BABEŞ-BOLYAI UNIVERSITY CLUJ-NAPOCA
Faculty of Chemistry and Chemical Engineering

NEW POLYOXOMETALATES KEGGIN-TYPE WITH MIXED ADDENDA ATOMS

PhD Thesis Summary

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CONTENT

Introduction……………………………………………………………………………..……....1
I. Literature review..……………………………………….……………………….……..3
I.1. Short history……………………………………..…………………………….……....3
I.2. General characterization of polyoxometalates……………………………...………3
I.3. Nomenclature of polyoxometalates ...……………………………………….....………4
I.4. Synthesis methods of polyoxometalates..………………………………….…………5
I.4.1. Synthesis in aqueous medium ..……………………………………….……..........5
I.4.1. Synthesis in nonaqueous medium..………………………………………………8
I.5. General properties of polyoxometalates…... ……………….....……………….……....9
I.6. Classification of polyoxometalates..……………...……………………………….....10
I.7. Keggin type polyoxometalates..……………………………….……………….......13
I.7.1. Keggin polyoxometalates with complete structure ………………...………………..13
I.7.2. Keggin polyoxometalates with lacunary structure ………………...………………..18
I.7.3. Keggin polyoxometalates as ligand………….........…………………………………20
I.8. *Keggin polyoxometalates with mixed addenda*…...……………..………………..……26
I.9. Applications of Keggin polyoxometalates ……………………………..……….......28
II. Experimental Detailes.....…………………………………………………………...31
II.1. General…..……………………………..……………………………………31
II.2. Equipment and reagents ……………………………………...……………….....32
II.3. Synthesis of polyoxoanions ligands ……………………….........………………33
II.3.1. Synthesis of monolacunary polyoxoanions $K_8[PVMo_{10}O_{39}]\cdot16H_2O$ (**L_1**)……..…..….33
II.3.2. Synthesis of monolacunary polyoxoanions $K_8[PVW_{10}O_{39}]\cdot15H_2O$ (**L_2**)……………..34
II.3.3. Synthesis of monolacunary polyoxoanions $K_8[AsVW_{10}O_{39}]\cdot16H_2O$ (**L_3**)……………..35
II.3.4. Synthesis of monolacunary polyoxoanions $K_9[SiVW_{10}O_{39}]\cdot13H_2O$ (**L_4**)………………35
II.3.5. *Synthesis of monolacunary polyoxoanions* $K_9[SiVMo_{10}O_{39}]\cdot18H_2O$ (**L_5**)....................36
II.4. Synthesis study of polyoxoanions complexes……………….………..……...…37
II.4.1. Determination of the stability range of monolacunary polyoxoanions ……………….37
II.4.2. Determination of the stoichiometry for the synthesis of poloyxoanions complexes ..…………………………………………………………………………………….……..40
II.4.3. *Determination of optimal reaction conditions for the synthesis of poloyxoanions complexes* ……………………………………………………………………………..….43
II.5. Synthesis of polyoxometalate complexes...………………………..……………51

II.5.1. Synthesis of the polyoxoanion complex $K_6[MnPVMo_{10}O_{39}(H_2O)]\cdot 10H_2O$ (**1**)……....51
II.5.2. Synthesis of the polyoxoanion complex $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot 8H_2O$ (**2**)……..…..51
II.5.3. Synthesis of the polyoxoanion complex $K_6[CoPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$ (**3**)………..52
II.5.4. Synthesis of the polyoxoanion complex $K_6[NiPVMo_{10}O_{39}(H_2O)]\cdot 21H_2O$ (**4**)…..……52
II.5.5. Synthesis of the polyoxoanion complex $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$ (**5**)………...53
II.5.6. Synthesis of the polyoxoanion complex $K_6[MnPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$ (**6**)……..…54
II.5.7. Synthesis of the polyoxoanion complex $K_5[FePVW_{10}O_{39}(H_2O)]\cdot 11H_2O$ (**7**)…….…….54
II.5.8. Synthesis of the polyoxoanion complex $K_6[CoPVW_{10}O_{39}(H_2O)]\cdot 21H_2O$ (**8**)……..…..55
II.5.9. Synthesis of the polyoxoanion complex $K_6[NiPVW_{10}O_{39}(H_2O)]\cdot 19H_2O$ (**9**)…………....55
II.5.10. Synthesis of the polyoxoanion complex $K_6[CuPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$ (**10**)…..…...56
II.5.11. Synthesis of the polyoxoanion complex $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$ ($\mathbf{ZnL_3}$)…...56
II.5.12. Synthesis of the polyoxoanion complex $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$ ($\mathbf{ZnL_4}$)…....57
II.5.13. Synthesis of the polyoxoanion complex $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$ ($\mathbf{ZnL_5}$)…..57
III. Results and Discussions ……………………………………………..……………58
III.1. Chemical analyses of synthesized Keggin polyoxometalates..……………...……....58
III.2. Thermogravimetric analysis of synthesized Keggin polyoxometalates...…………....63
III.2.1. Thermogravimetric analysis of polyoxometalates $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVMo_{10}O_{39}]\cdot xH_2O$ ($M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$)………………………63
III.2.2. Thermogravimetric analysis of polyoxometalates $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVW_{10}O_{39}]\cdot xH_2O$ ($M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$)…………………………67
III.2.3. Thermogravimetric analysis of polyoxometalates $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$, $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$ *and* $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$ ……………………70
III.3. FT-IR vibrational spectra analysis of synthesized Keggin polyoxometalates 71
III.3.1. FT-IR vibrational spectra analysis of polyoxometalates $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVMo_{10}O_{39}]\cdot xH_2O$ ($M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$)……………………..71
III.3.2. FT-IR vibrational spectra analysis of polyoxometalates $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVW_{10}O_{39}]\cdot xH_2O$ ($M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$)……………..……..……73
III.3.3. FT-IR vibrational spectra analysis of polyoxometalates $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$, $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$ *and* $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$……………………………………………………77
III.4. Raman spectral analysis of synthesized Keggin polyoxometalates ………………….78
III.4.1. Raman spectral analysis of polyoxometalates $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$ *and* $K_{8n}[M^{n+}(H_2O)PVMo_{10}O_{39}]\cdot xH_2O$ ($M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$)…………………….…79

III.4.2. Raman spectral analysis of polyoxometalates $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVW_{10}O_{39}]\cdot xH_2O$ *(M =* Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}*)*…………………………80

III.5. UV absorption spectra analysis of synthesized Keggin polyoxometalates ………….81

III.5.1. UV absorption spectra analysis of polyoxometalates $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVMo_{10}O_{39}]\cdot xH_2O$ *(M =* Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}*)*…………………………..81

III.5.2. UV absorption spectra analysis of polyoxometalates $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVW_{10}O_{39}]\cdot xH_2O$ *(M =* Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}*)*…………………………83

III.5.3. UV absorption spectra analysis of polyoxometalates $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$, $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$ *and* $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$……………………..…..85

III.6. Visible electronic absorption spectra of synthesized Keggin polyoxometalates ……..86

III.7. EPR spectroscopy analysis of Keggin polyoxometalates $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot 8H_2O$ and $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$…………..…………..90

III.8. X-ray diffraction analysis of synthesized Keggin polyoxometalates …………….92

III.8.1. X-ray diffraction analysis of polyoxometalates $K_6[NiPVMo_{10}O_{39}]\cdot xH_2O$ *and* $K_6[CuPVMo_{10}O_{39}]\cdot 17H_2O$………………………………………………………...93

III.8.2. X-ray diffraction analysis of polyoxometalates $K_8[PVW_{10}O_{39}]\cdot 15H_2O$, $K_6[MnPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$, $K_6[NiPVW_{10}O_{39}(H_2O)]\cdot 19H_2O$..95

III.8.3. X -ray diffraction analysis of polyoxometalates $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$, $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$ *and* $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$………………………97

III.9. Cyclic voltammetry analysis of Keggin polyoxometalates $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot 8H_2O$ and $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$……………………...98

IV. Using of polyoxometalates in *Triticale* seeds germination ………………………....103

IV.1. Preparation of samples for the study of *Triticale* seeds germination ………..……..104

IV.2. Statistical processing of results obtained from the study of *Triticale* seeds germination ...……………………………………………………………………………..…106

IV.2.1. Yield determination of Triticale seeds germination …………………………..……108

IV.2.2.Statistical processing of results from the use of polyoxometalates $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVMo_{10}O_{39}]\cdot xH_2O$ *(M =* Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}*) for Triticale seeds germination* ……………………...……………………….……109

IV.2.3. Statistical processing of results from the use of polyoxometalates $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ *and* $K_{8-n}[M^{n+}(H_2O)PVW_{10}O_{39}]\cdot xH_2O$ *(M =* Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}*) (M =* Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}*) for Triticale seeds germination* ………………..122

Conclusions……………………………………………………………...……….136

References.……………………………………………………...…………....…….142

Appendix 1………………………………………………………………………...155
Appendix 2………………………………………………………………………...156
Appendix 3………………………………………………………………………...157
Appendix 4………………………………………………………………………...158
Appendix 5………………………………………………………………………...159
Appendix 6………………………………………………………………………...160
Appendix 7………………………………………………………………………...161
Appendix 8…………………………………………………………………………162
Appendix 9………………………………………………………………………...163
Appendix 10……………………………………………………………………….164
Appendix 11……………………………………………………………………….165
Appendix 12……………………………………………………………………….166

Key words: polyoxometalates, mixed addenda, Keggin, spectral methods, *Triticale*

INTRODUCTION

Polioxometalates are inorganic compounds resulting from the polycondensation reactions between oxoanions of transition metals (molybdenum, tungsten, vanadium, niobium and tantalum) around of someone metal or nonmetal oxoanion.

In this thesis we focused on Keggin-type polyoxometalate of the formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$. Keggin polyoxometalales have a structure consisting of a tetrahedral unit XO_4 as primary heteroatom surrounded by twelve octahedral MO_6 of addenda atoms. MO_6 octahedral are connected together by common edges in four M_3O_{13} units, which in turn are connected by common corners (Figure 1).

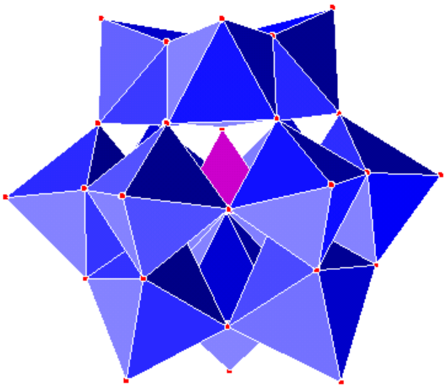


Figure 1. Keggin polyoxoanion with complete structure

Sidgwick proposed a planar model of the M_3O_{13} unit from α-Keggin structure. In Figure 2 can see that inside the M_3O_{13} unit, heteroatom X is surrounded by four oxygen atoms.

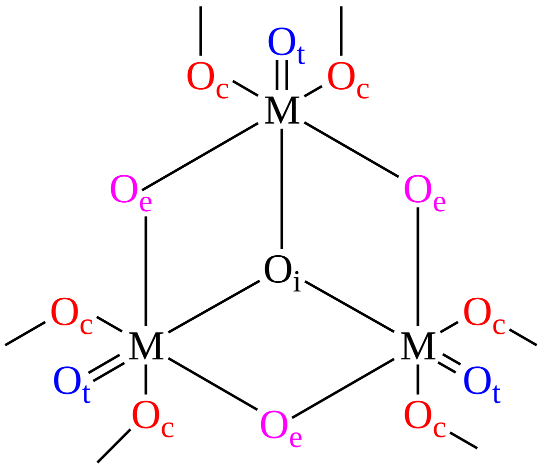


Figure 2. Planar image of the M_3O_{13} units inside of Keggin polyoxoanion

Oxygen atoms can be distinguished among the nature of the connection realised with the primary heteroatom X and addenda atoms M (Figure 2) in:

- Oi are oxygen atoms between the primary heteroatom X and addenda atoms M, in X-O_i-M bonds;
- Oe are oxygen atoms find inside of M_3O_{13} unit, in common edges of MO_6 octhaedral, in M-O_e-M bonds;
- Oc are oxygen atoms connecting bridge between M_3O_{13}, find in common corners of MO_6 octhaedral, in M-O_c-M bonds;
- Ot are terminal oxygen atoms atom bonded to each addenda atom, in order to achieve octahedral coordination, in M=O_t bonds.

A monolacunary Keggin structure can form by removal of one MO_6 octahedron. The monolacunary polyoxometalate is unsaturated with enhanced reactivity and lower stability than complete Keggin structure and is able to coordinate to metal cations.

The lacunary polyoxoanions chelated to a metal ion **M**, and if the coordination geometry of **M** is not achieved, **M** will coordinated ligands **L** of the reaction medium. (H_2O, O_2^-, F^-). The metal ion **M** can be removed from the structure of the new complex without destroying the framework of monolacunary polyoxoanion acting as ligand.(Figure 7).

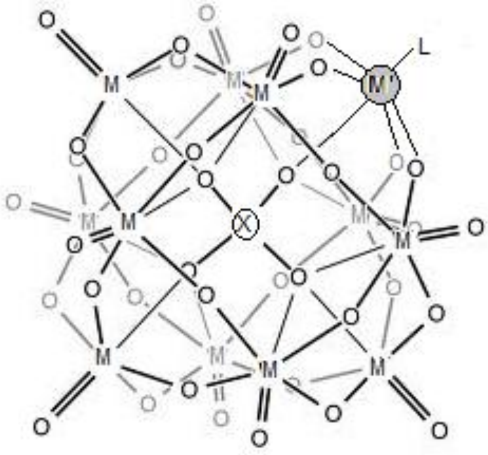


Figure 7. Structure of Keggin polyoxoanion complex with general molecular formula $[\mathbf{M}(XM_{11}O_{39})\mathbf{L}]^{q-}$

Up to now, in general, Keggin polyoxometalates monolacunary and their complexes with a single species of addenda atoms (molybdenum and tungsten) or a mixed addenda atoms type molibdotungstate have been synthesized. In the case of Keggin compounds with vanadium addenda atoms, only polyoxometalates with complete structure were synthesized and studied until now. Keggin polyoxometalates with vanadium addenda atoms have been proved to be compounds with remarkable properties, in particular in homogeneous and heterogeneous catalysis in synthesis of organic chemistry, but also in other fields such as medicine and biology.

In this thesis we have proposed to synthesize Keggin polyoxometalates with mixed addenda, monolacunary and their complexes, monovanadodecamolibdate and monovanadodecatungstate type with primary heteroatom P (V), As (V) or Si (IV), as potassium salts. Polyoxoanion complexes of $[PVW_{10}O_{39}]^{8-}$ and $[PVMo_{10}O_{39}]^{8-}$ with cations of transition metals **M** (Mn(II), Fe(III), Co(II), Ni(II) și Cu(II)) and complexes of Zn(II) cation with polyoxoanions $[AsVW_{10}O_{39}]^{8-}$, $[SiVW_{10}O_{39}]^{9-}$ and $[SiVMo_{10}O_{39}]^{9-}$ were prepared after a synthesis study.

The thesis were organised in four chapters, general conclusions about experimental part and interpretation of results, also bibliography are included at the end.

THE RESUME OF THESIS CHAPTERS

Chapter I present a theoretical part of thesis. In this part, polyoxometalates are definied and a short history of them is presented. General characterization, nomenclature, physical and chemical properties of polyoxometalates are also presenting here. Further, the methods for the synthesis of polyoxometalate in both aqueous and organic solvents are presented. Reaction conditions, methods of separation and isolation of polyoxometalates from synthesis medium were given special attention. Keggin polyoxometalates including complete and lacunary structures, and also complexes of these were discussed in more detail. In this chapter, Keggin polyoxometalates with mixed addenda were included. At the end of the chapter reviews the areas where polioxometalații Keggin type have been used until now.

Chapter 2 presents the experimental part of the work. Synthesis of monolacunary polyoxoanions with mied addenda, $K_8[PVMo_{10}O_{39}]\cdot16H_2O$ (**L_1**), $K_8[PVW_{10}O_{39}]\cdot15H_2O$ (**L_2**), $K_8[AsVW_{10}O_{39}]\cdot16H_2O$ (**L_3**), $K_9[SiVW_{10}O_{39}]\cdot13H_2O$ (**L_4**) and $K_9[SiVMo_{10}O_{39}]\cdot18H_2O$ (**L_5**), were printed in the first part of chapter. In the second part, the study of synthesis between monolacunary polyoxoanions and metal cations **M** (Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} și Zn^{2+}) was approached step by step. Determination of optimal synthesis conditions of complexes was effectuated after finding of stability pH range for monolacunary polyoxoanions used. First, stoichiometry of complexation reactions between polyoxoanions and metal cations was occured with conductometer method. pH, reaction time and temperature, that obtain the best results, were achieved with spectrofotometric method. This chapter concludes with synthesis of polyoxoanion complexes, which were studied:
$K_6[Mn(H_2O)PVMo_{10}O_{39}]\cdot10H_2O$ (**1**), $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot8H_2O$ (**2**), $K_6[CoPVMo_{10}O_{39}(H_2O)]\cdot17H_2O$ (**3**), $K_6[NiPVMo_{10}O_{39}(H_2O)]\cdot21H_2O$ (**4**), $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot17H_2O$ (**5**), $K_6[MnPVW_{10}O_{39}(H_2O)]\cdot14H_2O$ (**6**), $K_5[FePVW_{10}O_{39}(H_2O)]\cdot11H_2O$ (**7**), $K_6[CoPVW_{10}O_{39}(H_2O)]\cdot21H_2O$ (**8**), $K_6[NiPVW_{10}O_{39}(H_2O)]\cdot19H_2O$ (**9**), $K_6[CuPVW_{10}O_{39}(H_2O)]\cdot14H_2O$ (**10**); $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot15H_2O$ (**ZnL_3**), $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot16H_2O$ (**ZnL_4**), $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot11H_2O$ (**ZnL_5**).

Results obtained from the use of chemical analysis, thermogravimetry, FT-IR, Raman, UV-VIS, EPR, X-ray spectroscopy and cyclic voltammetry, for all synthesized compounds, are presented in Chapter 3. Results were shown in figures and tables, and were discussed on the basis of information acquired from the study of the scientific literature.

For a comparative study, synthesized Keggin polyoxometalates were divided into three groups. The first group comprised the monolacunary polyoxometalate $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$ (**L_1**) and its complexes $K_{8-n}[M^{n+}(H_2O)PVMo_{10}O_{39}]\cdot xH_2O$ (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) (**1-5**); the second group included the monolacunary polyoxometalate $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ (**L_2**) and its complexes $K_{8-n}[M^{n+}(H_2O)PVW_{10}O_{39}]\cdot xH_2O$ (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) (**6-10**) and the third group formed zinc complexes, $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$ (**ZnL_3**), $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$ (**ZnL_4**), $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$ (**ZnL_5**).

Chemical analysis resulted to the precise determination of the polyoxometalates composition [5, 238, 239]. Thermal analysis gave us information on the thermal stability of the polyoxometalate and the number and nature of the water molecules of the compounds studied [53-55, 240].

The FT-IR analysis has revealed the characteristic vibrational bands of Keggin-type compounds:, ν_{as}(OH) in range 3000-3600 cm^{-1} and δ(OH) to 1600-1650 cm^{-1} were assigned to water molecules; antisimmetrical stretching, ν_{as}(X-Oi) (X is P(V), Si (IV) or As(V) heteroatom) to 1000-1100 cm^{-1}, vibrational bands ν_{as}(M-Ot) (M is Mo(VI) orW (VI)) to 950 – 1000 cm^{-1}; ν_{as}(Mo-Oc-Mo) and ν_{as}(Mo-Oe-Mo) from 700 to 950 cm^{-1}. These vibrational bands were shifted and were modified to complexes than to monolacunary polyoxoanions, as result of metal cation coordination [14, 55, 95, 96, 103, 109, 135].

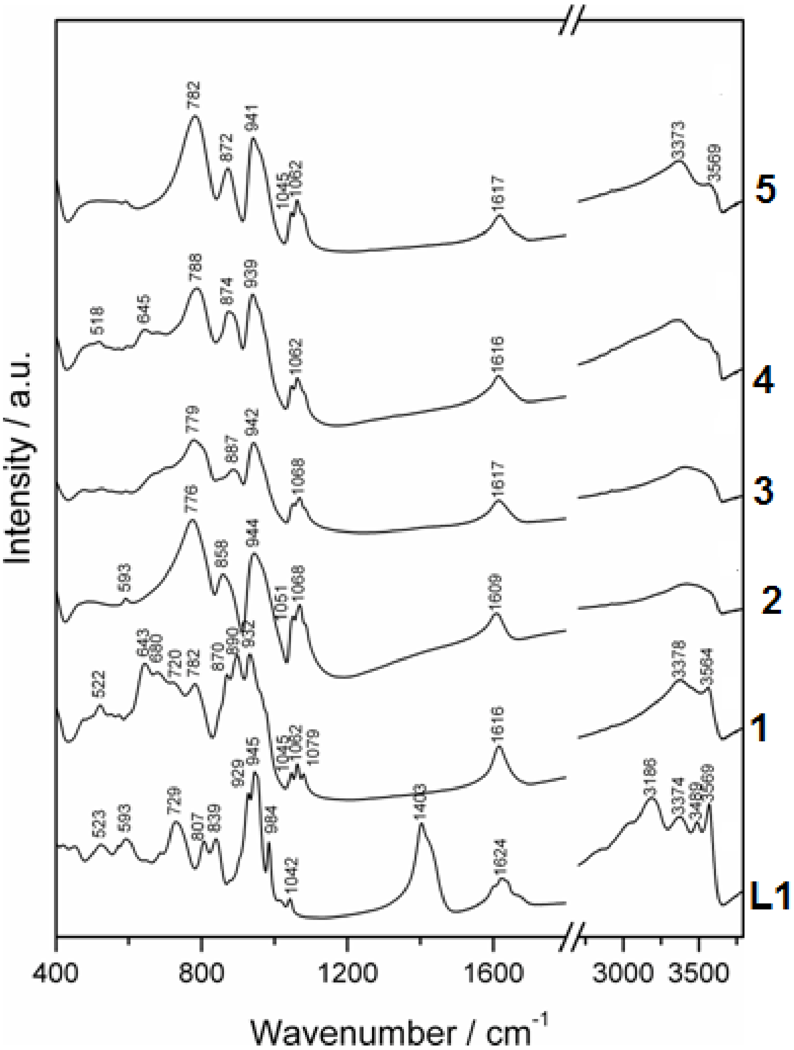


Figure 26. FT-IR vibrational spectra of **L_1** and **1 -5**

In Raman spectra, recorded in 1200-100 cm^{-1} range, characteristc bands were obtained for symmetric stretching vibration, ν_s(M-Ot) (M is Mo(VI) or W (VI)) in 900-1000 cm^{-1}, for antisymmetric stretching vibration, ν_{as}(M-Ot), to 850-900 cm^{-1}, and for symetric stretching vibration of M-Oi bond (ν_s(M-Oi)) arround to 250 cm^{-1}. These three bands were slightly shifted in polyoxoanion complexes than in monolacunary polyoxoanions, because the structural stability increased after coordination of metal cation **M** [13, 61, 152, 159].

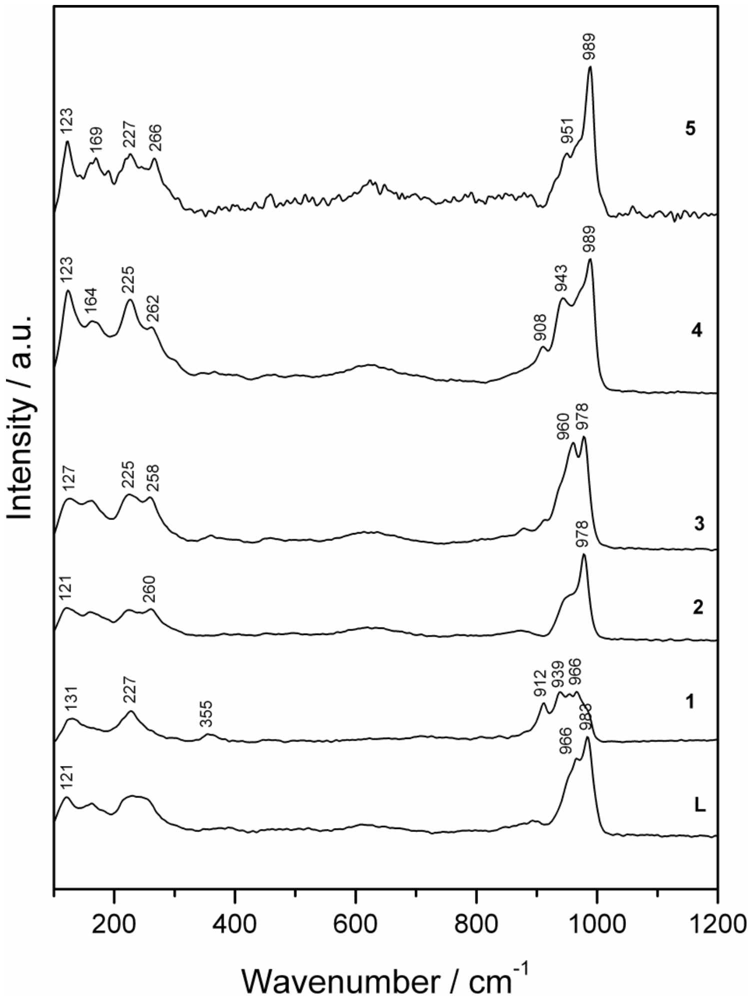


Figure 29. Raman spectra of polyoxometalates **L_1** and **1-5**

All electronic absorption spectra in UV, obtained for synthesized Keggin polyoxometalates contained two charge transfer bands characteristic and relatively intense.
The first absorption band (ν_1), approximately to 40000 cm^{-1} (250 nm), was attributed to electron transitions within W-Oc,e-W tricenter bonds of polyoxoanionic framework. This band was recorded in range 3100-3250 cm^{-1} in spectra of polyoxoanions with molibden addenda atoms and was shifted to higher energies as the stability of the resulting complex is higher.

The second most intense band (ν_2), around to 50000 cm^{-1} (200 nm) was assigned to the transition d_π-p_π of electrons from M=Ot bond, (where M is addenda atom). This band are independent by the polyoxoanion structure, and its position is unaffected by the nature of primary heteroatom [14, 61, 109, 234, 235].

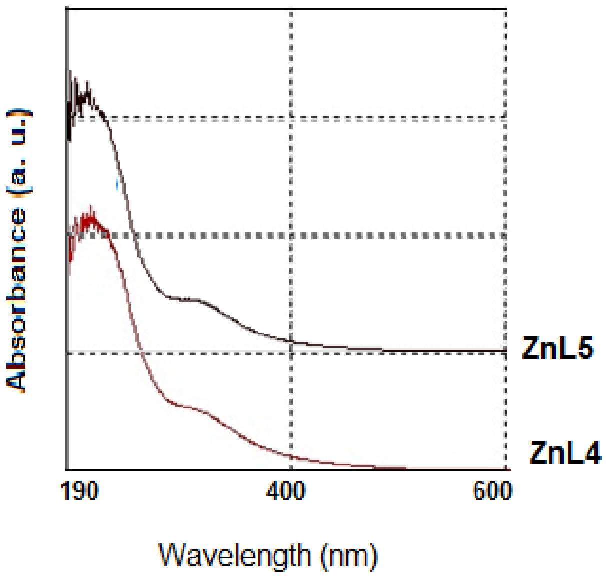
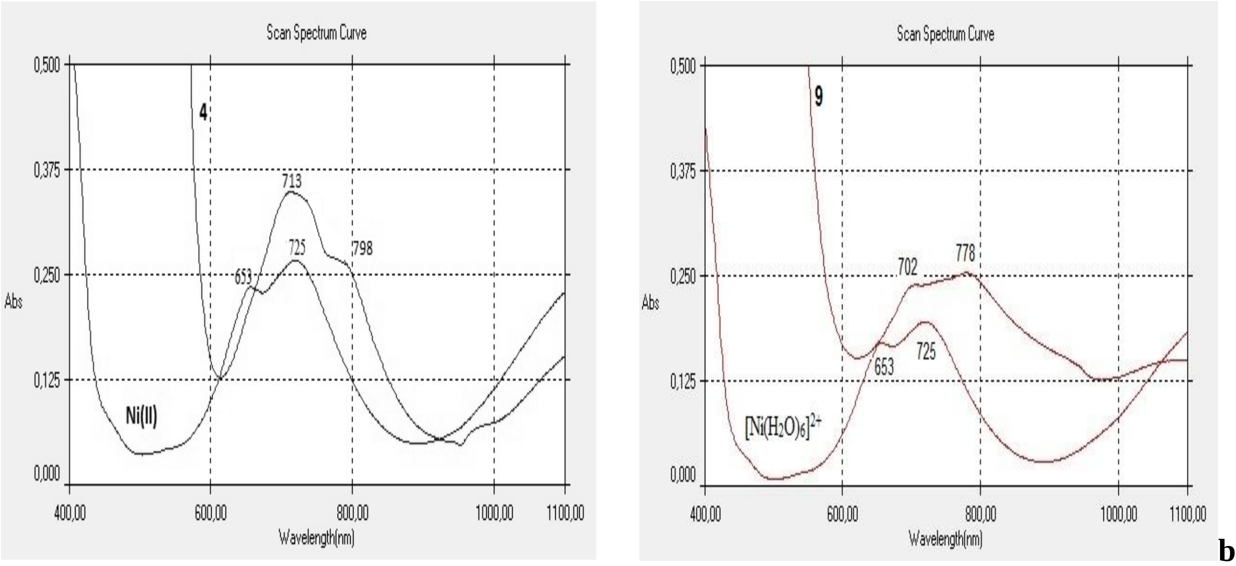


Figure 33. Absorption electronic spectra in UV of polyoxometalates **ZnL_4** şi **ZnL_5**

As expected, the electron transfer bands in VIS of Zn^{2+}, Mn^{2+}, Fe^{3+} cations were not observed. Electronic transitions d-d were masked by charge transfer band ν_1 of polyoxoanion ligands, which extanded from UV to VIS. For complexes of Co^{2+} cation assigned to electronic transition ν_3 $^4T_{1g}(F) \leftarrow {}^4T_{1g}(P)$ were shifted to lower energies than $[Co(H_2O)_6]^{2+}$ [6, 184, 242].

In VIS spectra of Figure 36, two electronic transfere bands d-d corresponding to transitions $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ şi $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ can see for both **4** and **9** complexes of Ni^{2+}. In polyoxoanion complexes, **4** and **9**, the two bands were asymmetric and were shifted to lower energy than in $[Ni(H_2O)_6]^{2+}$ [6, 184, 242]. In VIS spectra of Cu^{2+} complexes, characteristic absorption band of copper cation appeared to lower energies than in $[Cu(H_2O)_6]^{2+}$. In conclusion, Cu^{2+} was weaker bound in coordinative binds to polyoxoanions ligans than in aquaion, $[Cu(H_2O)_6]^{2+}$ [97, 242].



b)

a)

Figure 36. VIS absorption spectra of a) $[Ni(H_2O)_6]^{2+}$ and **4**; b) $[Ni(H_2O)_6]^{2+}$ and **9**

EPR spectra of complexes $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot 8H_2O$ **(2)** şi $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$ **(5)** were interpreted by considering the octahedral geometry of the Fe^{3+} and Cu^{2+} into monolacunary $[PVMo_{10}O_{39}]^{8-}$ ligand, and were discussed by considering noninteracting Fe^{3+} and Cu^{2+} ions, respectively. Both the higher change in polyoxoanionic complex of copper ions than in copper aquacomplex and the band asymmetry may be due to Jahn-Teller distortion. EPR spectra obtained are typical for mononuclear iron and copper species surrounded octahedrally [245-247].

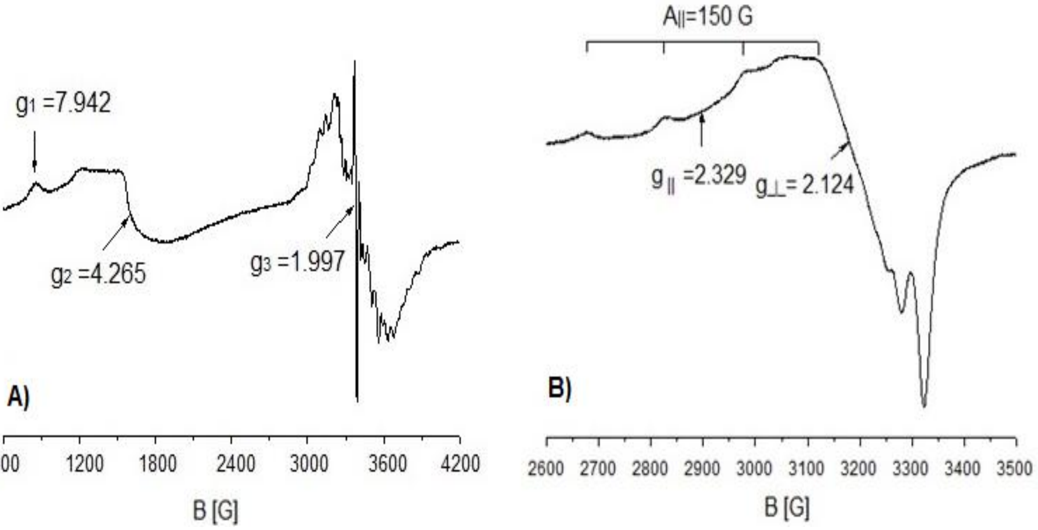


Figure 39. EPR spectra recorded at room temperature in X band for: A) polyoxoanionc complex **2**; B) polyoxoanionic complex **5**

X-ray diffraction analysis was performed in the powder of $K_6[NiPVMo_{10}O_{39}]\cdot xH_2O$ (**4** and **4'**), $K_6[CuPVMo_{10}O_{39}]\cdot 17H_2O$ (**5**), $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ (**L_1**), $K_6[MnPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$ (**6**), $K_6[NiPVW_{10}O_{39}(H_2O)]\cdot 19H_2O$ (**9**), $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$ (**ZnL_3**), $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$ (**ZnL_4**) and $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$ (**ZnL_5**). X-ray spectra were recorded, the unit cell parameters were calculated and the crystallization system was determined for all of these polyoxometalates. Two different samples were investigated with X-ray diffraction for polyoxometalate complex of Ni^{2+} cation and two polyoxometalate complexes with different numbers of hydration water molecules were found: $K_6[NiPVMo_{10}O_{39}]\cdot 21H_2O$ (**4**) și $K_6[NiPVMo_{10}O_{39}]\cdot 16H_2O$ (**4'**) [248-252].

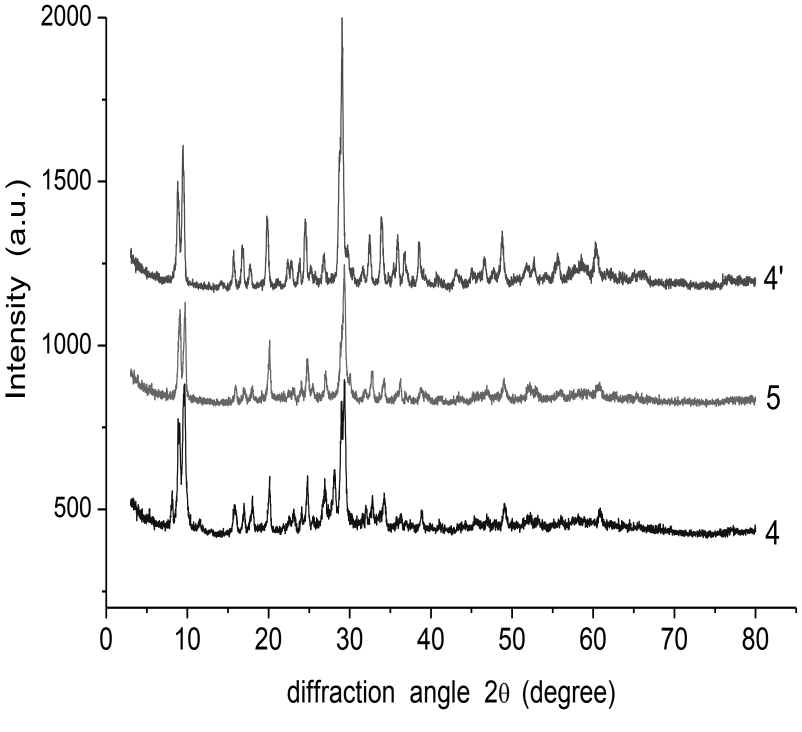


Figure 40. X-ray diffraction spectra of polioxoanionic complexes **4**, **4'**and **5**

Electrochemical behavior of polyoxometalate complexes $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot 8H_2O$ (**2**) and $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$ **(5)** was studied and recorded with cyclic voltametry in 0,25 M Na_2SO_4 solution to pH 2.5 and 5.1. The cvasi-reversibile redox process (wave I) was assumed to belong reduction process Cu(II) → Cu(0) and irreversible processes (undele II și III) corresponding to the reduction of V and Mo ions in the structure of phosphovanadomolibdate [253, 254]. Electrocatalytic activity of polyoxoanion $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$ was studied on H_2O_2 reduction [256-263].

In Chapter IV has aimed to determine the influence of synthesized polyoxometalates over germination of *Triticale* seeds. The germination yield, plant growth on the sixth day after germination (embryonic root length, length of adventitious roots, coleoptile length, length of the first leaflets) and biomass were monitored in these experiments [267-301].

The study was comparative for each series of polyoxometalates. The first series included compounds studied: $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$ and its complexes $K_{8-n}[M^{n+}(H_2O)PVMo_{10}O_{39}]\cdot xH_2O$ (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}), the second series was composed of $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ and its complexes $K_{8-n}[M^{n+}(H_2O)PVW_{10}O_{39}]\cdot xH_2O$ (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}). Solutions of concentration 0.1 μM, 1.0 μM, 10 μM și 100 μM have been prepared for each compound used. Control sample was distilled water.

Determinations effectuated for each set of *Triticale* grains were compared with the control and were statistically analyzed with functions of Excel 2007. Statistical parameters were determined: arithmetic average, standard deviation, coefficient of variation, percentage differences, TTEST function. Conclusions about the influence of polyoxometalate solutions on germination of *Triticale* seeds were obtained after analysis of the obtained results, especially percentage differences between polyoxometalates solutions and control.

CONCLUSION

1. In this thesis were synthesised nineteen Keggin polyoxometales, in which fifteen were new:
- monolacunary polyoxoanion as ligand $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$ and its complexes with metal cation: $K_6[Mn(H_2O)PVMo_{10}O_{39}]\cdot 10H_2O$, $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot 8H_2O$, $K_6[CoPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$, $K_6[NiPVMo_{10}O_{39}(H_2O)]\cdot 21H_2O$, $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$;
- monolacunary polyoxoanion as ligand $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ and its complexes with metal cation: $K_6[MnPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$, $K_5[FePVW_{10}O_{39}(H_2O)]\cdot 11H_2O$, $K_6[CoPVW_{10}O_{39}(H_2O)]\cdot 21H_2O$, $K_6[NiPVW_{10}O_{39}(H_2O)]\cdot 19H_2O$, $K_6[CuPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$;
- complexes with Zn (II) , $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$, $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$, $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$ of monolacunary polyoxoanions $K_8[AsVW_{10}O_{39}]\cdot 16H_2O$, $K_9[SiVW_{10}O_{39}]\cdot 13H_2O$ and $K_9[SiVMo_{10}O_{39}]\cdot 18H_2O$.

2. Determination of the stability range of monolacunary polyoxoanions $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$, $K_8[PVW_{10}O_{39}]\cdot 15H_2O$, $K_8[AsVW_{10}O_{39}]\cdot 16H_2O$, $K_9[SiVW_{10}O_{39}]\cdot 13H_2O$ şi $K_9[SiVMo_{10}O_{39}]\cdot 18H_2O$ realised with both conductometric and spectrophotometric methods permitted to establish the optimal pH range, in which the study of optimal reaction conditions, for syntheses of complexes between monolacunary polyoxoanions and metal cations is recomanded to realise.

3. The determination of chemical reactions stoichiometry between synthesised monolacunary polyoxometalates and metal cations **M**, eas effectuated with conductometric method to different combination rate, metal/ligand, and resulted in 1:1 rate for all compounds. This result is in concordance with literarure data, mentioned for other Keggin monolacunary polyoxoanions coordinated in complexes with metal cations **M** (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} şi Zn^{2+}), those we use in this study [1-5, 16].

4. Determination of optimal conditions for synthesis included finding the optimal pH, the reaction time and the temperature, at which the reactions forming complexes beteewn metal cations and monolacunary polyoxometalate derives as good yield. Spetrophotometric method was used for these experiments. pH values finding for complexes preparation are in good

concordance with literature data for related compounds [1-5, 16]. Synthetic time, relative shortly, necessary for obtaining the complexes may be due to the very high reactivity of the monolacunary polyoxometalate. Synteses of monovanadodecamolibdate with P (V) or Si(IV) take place better at room temperature and are disadvantaged by increasing of temperature, because monolacunary polyoxometalates with molibden as addenda atoms are very unstable and decompose in solution at higher temperature.

5. Chemical analysis of syntheses compounds together with thermogravimetry data permited to establish with precision of molecular formulas, and experimental results were in concordance with theoretical result from mathematical computations.

6. From curves of thermal analysis, TG-DTG-DTA, resulted that all prepared compounds suffered three important transformations: an endotherm process, in more steps, the lost of christalisation water molecules into a large range of temperature (60-180 °C), following by a exotherm process due of multiple transformations of oxides from polyoxoanions decomposition. This sequence of processes occured in characteristic temperature range of Keggin polyoxometalates. From thermal analysis resulted that synthesised complexes of transition metal cations were more stabile than “parents” monolacunary polyoxoanions. Complexes with molibden addenda atoms were less stable than their omologues with tungsten addenda atoms. The thermal stability of polyoxoanion complexes with zinc cation increased in order: $K_9[SiVMo_{10}O_{39}]\cdot 18H_2O \approx K_8[AsVW_{10}O_{39}]\cdot 16H_2O < K_9[SiVW_{10}O_{39}]\cdot 13H_2O$. A water molecule was coordinated to metal cation **M** (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} şi Zn^{2+}), so result from thermogravimeter analysis.

7. FT-IR spectra of all synthesised polyoxoanions exhibited characteristic vibrational bands of Keggin polyoxometalates and their water molecules. For Keggin complexes, these bands were better definied and shifted to higher energies, indicated the coordination of metal cation and the rebuilding of polyoxoanion framework after binding of metal cation. FT-IR spectra proved a higher stability of polyoxoanions with tungsten addenda atoms than omologues with molibden addenda atoms. Significant deplacement to higher energies of vibrational bands of bond P-Oi and M-Oc,e-M (M are addenda atoms Mo, W or V) showed that oxygen atoms involved in coordination of metal cations could be intern oxygen (Oi), common corners oxygen (Oc) and common edges oxygen (Oe).

These results are consistent with literature data for complexes of monolacunary polyoxometalate Keggin-type, which shows that the polyoxoanion acts as a pentadentate ligand. The sixth position was occupied by a water molecule, according to the results of chemical and thermal analysis, and characteristic marked in vibrational band of OH bonds in IR spectra.

8. In the spectra of the Raman vibrational bands characteristic of symmetrical and asymmetrical connections are evident from the Keggin polioxometalaţii both the two monolacunary polyoxometalates $K_8[PVMo_{10}O_{39}]\cdot16H_2O$ şi $K_8[PVW_{10}O_{39}]\cdot15H_2O$, as well as their complexes with metal cations. The vibration spectra of these complexes are well defined and shifted to higher frequencies, indicating an increase in stability and symmetry from the coordination of the metal cation.

9. UV electronic absorption spectra of the ligands $K_8[PVMo_{10}O_{39}]\cdot16H_2O$ şi $K_8[PVW_{10}O_{39}]\cdot15H_2O$ and their complexes with metal cations, and spectra of polyoxoanions $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot15H_2O$, $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot16H_2O$, $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot11H_2O$ exposed two charge transfer characteristic bands:: ν_1 due to transitions of electrons from tricenter bonds M-Oc,e-M and ν_2 attributed to the transition d_π-p_π of electrons involved in M=Ot bonds (M are addenda atoms). For complexes, the position of charge transfer band ν_1 is shifted to higher energies and this band is much better defined than in the spectrum of ligands, due to the increased symmetry of MO_6 octahedron of addenda atoms following metal cation coordination to polyoxoanionic framework. The second charge transfer band ν_2 was shifted insignificantly, because M=Ot bond were not involved in transition metal cation coordination.

10. VIS spectra have been recorded only for cations of Co^{2+}, Ni^{2+}, Cu^{2+}, because electronic transfer bands characteristic for ions of Zn^{2+}, Mn^{2+},Fe^{3+} in octahedral ligand field was masked by the charge transfer band ν_1 of the ligands wich have been extended from UV to VIS.

The results obtained for complexes with cation of Co^{2+}, $K_6[CoPVMo_{10}O_{39}(H_2O)]\cdot17H_2O$ and $K_6[CoPVW_{10}O_{39}(H_2O)]\cdot21H_2O$, proved that Co^{2+} ion was surrounded octahedrally in both complexes, but coordination around Co^{2+} ions is low and disorderly, compared to that of $[Co(H_2O)_6]^{2+}$ aquaion.

Two bands of electronic transfer d – d characteristic of octahedrally coordination of Ni^{2+} cation were obtained in VIS spectra of Ni^{2+} complexes, $K_6[NiPVMo_{10}O_{39}(H_2O)]\cdot 21H_2O$ and $K_6[NiPVW_{10}O_{39}(H_2O)]\cdot 19H_2O$. Both bands of polyoxometalate complexes are more asymmetric and shifted to lower energies than aquaion $[Ni(H_2O)_6]^{2+}$, indicating a weaker coordination of Ni^{2+} cation in the polyoxoanions complexes and a distortion of the octahedron due to coordination with non-equivalence of ligands.

A single wider band characteristic for ions of Cu^{2+} octahedrally surrounded was obtained for $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$ and $K_6[CuPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$ complexes, which occurs at lower energies in the spectra of two complexes, compared to the absorption band registered for $[Cu(H_2O)_6]^{2+}$ aquaion. This is due to weaker ligand field created at coordination of polyoxoanionic ligands compared to that of water molecules in aquaion.

11. 11. From results of EPR method, it follows that in the case of polyoxometalates complexes, $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot 8H_2O$ and $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$, each polyoxoanionic structural unit contains a single metalic cation Fe^{3+} and respectively Cu^{2+}, coordinated at monolacunar polyoxoanion with ligand role, $[PVMo_{10}O_{39}]^{8-}$. Both, Fe^{3+} and Cu^{2+} metal are in an octahedral ligand field.

12. X -ray diffraction analyses have been carried out only on the powder and revealed that for the same polyoxometalate can be obtained compounds with different numbers of water molecules of hydration: $K_6[NiPVMo_{10}O_{39}(H_2O)]\cdot 21H_2O$ and $K_6[NiPVMo_{10}O_{39}(H_2O)]\cdot 16H_2O$. The different number of water molecules affected only the cell unit dimensions and not the crystallization system. As a result of X -ray diffraction analysis $K_6[NiPVMo_{10}O_{39}(H_2O)]\cdot H_2O$ and $K_6[CuPVMo_{10}O_{39}(H2O)]\cdot 17H_2O$ crystallizes in the monoclinic system and belong to space group $P2_{1/c}$; $K_6[MnPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$, $K_6[NiPVW_{10}O_{39}(H_2O)]\cdot 19H_2O$ crystallizes in the primary cubic system, belonging to the space group P_{m-3n}, $K_6[ZnAsVW_{10}O_{39}(H_2O)]\cdot 15H_2O$ crystallizes in the tetragonal system and $K_7[ZnSiVW_{10}O_{39}(H_2O)]\cdot 16H_2O$ and $K_7[ZnSiVMo_{10}O_{39}(H_2O)]\cdot 11H_2O$ complexes crystallizes in the monoclinic system belonging to the space group C_m. In the case of monlacunar polyoxoanion $K_8[PVW_{10}O_{39}]\cdot 15H_2O$, the sample presented an amorphous part which made difficult the interpretation of the diffractogram , but the calculation of unit cell parameters indicated however a tetragonal crystal system.

13. Electrochemical behavior of polyoxometalate $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$ investigated at different scanning speed and pH shows successive quasi-reversible waves (peak Ia / Ic) attributed to the reduction of ions of Cu^{2+} to Cu^0 and irreversible wave (peaks IIc, IIIc) assigned to the reduction of molybdenum or vanadium addenda atoms. The H_2O_2 electroreduction assisted by compound $K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$, highlights the possibilities of using these compounds as electrocatalysts and electron transfer devices.

14. Using of 0. 1 - 100 μM polyoxoanion solutions $K_8[PVMo_{10}O_{39}]\cdot 16H_2O$,
$K_6[Mn(H_2O)PVMo_{10}O_{39}]\cdot 10H_2O$, $K_5[FePVMo_{10}O_{39}(H_2O)]\cdot 8H_2O$,
$K_6[CoPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$, $K_6[NiPVMo_{10}O_{39}(H_2O)]\cdot 21H_2O$,
$K_6[CuPVMo_{10}O_{39}(H_2O)]\cdot 17H_2O$ in *Triticale* seed germination was found that:

- the growth of roots, coleoptiles and leaflet were stimulated mostly by iron and nickel complexes solutions and inhibited by cobalt complex ;
- Biomass growth was stimulated mainly by cobalt and copper solutions in the whole range of concentrations and inhibited by iron and nickel solutions of 100 μM.

When using polyoxoanion 0.1 - 100 μM solutions of $K_8[PVW_{10}O_{39}]\cdot 15H_2O$,
$K_6[MnPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$, $K_5[FePVW_{10}O_{39}(H_2O)]\cdot 11H_2O$,
$K_6[CoPVW_{10}O_{39}(H_2O)]\cdot 21H_2O$, $K_6[NiPVW_{10}O_{39}(H_2O)]\cdot 19H_2O$,
$K_6[CuPVW_{10}O_{39}(H_2O)]\cdot 14H_2O$, in Triticale seed germination was found that:

- Roots growth was inhibited only by the copper complex solutions ;
- Coleoptile growth was not significantly affected by anyone solutions using;
- First leaflet growth was significantly stimulated by 100 μM $K_8[PVW_{10}O_{39}]\cdot 15H_2O$ monolacunary polyoxoanion solution and slightly inhibited by copper complex solutions;
- biomass growth was inhibited by almost of the solutions used, except those of the copper complex and of monolacunary ligand at concentrations from 1.0 to 100 μM.

In conclusion it can be said that both complexes with copper cation play an important role in biomass growth. Otherwise, it can't be done a parallel between the results obtained for the series of complexes with molybdenum adenzi atoms and tungsten adenzi atoms.The complexity and diversity of the results obtained on one hand is due to the different degree of dissociation molybdenum compounds beside those of tungsten in aqueous solution and, on the other hand, is caused by the transmission system and the enzymatic catalysis, specific to *Triticale* grains during germination.

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