Hydrothermal Synthesis and Comparative Study of Two Silicium Monolacunar Polyoxometalates Zn Complexes

K₇[Zn(SiM₁₀VO₃₉)(H₂O)] . nH₂O; (M=Mo,W)

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Two new monolacunar polyoxometalates Zn complex: K₇[Zn(SiM₁₀VO₃₉)(H₂O)] . nH₂O; (M=Mo,W) were obtained by hydrothermal synthesis. The combination rate between ZnCl₂ and heteropolyoxometalate ligand [SiM₁₀VO₃₉]⁻⁹ and the optimal conditions for synthesis were determined by spectrophotometric and conductometric methods. Elemental analyses, TG/DTA, IR, UV-VIS spectroscopy and X-ray diffraction methods were carried out. The IR and UV spectrophotometric methods reveal the preservation of the Keggin framework in the new monolacunar heteropolyoxometalate complexes. The thermo gravimetric and thermo differential curves confirmed that those two compounds are Keggin type. X-ray diffraction method shows that the monolacunar Keggin structure is isomorphic with other monolacunar Keggin heteropolyoxanions containing P as central atom and reveals an orthorhombic structure.

Keywords: monolacunar Keggin triheteropolyacids, thermal behaviour, IR, UV-VIS spectroscopy, crystal structure

Polyoxometalates (POM) are a broad class of complexes which weak up an impressing interest from both theoretical and practical point of view[1-5]. Keggin type polyoxometalates with mixed addendum and their related lacunary compounds form a very interesting family. Lacunary oxoanions are generally good ligands for transition metals. During the last years, the related lacunary compounds form a very interesting family. Lacunary oxoanions are generally good ligands for transition metals. Transition metals. During the last years, the heteropolyoxometalates of the transition metals have received much attention being applied in medicine, catalyses, and material science.

Several monolacunar anions with general formula, [XM₉O₃₉]⁻⁹ may bind to a metal cation M as a pentadentate ligand and may form complexes by the type [(XM₉O₃₉)ML], where L is other monodentate ligand. The metallic cation takes the place of the MO group lost of the Keggin framework in the synthesis process of the monolacunar structure [6, 7].

As an expansion of the study on the POM chemistry, we attempted to explore the assembly of [SiM₁₀VO₃₉]⁻⁹, (M=Mo,W) in the presence of transition metal Zn under hydrothermal condition.

Here we report the hydrothermal synthesis, the thermal behaviour and crystal structure and properties of the two new Zn complex with [SiM₁₀VO₃₉(H₂O)]⁻⁹, (M=Mo,W) monolacunar polyoxometallate ligand.

Experimental part
Reagents
All reagents used were of analytical reagent grade (E. Merck) and the solutions were prepared with double distilled water. An acetic acid-sodium acetate buffer (pH= 4.5-5) was used for the conductometric studies.

Apparatus
The metallic ions (K, W, V) were determined using an atomic emission spectrometer Baird Spectrovac 2000.

The thermo gravimetric curves were register using a derivatograph OD-103 MOM. (Budapest), capacity: 200 ± 1-2 mg, sensitivity; 50 mg, temperature range: 10°C/min, reference material: Al₂O₃, atmosphere: air.

The combination rate among Zn²⁺ and heteropolyanion, [SiM₁₀VO₃₉]⁻⁹, (M=Mo,W), were determined using the conductometric method with a multimter Inolab Multi 720, in acetic buffer solution. The Inolab Multi 720 multimeter was use also for the pH and temperature monitoring connected with a thermostatic magnetic stirrer with temperature sensor.

An UV-VIS spectrometer Perkin Elmer Lambda was used to establish the best Zn complex formation conditions and to investigate the structure of the formed complex. The structure of the complex was investigated also in IR with an FTIR-JASCO 610 spectrometer, in KBr pellets.

The X-ray diffraction study was performed on crystalline powder using a PW 1050 Philips diffractometer, copper monochromatic radiation and Ni filter for the Kα emission.

The density measurement was performed using acetone liquid and picnometric method.

Results and discussions
Synthesis of K₇[SiW₁₀VO₃₉]·x H₂O
The monolacunar anion, [SiW₁₀VO₃₉]⁻⁹ was prepared in aqueous medium from Na₂SiO₃, NaVO₃· 2H₂O and Na₂WO₄· 2H₂O mixed in stoechiometric rate, with method according with literature by adapting reactions condition at: boiling temperature, pH=6,5 for 1 hour [8-11]. The heteropolyanion [SiW₁₀VO₃₉]⁻⁹ was separated from solution after precipitation with KCl salt in excess. The crystallisation process was made on an ice and ammonium chloride mixture (-4°C). The synthesis yield value was 65%.

Synthesis of K₇[SiMo₁₀VO₃₉]·y H₂O
A stoechiometric mixture between Na₂SiO₃, NaVO₃· 2H₂O and Na₂MoO₄· 2H₂O was kept at room temperature and pH = 5.5, under agitation, for 30 min. KCl salt was added in small quantities until the monolacunar anion started to precipitate. The crystallisation was realized on the ice bathroom, frozen with ammonium chloride(-4°C). The synthesis yield value was 40%.
Synthesis of $\text{K}_7\left[\text{Zn(SiW}_{10}\text{V}_{39})(\text{H}_2\text{O})\right]\cdot 16\text{H}_2\text{O}$

2 mL (4 mmol) solution 2M ZnCl$_2$ was added in drops under vigorously stirring to a equal quantity solution (4 mmol) $\text{K}_9\left[\text{SiW}_{10}\text{V}_{39}\right]\cdot n\text{H}_2\text{O}$ at room temperature. A 5% KHCO$_3$ solution and 5% HCl solution were used to maintain the $p\text{H}$ around 6. After addition of ZnCl$_2$, the reaction mixture was keep at boiling point for 15 min. The hot solution was filtered. It was added KCl salt in the filtrate. The precipitate solution was cooled to 5°C overnight. This was further purified by recrystallization from distilled water. The yield was 58%. In table 1 is presented $\text{K}_7\left[\text{Zn(SiW}_{10}\text{V}_{39})(\text{H}_2\text{O})\right]\cdot 16\text{H}_2\text{O}$ elementary analysis.

Synthesis of $\text{K}_7\left[\text{Zn(SiMo}_{10}\text{V}_{39})(\text{H}_2\text{O})\right]\cdot 11\text{H}_2\text{O}$

(4 mmol) $\text{K}_9\left[\text{SiMo}_{10}\text{V}_{39}\right]\cdot n\text{H}_2\text{O}$ solution was dissolved completely in water at room temperature. 2 M solution was added to arrive to $p\text{H} = 4.3$. 2 mL (4 mmol) solution 2M ZnCl$_2$ was added carefully in drops, under vigorously stirring, keeping $p\text{H} = 4.3$ with the help of 5% KHCO$_3$ and 5% HCl solutions. The mixture was kept to react for 30 min at room temperature and after was added KCl salt. The polyanion complex was started to precipitate and the reaction mixture was placed in a ice bath for a half of hour. The precipitate solution was cooled to 5°C overnight. This was further purified by recrystallization from distilled water. The yield was 58%. In table 1 is presented $\text{K}_7\left[\text{Zn(SiMo}_{10}\text{V}_{39})(\text{H}_2\text{O})\right]\cdot 11\text{H}_2\text{O}$ elementary analysis. Elemental analysis was done using a Baird I.C.P. 2070 optical emission spectrometer. The water content was determined on the basis of thermal analysis (DTG, TG, DTA) (table 2).

The stoichiometry of the two complexes synthesis reactions were determined by conductometric titration. The conductivity variation of the reactive solutions, ZnCl$_2$ and $\text{K}_9\left[\text{SiMo}_{10}\text{V}_{39}\right]\cdot n\text{H}_2\text{O}$; (M=Mo,W), (5 . 10$^{-3}$ M), in different molar ratios between 0,2:1 and 3:1 was recorded. The samples were prepared into acetate buffer solutions at $p\text{H}=4.5$ for M = Mo (VI) and at $p\text{H} = 6.0$ for M = W (VI).

The conductometric curve presents an inflexion point corresponding to a molar ratio between the reactants by 1:1, which show the obtaining of the anion complex.

The spectrophotometric registration was due on the aqueous solutions of the obtained Keggin monolacunar Zn complex in different conditions by changing successively one of the reaction parameters: $p\text{H}$, temperature and time. The concentrations for both reactive solutions (ZnCl$_2$ and $\text{K}_9\left[\text{SiMo}_{10}\text{V}_{39}\right]\cdot n\text{H}_2\text{O}$; (M=Mo,W)) were 5 . 10$^{-4}$ M, and the $p\text{H}$ values were adjusted with 5% KOH or 5% HCl. The final volume of the samples was 25 mL.

The variation of the absorbance values in the complexes formation study were measured at 400 nm. The maximum value of the absorbance for tungsten complex (compound 2.) were obtained at $p\text{H}=6.0$ at the boiling point for 15 min and for molybdenum complex (compound T.) were obtained the optimal reaction conditions at $p\text{H} = 4.3$, at room temperature, for 30 min.

Thermal Analyses of $\text{K}_7\left[\text{Zn(SiW}_{10}\text{V}_{39})(\text{H}_2\text{O})\right]\cdot n\text{H}_2\text{O}$; (M=Mo,W)

The thermal analyses of $\text{K}_7\left[\text{Zn(SiW}_{10}\text{V}_{39})(\text{H}_2\text{O})\right]\cdot n\text{H}_2\text{O}$; (M=Mo,W) indicate that the mass decrease occurs in the 20-800°C temperature range as a result of the dehydration process and their thermal stability.

The study of the polyoxometalate complex thermal behaviour depicts three main processes, two endothermic and one exothermic (table 2). On the thermo differential curve (DTA) the first endothermic effect corresponding to $\approx 120^\circ\text{C}$, was assigned to the loss of the crystallisation water (also named lattice water). This determines an increase of the lattice cohesion by the formation of hydrogen bonds, both with the constitution water and with the terminal oxygen atoms, confirmed by the $t_{\text{max}}$ value of the reaction, which decreases at $t_2<t_1$, in agreement with the increase of the number of the crystallisation water molecules[12-14].

The second process at $\approx 300^\circ\text{C}$ is exothermic and involves the loss of the constitution water (also named structure water). This loss significantly influences the geometry of the molecule, leading to a new structural rearrangement of the polyanionic complex for the compounds 1 and 2.

The endothermic reactions from 480, 600 and 715°C corresponding to the crystalline phase transformation of the oxides: at 480°C WO$_3$ changes its geometry from tetragonal to rhombic, at 600°C one can observe the melting of V$_2$O$_5$ and in the 715-720°C temperature range, the tetragonal MoO$_3$ and WO$_3$ becomes rhomic[15-19].

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<table>
<thead>
<tr>
<th>Compound / appearance</th>
<th>Analysis %</th>
</tr>
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<tbody>
<tr>
<td>$\text{K}<em>7\left[\text{Zn(SiW}</em>{10}\text{V}_{39})(\text{H}_2\text{O})\right]\cdot 11\text{H}_2\text{O}$ (Compound 1)</td>
<td>37</td>
</tr>
<tr>
<td>Red-orange square prism</td>
<td>Mo</td>
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<tr>
<td></td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>Si</td>
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<tr>
<td></td>
<td>Zn</td>
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<td>K</td>
</tr>
<tr>
<td></td>
<td>H$_2$O crystallization</td>
</tr>
<tr>
<td></td>
<td>H$_2$O solution</td>
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<tr>
<td>$\text{K}<em>7\left[\text{Zn(SiMo}</em>{10}\text{V}_{39})(\text{H}_2\text{O})\right]\cdot 16\text{H}_2\text{O}$ (Compound 2)</td>
<td>58</td>
</tr>
<tr>
<td>Brick-red octaedra</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>Si</td>
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<tr>
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<td>H$_2$O crystallization</td>
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IR Spectra
The IR spectra of the Keggin complexes are looking alike with the corresponding ligands, suggesting the same framework. It was registered a slight shift of the absorption bands towards higher energies, demonstrating that the Keggin monolacunary, K₉[SiM₁₀VO₃₉] . nH₂O, was stabilized by coordination with zinc.

The asymmetric stretching vibration of the Si-O present in polyanion ligand around 1000 cm⁻¹ has been shifted to higher frequencies (1050 cm⁻¹), in zinc polyanionic complex. This is consistent with an increase in anion cohesion at attached zinc atom at heteropolyanion framework in the vacant position [20].

The heteropolyanion complex, K₇[Zn(SiMo₁₀VO₃₉)(H₂O)] . 11H₂O, has more vibration corresponding to the addendum-oxygen bonds in 1000-700 cm⁻¹ range, which are modified higher frequencies compared with the ligand (table 3).

UV Spectra
The UV electronic spectra and the maximum absorbance values are presented below in table 4.

With respect to the polyoxometalate complex, the shift in the higher energy band, due to the dx-px proper transitions from the addendum atom to the terminal oxygen atom (M-O bonds) was insignificant when compared to that of the polyanion ligand. This may be related the involvement of only one terminal oxygen atom in coordination of zinc cation. The lower energy band due to the dπ-pπ-dπ electronic transitions from the M-O-M bonds displayed significant shift towards lower energy when compared with the ligand band, suggesting involvement of the oxygen atoms of these bonds in the coordination of the zinc cation [20,21].

The picnometric density measurement was performed using acetone as liquid and had a ± 0.05 g/cm³ precision. The experimental density value is 3.68 g/cm³ for compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>V-O (M=W, Mo)</th>
<th>M-O-M (M=W, Mo)</th>
<th>M-O (M=W, Mo)</th>
<th>Si-O (M=W, Mo)</th>
<th>H₂O (M=W, Mo)</th>
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<tbody>
<tr>
<td>1</td>
<td>530 cm⁻¹</td>
<td>800 cm⁻¹</td>
<td>950 cm⁻¹</td>
<td>1000 cm⁻¹</td>
<td>1680 cm⁻¹</td>
</tr>
<tr>
<td>2</td>
<td>525 cm⁻¹</td>
<td>810 cm⁻¹</td>
<td>952 cm⁻¹</td>
<td>998 cm⁻¹</td>
<td>1670 cm⁻¹</td>
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</table>

The vibrations at 1480 and 1680 cm⁻¹ were assigned at hydration water.

UV Spectra
The UV electronic spectra and the maximum absorbance values are presented below in table 4.

With respect to the polyoxometalate complex, the shift in the higher energy band, due to the dx-px proper transitions from the addendum atom to the terminal oxygen atom (M-O bonds) was insignificant when compared to that of the polyanion ligand. This may be related the involvement of only one terminal oxygen atom in coordination of zinc cation. The lower energy band due to the dπ-pπ-dπ electronic transitions from the M-O-M bonds displayed significant shift towards lower energy when compared with the ligand band, suggesting involvement of the oxygen atoms of these bonds in the coordination of the zinc cation [20,21].
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<td>K₃H₄ZnO₇SiVV₁₀</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>3186.7146</td>
</tr>
<tr>
<td>Crystal symmetry</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cm</td>
<td>Cm</td>
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<tr>
<td>a/Å</td>
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<td>14.982</td>
</tr>
<tr>
<td>b/Å</td>
<td>24.210</td>
<td>23.756</td>
</tr>
<tr>
<td>c/Å</td>
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<td>12.684</td>
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<td>β°</td>
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</tr>
<tr>
<td>v/Å³</td>
<td>4011.432</td>
<td>4000.520</td>
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<td>D/g/cm³</td>
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<td>3.758</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5

K₇[Zn(SiM₁₀VO₃₉)(H₂O)].nH₂O; (M=Mo,W) CRYSTAL DATA

1 and respectively 3.75 for compound 2. The number of SiM₁₀V groups (M=Mo,W) from elementary cell is Z = 4.

X-ray diffraction method

The anions reticular values (table 5) confirm the monolacunar Keggin heteropolyanions and reveal a monoclinic structure [21,22].

Conclusions

Polioxometalates anions [SiM₁₀VO₃₉]⁻⁹, (M=Mo,W) hydrothermal syntheses were based on literature data [8-10] by adapting reactions condition at: room temperature, pH=5.5, 30 min for K₃[SiMo₁₀VO₃₉]·x H₂O and boiling temperature, pH=6.5, 1 hour for K₃[SiW₁₀VO₃₉]·x H₂O [8-11]. To establish the synthesis product the crystallisation process was made on the ice bathroom frozen with ammonium chloride (-4°C). The synthesis yield value was 65% for K₃[SiW₁₀VO₃₉]·x H₂O respectively 40% for K₃[SiMo₁₀VO₃₉]·x H₂O.

The two polyoxygenates Zn complexes K₇[Zn(SiM₁₀VO₃₉)(H₂O)].11H₂O, (n=11 for M=Mo, and n=16 for M=W) synthesis conditions were establish using conduct metric method and visible spectrophotometric method (reagents rate 1:1, room temperature, pH=4.3 for 30 min for Mo polioxometalate and boiling temperature, pH=6 for 15 min for W polioxometalate). The crystallization process was at 5°C overnight. The synthesis yield value was 37% for Mo polioxometalate respectively 58% for W polioxometalate.

K₇[Zn(SiM₁₀VO₃₉)(H₂O)].nH₂O (n=11 for M=Mo, and n=16 for M=W) characterization were done using: elementary analysis, UV-IR-spectra and thermogravimetric treatment. The IR and UV spectrophotometric methods and thermo differential curves confirmed that those two compounds are Keggin type [8-10].

X-ray diffraction method reveal, for both studied Zn polioxometalates complexes, a monolacunar Keggin structure, monoclinic, isomorphic with other monolacunar Keggin heteropolyanions containing Si [21,22].

References

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