O$ at the 281 nm, absorbance is 0.2639 and the molar extinction is $1.09 \cdot 10^5$ ($cm^{-1}M^{-1}$).

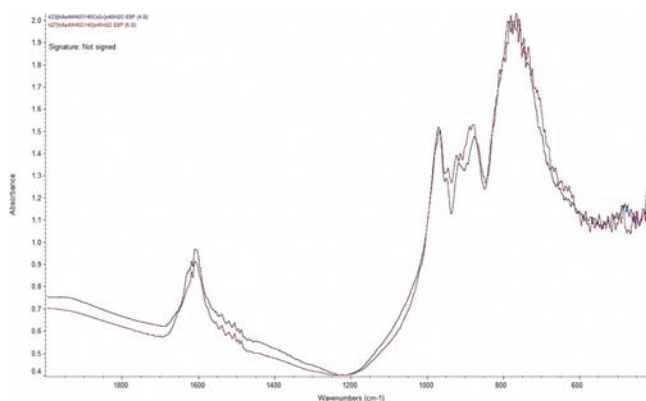
b) IR determinations

By absorption of energy quanta by simple or complex molecule and function of the energy absorbed, several types of molecular energy transitions at higher levels can occur. Information obtained by electronic spectra relates to the electronic structure, the nature of chemical bonds. Values in the spectra correspond to those found in the literature [13–18].

IR spectra study begins with saturated compounds marketed.

In all spectra a peak shows around 1600 cm^{-1} which is due to water molecules.

The saturated compounds spectra are presented in Figure 7. In compounds having the tungsten addenda atoms, a peak appears at 981 cm^{-1} corresponding $W = Od$ bond. In Mo compound, the peak corresponding to this connection is at 960 cm^{-1} . $W-O-W$ bridge bonds appear on a wider range, $785\text{--}923\text{ cm}^{-1}$, because there are several types of such bonds (Sidwick). $Si-O$ bonds appear at 712 cm^{-1} .



P-O bond appears at 1064 cm^{-1} in the molybdate complex and at 1080 cm^{-1} in the tungstate complex, this difference is due to the influence of established connections by octahedron coordination of W/Mo addenda. A slight peak shift appears in the third spectrum due to the sodium cation.

Between the two spectra (Figure 8) of the two isomers α and β of the monolacunary compound $\text{K}_7[\text{AsW}_{11}\text{O}_{39}]\cdot x\text{H}_2\text{O}$ very small differences appear, for peaks characterizing W = Od and W-O-W bonds. A significant difference appears at the As-O bond. While the peak occurs around the same values, the intensity is different.

In spectra of trilacunary compounds $\text{Na}_8[\text{HAsW}_9\text{O}_{33}]\cdot x\text{H}_2\text{O}/\text{Na}_8[\text{HSbW}_9\text{O}_{33}]\cdot x\text{H}_2\text{O}$ (Figure 9), the peaks characterizing the W = Od bonds appear at 931 cm^{-1} for As compound and 923.8 cm^{-1} for Sb compound. For W-O-W bonds: 782.7 to 900.3 cm^{-1} for As compound, from 770.8 to 892.6 cm^{-1} for Sb compound. For As-O bond the peak is at 729.1 cm^{-1} , while for Sb-O it is at 701.7 cm^{-1} . Smaller values of Sb compound show that the energy ties of this compound are smaller.

For the two clusters (Figure 10) one with Na and the other with K, characteristic peaks for W = Od bond occur at 963.7 cm^{-1} for Na compound and 968.2 cm^{-1} for K compound. For the K cluster compound the W-O-W bond peaks are intense. For Co^{2+} coordinated cluster peaks are well defined; 970.7 cm^{-1} peak is due to the newly formed W-O-Co bond from W = Od. These changes show that clusters are stabilized by coordination.

Conclusions

Similarities appear from the recorded UV and IR spectra, between compounds of the same class, by category association. Very fine displacements of peaks that occur explain the influence of heteroatoms, addenda atoms or coordinated cations.

Small displacements of the bands to higher energies, to higher frequencies, are due to the polioxometalate building flexibility, flexibility that allows cation coordination.

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