Hydrothermal Synthesis and Comparative Study of Two Silicium Monolacunar Polyoxometalates Zn Complexes $K_7[Zn(SiM_{10}VO_{39})(H_2O)]\ .\ nH_2O$; (M=Mo,W)

ALEXANDRINA FODOR[1]*, ANDA IOANA GRATIELA PETREHELE[1], SANDA RODICA BOTA[1], SIMONA BUNGAU[2]
[1]University of Oradea, Faculty of Sciences, 1 Universităţii Str.,410087, Oradea, Romania
[2]University of Oradea, Faculty of Medicine and Pharmacy, 1 Universităţii Str., 410087, Oradea, Romania

Two new monolacunar polyoxometalates Zn complex: $K_7[Zn(SiM_{10}VO_{39})(H_2O)]\ .\ nH_2O$; (M=Mo,W) were obtained by hydrothermal synthesis. The combination rate between $ZnCl_2$ and heteropolyoxometalate ligand $[SiM_{10}VO_{39}]^{9-}$ and the optimal conditions for synthesis were determined by spectrophotometric and conduct metric 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 conservation 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 heteropolyanions containing P as central atom and reveals an orthorhombic structure.

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

Polyoxometalates (POM) are a broad class of complexes which weak up an impressive 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 heteropolyoxometalates of the transition metals have received much attention being applied in medicine, catalyses, and material science.

Several monolacunary anions with general formula, $[XM_{11}O_{39}]^{n-}$ may bind to a metal cation M' as a pentadentate ligand and may form complexes by the type $[(XM_{11}O_{39})M'L]$, 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 monolacunary structure [6, 7].

As an expansion of the study on the POM chemistry, we attempted to explore the assembly of $(SiM_{10}VO_{39})^{7-}$, (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 $[SiM_{10}VO_{39}(H_2O)]^{9-}$, (M=Mo,W) monolacunary polyoxometalalte 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 (*p*H= 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: Al_2O_3, atmosphere: air.

The combination rate among Zn^{2+} and heteropolyanion, $[SiM_{10}VO_{39}]^{9-}$, (M=Mo,W), were determined using the conductometric method with a multimeter 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, cupper monochromatic radiation and Ni filter for the K_α emission.

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

Results and discussions

Synthesis of $K_9[SiW_{10}VO_{39})]\cdot x\ H_2O$

The monolacunary anion, $[SiW_{10}VO_{39}]^{9-}$ was prepared in aqueous medium from Na_2SiO_3, $NaVO_3\cdot\ 2H_2O$ and $Na_2WO_4\cdot\ 2H_2O$ mixed in stoechiometric rate, with method according with literature by adapting reactions condition at: boiling temperature, *p*H=6,5 for 1 hour [8-11]. The heteropolyanion $[SiW10VO_{39}]^{9-}$ 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 $K_9[SiMo_{10}VO_{39})]\ \cdot y\ H_2O$

A stoechiometric mixture between Na_2SiO_3, $NaVO_3\cdot 2H_2O$ and $Na_2MoO_4\cdot\ 2H_2O$ was kept at room temperature and *p*H = 5.5, under agitation, for 30 min. KCl salt was added in small quantities until the monolacunary anion started to precipitate. The crystallisation was realized on the ice bathroom, frozen with ammonium chloride(-4° C). The synthesis yield value was 40%.

---

* *email: afodor@uoradea.ro*

Table 1

$K_7[Zn(SiM_{10}VO_{39})(H_2O)]\ .\ nH_2O$; (M=Mo,W) ELEMENTARY ANALYSIS

Compound	Compound / appearance	η %	Analysis %	Found mg	Calculated mg	Calculated atom/mol
1	$K_7[Zn(SiMo_{10}VO_{39})(H_2O)]\cdot 11H_2O$ (Compound 1) Red-orange square prism	37	Mo	43.20	43.26	1
			V	2.23	2.29	1
			Si	1.24	1.26	1
			Zn	2.90	2.94	1
			K	12.29	12.34	7
			H_2O constitution	0.80	0.81	1
			H_2O crystallization	8.90	8.93	11
2	$K_7[Zn(SiW_{10}VO_{39})(H_2O)]\cdot 16H_2O$ (Compound 2) Brick-red octaedra	58	W	57.60	57.68	1
			V	1,52	1,59	1
			Si	0.82	0.88	1
			Zn	2.00	2.05	1
			K	8.50	8.58	7
			H_2O constitution	0.54	0.56	1
			H_2O crystallization	9.00	9.04	11

Synthesize of $K_7[Zn(SiW_{10}VO_{39})(H_2O)]\ .\ 16H_2O$

2 mL (4 mmol) solution 2M $ZnCl_2$ was added in drops under vigorously stirring to a equal quantity solution (4 mmol) $K_9[SiWVO_{39}]\ .\ nH_2O$ at room temperature. A 5% $KHCO_3$ solution and 5% HCl solution were used to maintain the *p*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 $K_7[Zn\ (SiW_{10}VO_{39})(H_2O)\ .\ 16H_2O$ elementary analysis.

Synthesis of $K_7[Zn(SiMo_{10}VO_{39})(H_2O)]\ .\ 11H_2O$

(4 mmol) $K_9[SiMoVO_{39}]\ .\ nH_2O$ solution was dissolved completely in water at room temperature. 2 M solution was added to arrive to *p*H = 4.3. 2 mL (4 mmol) solution 2M $ZnCl_2$ was added carefully in drops, under vigorously stirring, keeping *p*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 baker was placed in a ice bathroom 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 37%. In table 1 is presented $K_7[Zn(SiMo_{10}VO_{39})\ (H_2O)]\ .\ 11H_2O$ 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 $K_9[SiM_{10}VO_{39}]\ .\ nH_2O$; (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*H=4.5 for M = Mo (VI) and at *p*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*H, temperature and time. The concentrations for both reactive solutions ($ZnCl_2$ and $K_9[SiM_{10}VO_{39}]\ .\ nH_2O$; (M=Mo,W)) were $5\ .\ 10^{-6}$M, and the *p*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*H=6.0 at the boiling point for 15 min and for molybdenum complex (compound 1.) were obtained the optimal reaction conditions at *p*H = 4,3, at room temperature, for 30 min.

Thermal Analyses of $K_7[Zn(SiM_{10}VO_{39})(H_2O)]\ .\ nH_2O$; (M=Mo,W)

The thermal analyses of $K_7[Zn(SiM_{10}VO_{39})(H_2O)]\ .\ nH_2O$; (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°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_{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°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_2O_5 and in the 715-720°C temperature range, the tetragonal MoO_3 and WO_3 becomes rhombic[15-19].

Table 2

$K_7[Zn(SiM_{10}VO_{39})(H_2O)] . nH_2O$; (M=Mo,W) THERMOGRAVIMETRIC ANALYSIS DATA

Compound	Temperature range/°C	DTA peak/°C		TG data /%		Assigment
		endo	exo	calcd.	found	
1	25-1000	120	-	8.19	8.15	11 H_2O
		-	300	0.82	0.80	1 H_2O
		650	-			V_2O_5 MoO_3
		715	-			
2	20-400	126	-	11.13	11.10	16 H_2O
			310	0.66	0,61	1 H_2O
	400-1000	485	-			V_2O_5 WO_3
		600 720	- -			

Table 3

$K_7[Zn(SiM_{10}VO_{39})(H_2O)]$’”$nH_2O$; (M=Mo,W) IR SPECTRA VALUES

Compound	Peaks assign				
	V-O	M-O-M (M=W, Mo)	M-O	Si-O	H_2O crystallisation
1	530 cm^{-1}	800 cm^{-1}	950 cm^{-1}	1000 cm^{-1}	1680 cm^{-1}
2	525 cm^{-1}	810 cm^{-1}	952 cm^{-1}	998 cm^{-1}	1670 cm^{-1}

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, $K_9[SiM_{10}VO_{39}] . nH_2O$, 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, $K_7[Zn(SiMo_{10}VO_{39})(H_2O)] . 11H_2O$, 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).

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 d_x-p_x 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 d_π-p_π-d_π 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/cm^3 precision. The experimental density value is 3.68 $g/cm^3$for compound

Table 4

$K_7[Zn(SiM_{10}VO_{39})(H_2O)] . nH_2O$; (M=Mo,W) UV SPECTRA DATA

Keggin Heteropolyoxometalate	Bonds Type			
	M=O (M=Mo,W)		M-O-M (M=Mo,W)	
	ν (cm^{-1})	λ (nm)	ν (cm^{-1})	λ (nm)
$K_7[Zn(SiMo_{10}VO_{39})(H_2O)]\cdot 11H_2O$	46070	216	35700	290
$K_9[SiMo_{10}VO_{40}]\cdot 15H_2O$	46070	216	35000	285
$K_7[Zn(SiW_{10}VO_{39})(H_2O)]\cdot 16H_2O$	46080	220	35200	300
$K_9[SiW_{10}VO_{40}]\cdot 18H_2O$	46080	220	34800	290

Table 5
$K_7[Zn(SiM_{10}VO_{39})(H_2O)]$. nH_2O;
(M=Mo,W) CRYSTAL DATA

Compound	1	2
Molecular formula	$K_7H_{24}ZnO_{51}SiVMo_{10}$	$K_7H_{34}ZnO_{56}SiVW_{10}$
Formula weight	2217.6426	3186.7146
Crystal symmetry	Monoclinic	Monoclinic
Space group	C*m*	C*m*
a/Å	16.208	14.982
b/Å	24.210	23.756
c/Å	10.857	12.684
β/°	112.720	108.302
v/Å^3	4011.432	4000.520
D/g/cm^3	3.683	3.758
Z	4	4

1 and respectively 3.75 for compound 2. The number of $SiM_{10}V$ 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 $[SiM_{10}VO_{39}]^{-9}$, (M=Mo,W) hydrothermal syntheses were based on literature data [8-10] by adapting reactions condition at: room temperature, *p*H=5.5, 30 min for $K_9[SiMo_{10}VO_{39})]\cdot x\ H_2O$ and boiling temperature, *p*H=6.5, 1 hour for $K_9[SiW_{10}VO_{39})]\cdot x\ H_2O$ [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 $K_9[SiW_{10}VO_{39})]\cdot x\ H_2O$ respectively 40% for $K_9[SiMo_{10}VO_{39})]\cdot x\ H_2O$.

The two polyoxometalates Zn complexes $K_7[Zn(SiM_{10}VO_{39})(H_2O)]$. $11H_2O$, (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, *p*H=4.3 for 30 min for Mo polioxometalate and boiling temperature, *p*H=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.

$K_7[Zn(SiM_{10}VO_{39})(H_2O)]$. nH_2O (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

1. YAMASE, T., Mol. Eng., 3, 1993, p. 241
2. MISONO, M., Mol. Eng., 3, 1993, p.193
3. FEDOTOV, M.A., MKSIMORSKAYA, R.I., J. Struct. Chem., 57, 2006, p. 952
4. PAMIN, K., JAKIMSKA, B., ONIK, K., POLTOWICZ, J., GRABOWSKI, R., Catal. Lett., 27, 2009, p.167.
5. IZAROVA, N.V., KHOLDEEVA, O.A., SOKOLOV, M.V., FEDIN,V.P., Russian Chem. Bull., 158, 2009, p.134
6. HAB, X., YOU, W., DAI, L., QI, L., FANG, L.Y., LI, W. J., Clust. Sci., 20, 2009, p.707
7. TOURNE, C., TOURNE, G., Bull. Soc. Chim. France, 17, 1982, p. 64.
8. GHIZDAVU, L., FODOR, A., SZASZ, G.S., J.Therm. Anal. Cal., 63, 2001, p. 907
9. FODOR, A., ŞUTEU, A., Acta Chim. Slovenica., 50, 2003, p. 573
10. FODOR, A., GHIZDAVU, L., ŞUTEU, A., CARABAN, A., J.Therm. Anal. Cal., 74, 2004, p. 256
11. RUSU, D., RUSU, M., PĂTRUŢ, A., DAVID, L., Chem. Rev., 58, 2007. p. 484
12. PAULING, L., The nature of chemical bond, Ed. Cornel, New York, University Press,1960, p. 514
13. KAZANSKII, L.P., FEITHS, M., TROCHENKOVA, E.A., SPITSYN, V.I, Z., Anorg. Chem., 76, 1980, p.1201
14. SASCA, V., STEFĂNESCU, M., POPA, A., J.Therm. Anal. Cal., 72, 2003, p. 311
15. BIELANSKI, A., POZNICZEK, J., HASIK, M., J.Therm. Anal.Cal., 44, 1995, p. 717
16. MAROSI, L., ESCALONA, P.E., CIFRE, J., OTERO, A.C., J. Mater. Chem., 10, 2000, p.1949
17. POPE, M.T., Heteropoly and Isopoly Oxometalates New York Springer-Verlag; 1983, p.103
18. MASAHIRO, S., MICHIO, H.J., Chem.Soc., Dalton Trans., 2003, p. 659
19. GRIGORIEV, V.A., HILL, C.L., WEINSTOCK, J.A., J.Am.Chem.Soc., 122, 2000, p. 3544
20. GAMELAS, J., Polyhedron, J.A., 18, 1999, p.1163
21. PENG, J., MA, H.Y., HAN, Z.G., DONG, B.X., LI, W.Z., LU, J. WANG, E.B., Dalton Trans. 2003, p.3850
22. JIAN, F.F., WANG, X., WANG, J., XIAO, H., J. Clust. Sci., 21, 2010, p.57

Manuscript received: 19.08.2010