Rational Synthesis, Characterization and Crystal Structure Study of Keggin Monolacunar Arsenato (V)-Vanadium (V)-Tungsteno (VI) Zn (II) Complex

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A Keggin monolacunar heteropolianion Zn complex, $K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$, synthesis were rationalised by varying the reaction and crystalization conditions. The compound composition and structure were investigated by: elemental analysis, atomic absorption, spectral, thermo gravimetric and X-ray diffraction methods. The Zn complex formation was investigated using conductmetric and spectrophotometric method.

Keywords: Monolacunary Keggin Triheteropolyacids; IR, UV-VIS Spectra; thermal behaviour, crystal structure

Heteropolyacids, named also as polyoxometalates, application areas as: analytical, catalysis and biochemical [1-4], owing to their special redox properties [5-7], are in continuously expansion, therefore scientist are preoccupied to synthesizes new compounds from this class.

The hetero polyoxometalates containing As as heteroatom has been less synthesized and studied because of their instability and synthesis problems caused by their capacity to form large clusters [8].

The complexation with metallic ions can be a method to stabilize those compounds [9], and the clusters formation can be prevented by a rigorous synthesis conditions control [8].

For all these reasons the present paper focuses on the synthesis and analysis of the new Keggin monolacunar polyoxoanion containing As(V) as primer heteroatom and: V(V) and W(VI) as addends. The monolacunar anion stabilizations were done by Zn (II) complexation.

To establish the heteropolyanion synthesis recipe an important step were the study of optimum *p*H value (which decided the monolacunar form of the anion) [8,9] and the quick crystallization process, by a quick cooling on an ice and ammonium chloride mixture, for both: polyanion and Zn complex; to provide the stabilization of the polyanion desired form and to increase the synthesis efficiency [10,11].

Experimental part

Reagents

All reagents used were of analytical reagent grade (E. Merk) and the solutions were prepared with double distilled water. An acetic acid- sodium acetate buffer (*p*H= 4,5-5) was used for the conductmetric studies.

Apparatus

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

The thermo gravimetric curves were registered 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 between Zn^{2+} and heteropolyanion, $[AsW_{10}VO_{39}]^{8-}$, were determined using the conductmetric method with a multimeter Inolab Multi 720, in acetic tampon solution. The Inolab Multi 720 multimeter was used also for the *p*H and temperature monitoring connected with a thermostatic magnetic stirrer with temperature sensor.

An UV-VIS spectrometer Perkin Elmer Lambda3 was used to establish the optimal Zn complex formation conditions and to investigate the structure of the formed complex. The structure of the complex was investigated also in the IR dominium 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.

General procedure

The monolacunar heteropolyanion synthesis $K_8[AsW_{10}VO_{39}]\cdot 16\ H_2O$

0.01 mol $NaVO_3{\cdot}2H_2O$; 0,1 mol $Na_2WO_4{\cdot}2H_2O$ and 0.005 mol As_2O_5 were dissolved in 50 mL double distillate water with a continuous solution mixing. The solution *p*H value were regulate at *p*H=3,5 with H_2SO_4 1M, adding the acid drop by drop meantime continuous mixing (the *p*H value were monitorized using a pH-meter).

The resulting solution was maintained at room temperature under continuous mixing process for 1 h and then 7.5 g KCl, in small successive, quantities were added continuing the solution mixing. The final solution was cooled on an ice and ammonium chloride mixture (- 4°C) for 30 min.

The orange colour microcrystal of the desire product, $K_8[AsW_{10}VO_{39}]\cdot 16H_2O$ were obtained.

The Zn complex synthesis, $K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$

0.0065 mol $K_8[AsW_{10}VO_{39}]\cdot 15H_2O$ were dissolved in minimum water quantity and heated at 40°C. The obtained solution was maintained at constant temperature and an

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Tabel 1

$K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ ELEMENTARY ANALYSIS

Formula	η %	%	Determined	Calculated
$K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$	63	W	57.98	57.87
		V	1.54	1.60
		As	2.13	2.35
		Zn	2.05	2.05
		K	7.45	7.38
		H_2O (constitution)	0,57	0.56
		H_2O (crystallization)	8.65	8.50

Tabel 2

UV STUDY FOR COMPLEX $K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ FORMATION, CONC. $5\cdot 10^{-3}$M

Reaction conditions Temperature/time	Absorbance value (λ=280 nm)/pH					
	pH=3.6	pH=4	pH=4.5	pH=5	pH=5.5	pH=6
25 °C/30 minutes	0.730	0.745	0.752	0.750	0.740	0.730
40°C/30 minutes	0.750	0.752	0.755	0.750	0.745	0.700
60°C/30 minutes	0.742	0.745	0.747	0.742	0.735	0.680
80°C/30 minutes	0.740	0.742	0.745	0.740	0.735	0.680
100°C/30 minutes	0.730	0.735	0.740	0.735	0.730	0.670
40°C/30 minutes	0.760	0.765	0.770	0.765	0.752	0.700
40°C/60 minutes	0.763	0.767	0.772	0.763	0.755	0.700

equimolecular $ZnCl_2$ quantity were added under continuous stirring. The solution *p*H value was fixed at *p*H=4,5 with H_2SO_4 1 added drop by drop and then the reagents were stirred for 30 min at constant *p*H and temperature. The obtained solution was cooled for 30 min on an ice and NH_4Cl mixture. The obtained yellow-orange crystals $K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ were separated by filtration (yield 63% - table 1).

$K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$elemental analysis

The elemental analysis results are presented in table 1. The metal contents of the sample were determined by atomic emission spectrometry. For the As content determination the sample was treated with Zn and conc. HCl therefore AsH_3 was obtained. The AsH_3 were captured in HNO_3 to obtain H_3AsO_4 which was spectrometrically determined as reduced arsenomolybdate at 840 nm [12].

The optimum Zn complex formation conditions were established studding different molar reagents mixture, different temperature, *p*H values and temperature using spectrometric method (table 2).

The H_2O content was calculated from the TG curves (table 3). The combination rate between Zn^{2+} and polyanionic addend $[AsW_{10}VO_{39}]^{8-}$ were demined in acetate buffer using conduct metric method (table 4).

The obtained complex structure was investigating using UV-VIS and IR spectrometry (table 5).

Results and discussions

Zn complex formation conductmetric study

The conductmetric studies were performed on solutions: $5\cdot 10^{-3}$ M $K_8[AsW_{10}VO_{39}]\cdot 15H_2O$ and $5\cdot 10^{-3}$ $ZnCl_2$, in different ratio mixture (0.2-2.5) in acetic buffer (*p*H=5). The obtained curve shows an inflexion for the 1:1 molar ratio.

To investigate the optimum conditions for the complex formation were registered UV spectra for equimolecular mixture of reagents at different *p*H values (regulated with acetic buffer) at 280 nm, different temperature values and reaction time length. The maximum were registered at *p*H = 4,5, 40°C after 1h (table 2).

$K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ thermal analysis

The thermal analysis was performed to establish the crystallisation and constitution water and also for the structure evaluation; temperature range investigated was 20-800°C (table 3).

The dehydration is a two step process. The first loss of the crystallisation water (also named lattice water) occurs at ∼ 120 °C. The second step in the dehydration is also an endothermic process and it involves the loss of the constitution water (also named structure water) at ∼300 °C.

In the DTG curve were registered two picks: at 350°C and respectively 355°C, which were assigned to the As_2O_5 decomposition in As_2O_3 and to the As_2O_3volatilisation (in

Tabel 3

$K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ THERMOGRAVIMETRIC ANALYSIS DATA

Temperature/°C	DTA /°C endo	exo	TG /% Calculated	Registered.	assigned
20-40	120	-	8.50	8.55	15 H_2O
	-	300	0.56	0.5	1 H_2O
	350 355	-	3.91	3.56	0,5 As_2O_5
400-1000	470	-	-	-	-
	620	-	-	-	0,5 V_2O_5 10 WO_3
	720	-	-	-	

Tabel 4

$K_6[Zn(AsW_{10}VO_{39})(H_2O)]$. $15H_2O$ IR SPECTRA VALUES

V-O	M-O-M (M=W)	M-O	As-O	H_2O (crystallisation)
530m^{-1}	800cm^{-1}	950m^{-1}	1000 $^{-1}$	1680m^{-1}

Table 5

$K_8[AsW_{10}VO_{39}]$’”$15H_2O$ AND $K_6[Zn(AsW_{10}VO_{39})(H_2O)]$. $15H_2O$ UV SPECTRA DATA

Compound	Bond M=O M=W		M-O-M M=W	
	ν (cm^{-1})	λ (nm)	ν (cm^{-1})	λ (nm)
$K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$	46070	216	34700	290
$K_8[AsW_{10}VO_{39}]\cdot 15H_2O$	46070	216	35000	285

correspondence with As_2O_5 0,5 molls). The residual mass corresponds to the stoechiometric quantities of metal oxides. The elemental analysis shows the absence of As in solid residues.

The DTA curve endothermic reaction corresponding to the picks in the temperature range: 620-720°C was assigned to the oxides crystalline transformation: at ~ 480°C WO_3 tetragonal change to rhombic, at ~ 600°C V_2O_5 melts, and in the domain 720-740°C MoO_3 change from tetragonal into rhombic and WO_3 rhombic becomes powder [10,11].

The crystalline phase formed at 400°C is a mixture of metal oxides in stoichiometric ratios 10 WO_3/0.5 V_2O_5, results obtained by comparing the obtained and the calculated calcinations residue.

IR a $K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ spectrometric analysis

The complex $K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 17H_2O$ presents an absorption bands deviation in higher domain comparatively to the heteropolyacid. This deviation can be explained by the molecular stabilisation after the coordination with Zn(II) [10-13]. At the room temperature the IR spectrum presents absorption bands in domain: 500-1700 cm^{-1} (table 4). The 1680 cm^{-1} band were assigned to the crystallisation water molecules in agreement with X ray studies done for byheteropolyanions [10,12-14], studies which demonstrate the involving of this molecules in hydrogen bonds with heteropolyacids molecules and also between them.

In the 1000-700 cm^{-1} domain the picks were assigned to the M-O_b-M and M-O_t, (M = W, V) bonds.

The V-O, M-O, M-O-M (M = W) and As-O (table 4) picks were assigned in conformity with the literature dates regarding other Keggin triheteropolyacids [11,14,15].

The presence of a single unfork pick in the domain assigned for As valence reflects that all As-O bonds are equal therefore the structure of the heteropolyanion is Keggin type [16].

$K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ UV spectrometric analysis

The registered energy band assigned for d_x-p_x transition between the addend atom and O values for Zn(II) complex are removed to higher energy bands values comparatively to the corresponding triheteropolyacid. The shift to higher energy for the Zn(II) complex M=O energy bands values comparatively to heteropolyanions values is not significant (table 5). This can be explained by the using of only one donor terminal oxigen atom from AsO_4 group bond Zn(II). The energy bands values for the d_π-p_π-d_π electronic transitions in M-O-M bonds for the complex are at lower values that suggested the fact that the oxygen atoms from these bonds are involved in Zn(II) coordination [17].

The picnometric density measurement was performed using acetone as liquid and had a ± 0.05 g/cm^3 precision. The experimental density value is 3.75 g/cm^3. The number of $AsW_{10}V$ groups from elementary cell is Z=4.150H≈4.

The anion reticular values are: a=20.3Å, b= 15.3Å, C=18Å, $\alpha=\beta=\gamma=90^\circ$ characteristic for orthorhombic structure. That compound is isomorphic with other monolacunar Keggin heteropolyanions containing P [18].

Conclusions

$K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ synthesis rationalisation has been based on literature data [5,6,10,11] by adapting reactions condition for the reagents mixture at 25°, *p*H at 3.5 for 1h.

To establish the synthesis product the crystalization process was made on an ice and ammonium chloride mixture (-4° C). The synthesis yield value 63% can be due also to the increase of the crystalisation rate.

The $K_6[Zn(AsW_{10}VO_{39})(H_2O)]\cdot 15H_2O$ characterization was done using: elementary analysis, atomic absorption, UV-IR-spectra and thermogravimetric treatment.

The combination rate between Zn(II) and heteropolyanion was establish using conductmetric method and the conditions (40°C, *p*H=4.5 and 1h) for the complex formation using visible spectrophotometric method.

The crystal structural studies were based on X-ray diffraction method that confirm the monolacunar Keggin structure isomorphic with other monolacunar Keggin heteropolyanions containing P[18] and reveal an orthorhombic structure.

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