

SYNTHESIS AND TG/DTA STUDY ON TWO NEW METALLO(VI)–ARSENATO(V) HETEROPOLYACIDS CONTAINING VANADIUM(V)

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Abstract

An improved method for the synthesis of two heteropolyacids of the same type: $H_5[AsMo_{10}V_2O_{40}] \cdot 13H_2O$ and $H_5[AsW_{10}V_2O_{40}] \cdot 16H_2O$ was elaborated. The studied compounds were characterized by elemental analysis, IR spectra and thermal behaviour over 20–800°C temperature range.

Keywords: IR spectra, Keggin triheteropolyacids, thermal behaviour

Introduction

Keggin triheteropolyacids and their compounds have special redox properties that have been the subject of electrochemical studies in order to investigate their electrochemical [1–7] or analytical behaviour [8–10].

In this work the following heteropolyacids with 12 metal centres: $H_5[AsM_{10}V_2O_{40}] \cdot nH_2O$ ($M=Mo$ or W) were obtained and characterized (Table 1).

The thermal behaviour of these compounds was studied by means of TG/DTA measurements. To characterise the compounds atomic emission spectrometry and IR spectra were performed.

Experimental

The heteropolyacids were obtained by a modified version of Kokorin's synthesis $H_x[EM'_yM''_zO_{40}] \cdot nH_2O$ ($E=P, Si$; $M'=Mo, W$; $M''=V, W$) methods [11–14]. The new method used the following molar ratios between the reagents and the following recipe: an aqueous solution of As_2O_5 (0.005 mol) were treated with an aqueous solution

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of a mixture of: $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ (0.02 mol) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.10 mol), respectively, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 mol).

For either the compound, the obtained hot solution pH was adjusted to the value of 1.5 using 1 M H_2SO_4 and then 2 h boiled. The free $\text{H}_5[\text{AsM}_{10}\text{V}_2\text{O}_{40}] \cdot n\text{H}_2\text{O}$ ($M=\text{Mo}$ or W) with red-orange colours were obtained from the solution by double ether extraction and recrystallized in the presence of water at room temperature in darkness, with considerable yield, between 79 and 83% (Table 1).

Table 1 Some elemental analytical data of the studied heteropolyacids

Compound	η	Component	Analysis/%	
			calc.	found
1 $\text{H}_5[\text{AsW}_{10}\text{V}_2\text{O}_{40}] \cdot 16\text{H}_2\text{O}$	83%	W	62.35	62.21
		V	3.45	3.36
		As	2.54	2.45
		H_2O (constitution)	1.34	1.25
		H_2O (crystallization)	9.77	9.68
2 $\text{H}_5[\text{AsMo}_{10}\text{V}_2\text{O}_{40}] \cdot 13\text{H}_2\text{O}$	79%	Mo	47.60	47.43
		V	5.05	4.90
		As	3.71	3.39
		H_2O (constitution)	2.00	1.64
		H_2O (crystallization)	11.62	11.48

The metal contents (Mo, W, V) of the sample were determined by atomic emission spectrometry with frame on Baird Spectrovac 2000 (The Netherlands). For the As content determination the heteropolyacid was treated with Zn and conc. HCl therefore AsH_3 was obtained. Then AsH_3 were captured in HNO_3 to obtain H_3AsO_4 which was spectrophotometric determinate as reduced arsenomolybdate at 840 nm [15].

The H_2O content was calculated from the TG curves. The IR spectra were recorded in KBr pellets with an UR-20 spectrophotometer.

The thermal behaviour was studied with an OD-103 MOM derivatograph (Hungary), sample mass: $200 \pm 1-2$ mg, the sensitivity of the balance 50 mg, heating rate: $10^\circ\text{C min}^{-1}$, reference material: Al_2O_3 , atmosphere: static air.

Results and discussions

In the modified synthesis method suggested in the present paper the output increases from 50 to 83% comparatively to the classical method [11–14]. Two new factors optimizing the synthesis reaction of the two compounds, namely the reagents ratios and the value of the media pH-s stabilized at 1.5 (this class of heteropolyacids are stable in aqueous medium at this pH value, as was suggested in the electrochemical cyclic voltammetry studies [1–7]).

The obtained heteropolycompounds are highly soluble in water and decompose in aqueous medium at $\text{pH} > 5$.

IR spectra

At room temperature the IR spectra of the two compounds present absorption bands in the 468–1623 cm^{-1} region of the spectrum (Table 2).

Table 2 IR spectrum peaks and their assignment

Compound	Peaks/ cm^{-1} at assign ($M=W, Mo$)				
	V–O	M–O–M	M–O	As–O	H ₂ O (crystallization)
1 $\text{H}_5[\text{AsW}_{10}\text{V}_2\text{O}_{40}] \cdot 16\text{H}_2\text{O}$	518	780	902	983	1623
2 $\text{H}_5[\text{AsMo}_{10}\text{V}_2\text{O}_{40}] \cdot 13\text{H}_2\text{O}$	512	769	893	961	1617

The bands from 1623 and 1617 were assigned to the crystallization water molecules in agreement with X-ray diffraction effectuated on diheteropolyacids [15, 16]. The mentioned studies showed the involvement of these water molecules in hydrogen bonds between the molecules placed inside the heteropolyacid molecule or between the molecules themselves.

The other peaks were assigned to: V–O, M–O, M–O–M ($M=Mo, W$) and As–O valence vibration in conformity to other Keggin triheteropolyacids IR spectra [17–23].

The two obtained triheteropolyacids are Keggin ungapping type because the As–O valence vibration peak it is not fork [22–27], that means that all As–O bonds are length equal.

All the bands from those two studied compounds spectra are lightly displace in lower frequencies dominium 468–1623 cm^{-1} comparatively to 680–1700 cm^{-1} for the following triheteropolyacids: $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}] \cdot n\text{H}_2\text{O}$, $\text{H}_5[\text{PW}_{10}\text{V}_2\text{O}_{40}] \cdot n\text{H}_2\text{O}$, $\text{H}_5[\text{SiMo}_{10}\text{V}_2\text{O}_{40}] \cdot n\text{H}_2\text{O}$ and $\text{H}_4[\text{PMo}_6\text{W}_6\text{O}_{40}] \cdot n\text{H}_2\text{O}$, [22] fact that can be explained by the nature of P or Si central atom. Therefore the As–O bounds strength for the studied heteropolyacids are lower than the E–O ($E=P, Si$) bounds strength for the upper mentioned heteropolyacids.

Thermal analysis

The two studied compounds show similar thermal behaviour. Figure 1 shows one representative TG, DTG and DTA curves recorded for $\text{H}_5[\text{AsW}_{10}\text{V}_2\text{O}_{40}] \cdot 16\text{H}_2\text{O}$.

The main processes and their characterisation are given in Table 3. The dehydration is a two-step process. The first loss of the crystallisation water (also named lattice water) occurs at $\sim 120^\circ\text{C}$. The constitution water determines an increase of the lattice cohesion by the formation of hydrogen bonds with the terminal oxygen atom [16], confirmed by the t_{max} value of the reaction, which increases as $t_1 < t_2$, in agreement with the increase of number of the crystallisation water molecules.

The second step in the dehydration is also an endothermic process and it involves the loss of the constitution water (also named structure water). This loss sig-

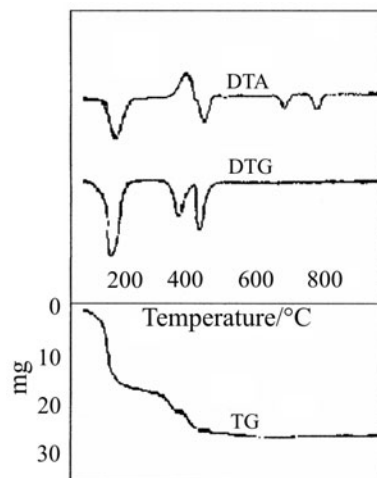


Fig. 1 TG, DTG and DTA curves of $H_5[AsW_{10}V_2O_{40}] \cdot 16H_2O$

nificantly influences the geometry of the molecule, leading to a new structural rearrangement of the polyanionic complex for the compounds at $\sim 300^\circ C$.

Table 3 Thermal data of the triheteropolyacids

Compound	Temp. range/ $^\circ C$	DTA peak/ $^\circ C$		TG data/%		Assign.
		endo	exo	calcd.	found	
1 $H_5[AsW_{10}V_2O_{40}] \cdot 16H_2O$	20–400	115	–	9.77	10.12	$16H_2O$
		–	303	1.53	1.94	$2.5H_2O$
		350	–	3.91	3.56	$0.5As_2O_5$
	400–1000	470	–	–	–	–
		610	–	–	–	V_2O_5
		722	–	–	–	and WO_3
20–400	108	–	11.62	12.50	$13H_2O$	
	–	307	2.25	2.48	$2.5H_2O$	
	355	–	5.73	5.40	$0.5As_2O_5$	
2 $H_5[AsMo_{10}V_2O_{40}] \cdot 13H_2O$	400–1000	485	–	–	–	–
		600	–	–	–	V_2O_5
		738	–	–	–	and MoO_3
	20–400	–	–	–	–	–

In the DTG curve of the compounds the peak at $350^\circ C$, respectively, at $355^\circ C$ was assigned to a mass loss corresponding both to 0.5 mol As_2O_5 (in good agreement with the transformation of As_2O_5 into As_2O_3 and the volatilization of As_2O_3) and to the obtained residue which corresponds to the stoichiometric ratio of the metal oxides. The elemental analysis shows the absence of As in the solid residues.

The endothermic reactions from 470–738°C in DTA curves correspond to the crystalline phase transformation of the oxides: at ~480°C WO₃ changes its geometry from tetragonal to rhombic, at ~600°C one can observe the melting of V₂O₅ and in the 720–740°C temperature range, the tetragonal MoO₃ and WO₃ becomes rhombic [28].

The crystalline phase formed at 400°C is a mixture of metal oxides in stoichiometric ratios 10WO₃+V₂O₅ and 10MoO₃+V₂O₅, results obtained by comparing the obtained and the calculated calcinations residue.

Conclusions

The triheteropolyacids synthesis method suggested in the present paper increases the efficiency comparatively to the classical method. The obtained compounds were characterized by elemental analysis, IR spectra and thermal behaviour over 20–800°C temperature range and their determinate formula is:



The crystalline phase formed at 400°C is a mixture of metal oxides in stoichiometric ratios, results that allow us to propose an alternative method for the synthesis of a mixture of two oxides with a known composition, a method which consists of calcinations of the compounds at ~400°C.

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