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E.S. Duvanova, S.V. Radio, G.M. Rozantsev, K.S. Yutilova

SYNTHESIS AND THERMOLYSIS OF SODIUM–MANGANESE PARATUNGSTATE



Vasyl' Stus Donetsk National University, Vinnytsia, Ukraine

A new procedure for the preparation of sodium–manganese paratungstate was developed and used to synthesize $\text{Na}_5[\text{Mn}_{2.5}(\text{W}_{12}\text{O}_{40}(\text{OH})_2)] \cdot 36\text{H}_2\text{O}$. This procedure implies an acidity ratio represented as $Z=C(\text{H}^+)/C(\text{WO}_4^{2-})=1.00$ and a component ratio of $C_{\text{W}}:C_{\text{Mn}}=6:1$, which enables the synthesis of compounds to be faster, more cost-effective, and with lower energy consumption. The composition and single-phase nature of the compound was confirmed by elemental analysis and scanning electron microscopy. Furthermore, the nature of the paratungstate anion within its composition was determined by IR spectroscopy. Thermolysis of synthesized $\text{Na}_5[\text{Mn}_{2.5}(\text{W}_{12}\text{O}_{40}(\text{OH})_2)] \cdot 36\text{H}_2\text{O}$ was studied, revealing that the dehydration process proceeds in a full accordance with the entry of water molecules into the coordination spheres of cations and anions. The sequence of H_2O removal with increasing temperature is as follows: outer sphere; H_2O molecules from the Na coordination environment; H_2O molecules from the Mn coordination environment; and constitutional H_2O molecule from the anion composition.

Keywords: polyoxometalate, manganese, IR spectroscopy, synthesis, thermolysis, scanning electron microscopy, water.

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Introduction

One of the essential topics of modern research is the optimization of synthesis conditions for various isopoly- and heteropoly salts, as well as the investigation of their properties and thermodynamic stability. The lack of a reliable database of thermodynamic characteristics for polycondensation processes leading to the formation of polyoxometalate anions (POMA) often hinders the development of consistent and reproducible methods for salt synthesis. However, some of the salts among POMA have found applications in science, technology, and medicine.

Notably, the use of polyoxotungstates with various cations of d- and f-metals plays a significant role in diverse fields such as analytical chemistry, medicine, electronics, industrial organic synthesis, nanotechnologies, and material science [1–5]. For instance, polyoxotungstates serve as catalysts for olefin oxidation, materials with photochromic properties, sorbents, proton and ion conductors, luminescent compositions, and more. In recent years,

their potential has also been explored in the development of antitumor drugs and antibacterial agents.

In the case of manganese paratungstates B, there is limited information available regarding synthesis methods, and no clear correlation can be established between the composition of the resulting compounds and the synthesis conditions. Typically, these compounds, which exhibit poor reproducibility, are obtained using acetate buffer solutions (pH 4.5–6.0) through exchange reactions or self-assembly methods.

For instance, the salt $\text{Na}_5[\text{Mn}_{2.5}(\text{W}_{12}\text{O}_{40}(\text{OH})_2)] \cdot 36\text{H}_2\text{O}$ was synthesized [6] through a self-assembly reaction involving the mixing of Na_2WO_4 and MnSO_4 (in a molar ratio of 12:1) at 80°C in an acetate buffer solution with pH 4.5. Following cooling to room temperature, pale yellow crystals of the double sodium–manganese(II) paratungstate B $\text{Na}_5[\text{Mn}_{2.5}(\text{W}_{12}\text{O}_{40}(\text{OH})_2)] \cdot 36\text{H}_2\text{O}$ were isolated. The limited reproducibility of this synthesis primarily arises from the fact that, at such a low pH value,

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hydrohepta- and metatungstate anions [7] are expected to predominate in the solution, which should be incorporated into the composition of the synthesized salt. As demonstrated in ref. [8], the use of acetic acid as a proton source stabilizes the paratungstate anion in the solution. Moreover, controlling the yield based on pH value presents challenges because this value is a function of the solution's concentration. Replacing it with acidity represented as $Z=C(H^+)/C(WO_4^{2-})$, which is independent of the solution's concentration, and using nitric acid instead of an acetate buffer, can resolve these issues.

Materials and methods

It is known that the stabilization of paratungstate anions as a result of the formation of ionic associates allows synthesizing d-metal paratungstates in a wide range of acidity. The zone of dominance of the paratungstate-B anion corresponds to acidity range of $Z=1.00-1.17$. Consequently, the lower borderline value was selected for the synthesis process.

Furthermore, it was observed that when using a stoichiometric ratio or an excess of metal cations, or when conducting the reaction at an elevated temperature, an amorphous precipitate forms in the solution. Conversely, when the ratio falls below stoichiometric, the solution remains homogeneous for a certain period, after which crystals of varying sizes and habits begin to form. All of these factors were taken into consideration during the synthesis of manganese paratungstate.

Synthesis of $Na_5Mn_{2.5}[W_{12}O_{40}(OH)_2] \cdot 36H_2O$

At the first stage of the synthesis of sodium–manganese(II) paratungstate, 38.60 mL of Na_2WO_4 solution with $C=0.2591$ mol/L was acidified to the value of $Z=1.00$ with 25.52 mL of HNO_3 solution with $C=0.3919$ mol/L at $T=298$ K. Then, 14.84 mL of $MnCl_2$ solution, $C=0.1123$ mol/L, were added dropwise to it during intensive stirring ($C_w:C_{Mn}=6:1=0.0167$ mol/L), provided that the addition of the next portion of the solution occurred only after the disappearance of the opalescence. In the homogenous system obtained in this way, after 2–3 weeks, pale yellow crystals were isolated and then filtered from the mother liquor, washed with cold water and air-dried to a constant weight.

Infrared (IR) spectroscopy

Pressed thin discs prepared from an exact weight (0.0030 g) of air-dry samples of the obtained salts in the KBr matrix (*puriss. spec.*; 0.6000 g) were used to capture the IR spectra of the synthesized

polyoxotungstate. The imaging was carried out on an IR spectrometer with a Fourier transform (FTIR) «Spectrum BXII» (Perkin-Elmer) in the wavenumbers range of $\lambda=400-4000$ cm^{-1} .

Differential thermal analysis (DTA)

Differential thermal analysis of the salts was performed on a Shimadzu DTG-60H synchronous TG/DTA analyzer in the temperature range from 0°C to 600°C in an air atmosphere (100 mL/min) at a rate of 10°C/min; $\alpha-Al_2O_3$ was used as a standard.

Scanning electron microscopy

The study of the surface morphology and confirmation of the single phase of ground air-dry samples of synthesized salts was carried out by scanning electron (raster) microscopy (SEM) and EDX analysis (analytical complex JSM 6490 LV, JEOL using air-dry samples applied to graphite tape in the mode of backscattered electrons (BES). Elemental analysis was performed using an energy-dispersive X-ray spectrometer and INCA PentaFETx3, Oxford Instruments).

Chemical analysis

For the selected salts, chemical analysis was performed according to the following procedure. The water content in samples of air-dry synthesized salts was determined based on the mass loss after calcination of samples at 773 K ($\delta=0.5\%$).

Initially, to determine the tungsten content, an exact weight of salts (≥ 0.15 g) was treated with a mixture consisting of 15 mL of concentrated HCl and 5 mL of concentrated HNO_3 until the formation of a precipitate of white tungstic acid. The calcination of the precipitate at 1073 K made it possible to obtain the gravimetric form of WO_3 ($\delta=0.5\%$).

The content of manganese (+2) ($\delta=0.8\%$) in the filtrate remaining after separation of $WO_3 \cdot H_2O$, was determined by complexometric titration at pH 9–10 in the presence of Eriochrome Black T.

After the separation of $WO_3 \cdot xH_2O$, in parallel with the determination of the content of M^{2+} Mn^{2+} , Co^{2+} , Cu^{2+} in the filtrate, the volume of which is brought up to 200 ml, the analysis of the content of sodium (I) ($\delta=2\%$) was carried out by the method of atomic absorption spectroscopy. The sodium(I) content was determined using the «Saturn 3» atomic absorption spectrometer in an acetylene-air flame (analytical line 589.6 nm), with a high-frequency electrodeless lamp VSB 2 as the source of resonant radiation (operating at a current of 70 mA).

Results and discussion

The brutto formula of $2.5Na_3O \cdot 2.5MnO \cdot 12WO_3 \cdot 37H_2O$ was derived from the results of chemical elemental analysis. For the pale yellow sample, it was found (calculated), wt.%: Na_2O 4.08 (4.10), MnO 4.67

(4.69), WO_3 73.59 (73.58), H_2O 17.61 (17.63), which can correspond to $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ paratungstate.

To identify the nature of the isopolyanion, an IR spectroscopic analysis was used. This method is considered reliable, especially for compounds with an island structure like metal paratungstates synthesized from solutions. The resulting IR spectrum of the salt shown in Fig. 1 confirms that the compound belongs to paratungstates B, based on the positions of the absorption maxima in the oscillation zone of the tungsten–oxygen framework.

The paratungstate B–anion has a characteristic IR spectrum in the range of $500\text{--}1000\text{ cm}^{-1}$ both in terms of the position of the absorption bands and their intensity. In the spectrum, absorption bands of tungsten-terminal oxygen ($\text{W}=\text{O}$) type $\nu(\text{A}_1)$, valence symmetric $\nu_1(\text{A}_1)$ and valence asymmetric $\nu_3(\text{B}_2)$ oscillations of angular bridging groups tungsten–oxygen–tungsten (C_{2v} point group) are recorded. Deformation $\nu(\text{A}_1)$ oscillations recorded in the area of $\nu < 500\text{ cm}^{-1}$ in the paratungstate anion are not characteristic and cannot be used to determine the nature of the anion. Thus, the IR spectrum of $2.5\text{Na}_2\text{O}\cdot 2.5\text{MnO}\cdot 12\text{WO}_3\cdot 37\text{H}_2\text{O}$ is in the agreement with the IR spectra of other paratungstates B, for which the crystal structure has already been determined [9–11], which indicates the presence of paratungstate B–anion $[\text{W}_{12}\text{O}_{40}(\text{OH})_2]^{10-}$ in its composition.

In parallel, the gross composition of the salt and its formula $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ were confirmed by scanning electron microscopy. The averaged EDX analysis was conducted in various zones of the crystal (Table 1) confirmed the molar ratio of $\text{Mn}:\text{W}$ as 2.5:12.

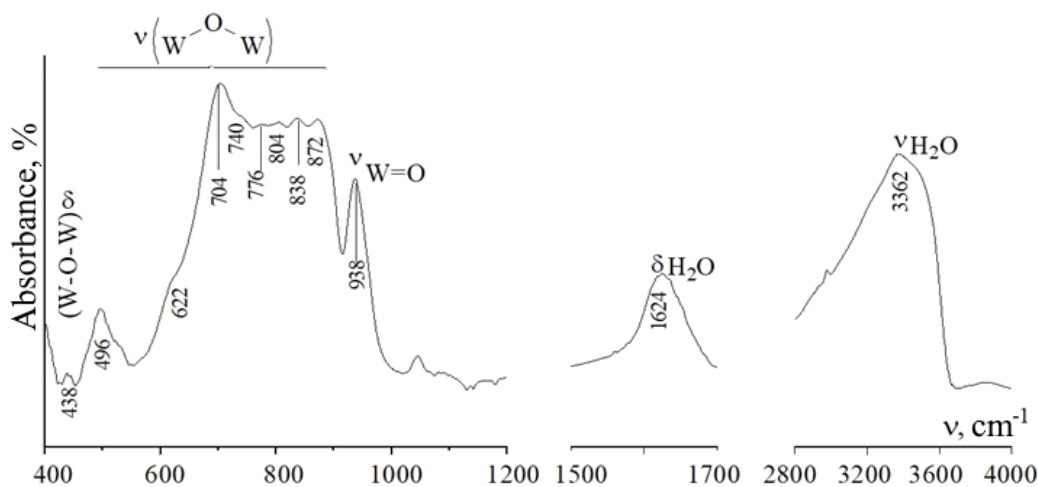


Fig. 1. IR spectrum of $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$

Table 1

Molar ratio* of elements $\text{Na}:\text{Mn}:\text{W}$ in different zones

	Theoretical ratio	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Average value	Standard deviation S
$\nu(\text{Na})$	5.00	5.07	5.13	5.02	5.15	5.12	5.10	0.0526
$\nu(\text{Mn})$	2.50	2.57	2.52	2.59	2.45	2.43	2.51	0.0709
$\nu(\text{W})$	12.00	12.00	12.00	12.00	12.00	12.00	12.00	–

Note: * – ratio is calculated for 12 W atoms.

The SEM images of the $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ sample (Fig. 2) indicates the absence of zones with different surface morphology.

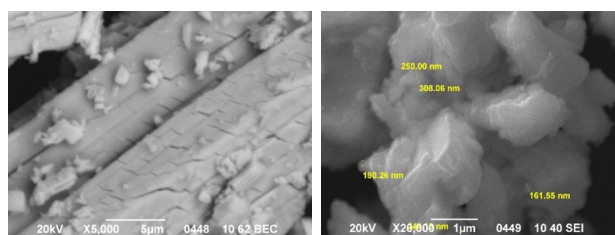


Fig. 2. SEM images of the surface of $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ salt at $\times 5000$ and $\times 20000$ magnification

The uniform contrast of the $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ powder surface in the characteristic X-ray radiation (Fig. 3) indicates a uniform distribution of metals and allows us to confidently state the formation of a single-phase sample.

As already mentioned, paratungstate $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ was previously synthesized [6], and its structure was investigated by

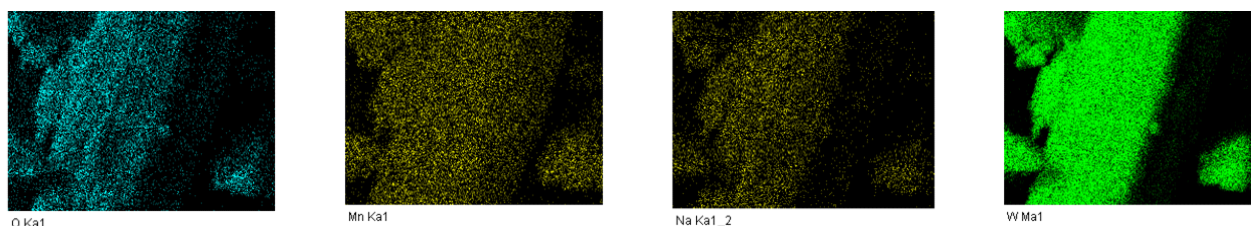


Fig. 3. Surface images of $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ powder in characteristic X-ray radiation (O $\text{K}\alpha_1$, Na $\text{K}\alpha_{1,2}$, Mn $\text{K}\alpha_1$, W $\text{M}\alpha_1$)

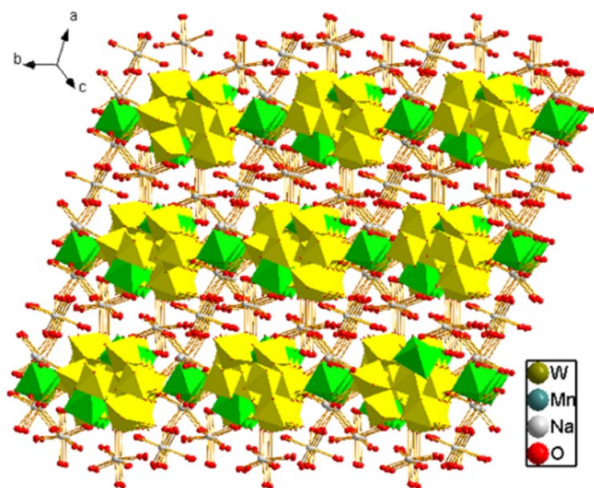


Fig. 4. Combined polyhedral/ball-and-rod representation of a three-dimensional $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ framework [6]

X-ray structural analysis. The resulting structure in the form of a three-dimensional framework is shown

in Fig. 4. Modeling of water molecules made it possible to predict its coordination to cations and present the formula in the form $\text{Na}_{10}\{[\text{Mn}(\text{H}_2\text{O})_3]_2[\text{H}_2\text{W}_{12}\text{O}_{42}]\}\{[\text{Mn}(\text{H}_2\text{O})_3]_2\cdot[\text{Mn}(\text{H}_2\text{O})_4][\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot(6\text{H}_2\text{O})\}$.

As evident, water molecules play a significant role in the structure of sodium–manganese(II) tungstate polyhydric crystal hydrate. They serve as bridges of various types, connecting cationic and anionic fragments. Importantly, these water molecules are known to contribute to the thermal stability of the salt. It is noteworthy that prior to this study, there was a lack of investigation into the thermal behavior of this compound, and no data were available in the existing literature. Therefore, a thermogravimetric analysis was conducted, and the results are presented in the form of a thermogravigram in Fig. 5 and summarized in Table 2.

The results of thermogravimetric analysis for each stage of dehydration can be reconciled according to the data for the type of water given in ref. [6].

At the first stage (up to 75°C), 23 molecules of

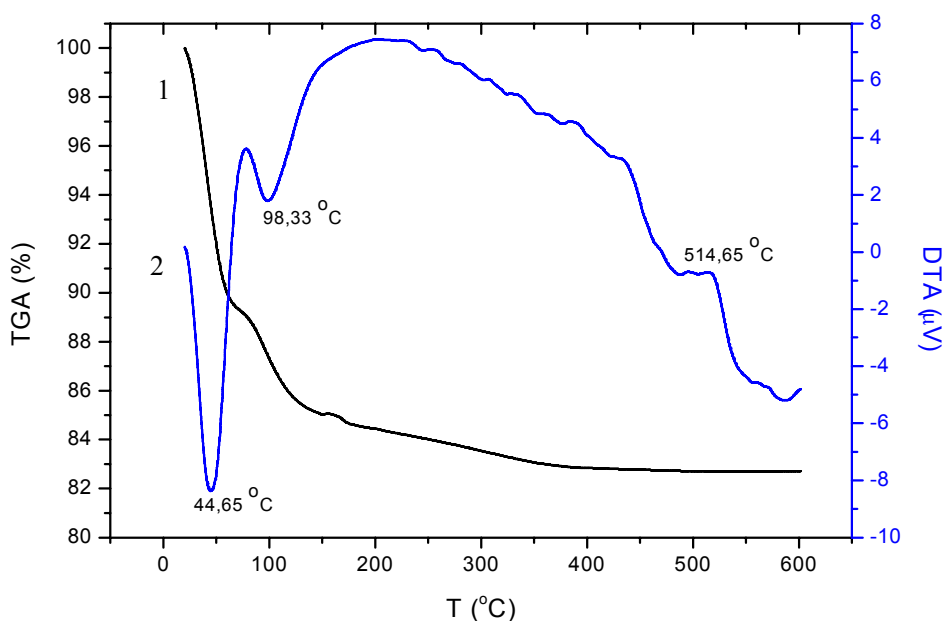


Fig. 5. Thermogravigram of $\text{Na}_5\text{Mn}_{2.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot 36\text{H}_2\text{O}$ (1 – TGA; and 2 – DTA)

Table 2

Thermolysis data on $\{[\text{Na}(\text{H}_2\text{O})_5][\text{Mn}(\text{H}_2\text{O})_3]_2[\text{Mn}(\text{H}_2\text{O})_4]_{0.5}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\} \cdot 23\text{H}_2\text{O}$ sodium–manganese(II) paratungstate B

Stage	T, °C	Weight loss (exp.), %	n(exp.), mol	Weight loss (theor.), %	n(theor.), mol
I	40–75	10.75	–22.56 H ₂ O	10.96	–23.0 H ₂ O
II	75–158	4.21	–8.84 H ₂ O	4.29	–9.0 H ₂ O
III	158–350	1.85	–3.88 H ₂ O	1.91	–4.0 H ₂ O
IV	350–405	0.43	–0.90 H ₂ O	0.48	–1.0 H ₂ O

outer-sphere water, which have the lowest binding energy in the compound, are removed. Most likely, this type of water in the compound is held due to hydrogen bonds. When the temperature increases to 160°C in the second stage, water is released from the $[\text{Na}(\text{H}_2\text{O})_5]$ fragment, which structurally connects adjacent 2-D layers with lamellar Na–O bonds into a three-dimensional framework (Fig. 4).

Heating the samples to the temperature of the first two stages does not affect the structure of the salt anion, and IR spectra retain the oscillations characteristic of the paratungstate tungsten–oxygen skeleton. At the third stage of dehydration, the water included in the fragments of the Mn^{2+} cation is removed. $[\text{Mn}(\text{H}_2\text{O})_3]^{2+}$ groups in the salt structure connect adjacent clusters of paratungstate B $[\text{W}_{12}\text{O}_{40}(\text{OH})_2]^{10-}$ through double bridging groups, forming a one-dimensional anionic chain $\{[\text{Mn}(\text{H}_2\text{O})_3]_2[\text{W}_{12}\text{O}_{40}(\text{OH})_2]_n\}^{6n-}$ along the [1 1 1] direction, and the 1D anionic chains $\{[\text{Mn}(\text{H}_2\text{O})_3]_2[\text{W}_{12}\text{O}_{40}(\text{OH})_2]_n\}^{6n-}$ are connected by cations $[\text{Mn}(\text{H}_2\text{O})_4]^{2+}$ with the formation of 2D layers in the (0 –1 1) plane. Based on this, the removal of H₂O from these fragments should not destroy the isopolyanion itself, but it was not possible to confirm this due to the low resolution of X-ray and IR spectra.

Finally, at the last fourth stage (above 405°C), dehydration of the last water molecule takes place, which is accompanied by the destruction of paratungstate B anion, and exo-effects at temperatures of 510–520°C likely indicate the formation of decomposition products, which can be either Na_2WO_4 , MnWO_4 , and WO_3 .

Conclusions

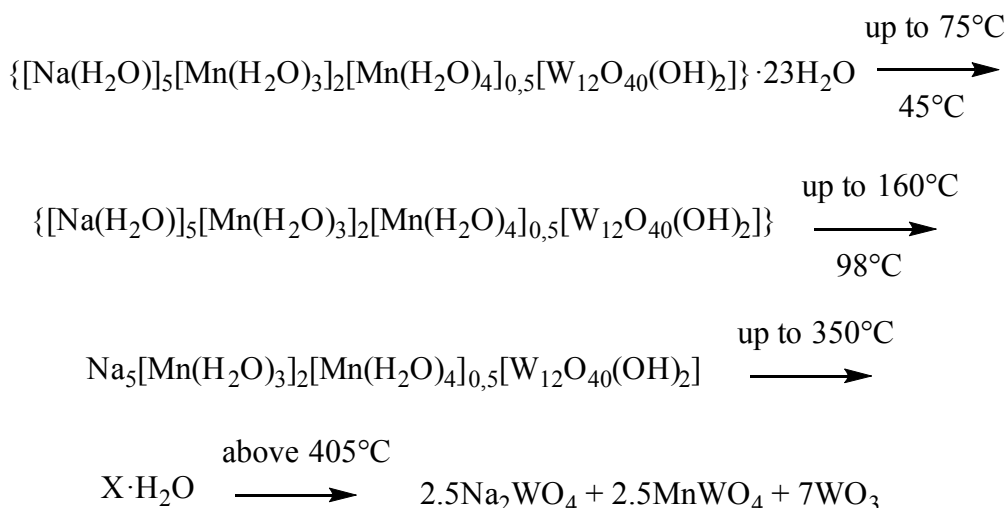
A new procedure for the synthesis of sodium–manganese paratungstate $\text{Na}_5[\text{Mn}_{2.5}(\text{W}_{12}\text{O}_{40}(\text{OH})_2)] \cdot 36\text{H}_2\text{O}$ was developed, the feature of which is the use of solution acidity $Z=1.00$, which, unlike the generally accepted pH value, does not depend on the concentration of the original sodium orthotungstate solution. This approach ensures the necessary predominance of the paratungstate B anion in the presence of d-metal cations, achieved by using nitric

acid instead of an acetate buffer. The low pH value (pH 4.00) of the acetate buffer typically used in such syntheses does not guarantee the unambiguous predominance of the target anion, leading to issues with reproducibility. Consequently, the new synthesis procedure proves to be more efficient, cost-effective, and energy-efficient. It also confirms the stabilization of paratungstate anions in an aqueous solution by d-metal cations.

The dehydration process of the synthesized sodium–manganese paratungstate $\text{Na}_5[\text{Mn}_{2.5}(\text{W}_{12}\text{O}_{40}(\text{OH})_2)] \cdot 36\text{H}_2\text{O}$ follows the characteristic sequence of water removal in aqua-coordinated polyoxometalates, which is associated with varying binding energies, particularly with respect to the available cations. Based on thermolysis data, calculations revealed a complete correspondence between the number of moles of H₂O molecules within the coordination environments of sodium(+) and manganese(2+) cations and their subsequent dehydration. The four-stage dehydration process can be represented as in Scheme.

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Scheme

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СИНТЕЗ ТА ТЕРМОЛІЗ НАТРІЙ–МАНГАН ПАРАВОЛЬФРАМАТУ Na₅[Mn_{2,5}(W₁₂O₄₀(OH)₂)]·36H₂O

Е.С. Дуванова, С.В. Радио, Г.М. Розанцев, К.С. Ютілова

Розроблена і застосована для синтезу нова методика добування натрій–манган. Синтез та термоліз натрій–манган паравольфрамату Na₅[Mn_{2,5}(W₁₂O₄₀(OH)₂)]·36H₂O паравольфрамату Na₅[Mn_{2,5}(W₁₂O₄₀(OH)₂)]·36H₂O, яка полягає у використанні кислотності $Z=C(\text{H}^+)/C(\text{WO}_4^{2-})=1,00$ та співвідношення компонентів $C_{\text{W}}:C_{\text{Mn}}=6:1$, що дозволяє синтезувати сполуки більш експресно, дешево, з меншими енергозатратами. Склад та однофазність сполуки підтверджено методами елементного аналізу та скануючою електронною мікроскопією, а природу паравольфрамат–аніона в її складі встановлено методом ІЧ-спектроскопії. Досліджено термоліз синтезованого Na₅[Mn_{2,5}(W₁₂O₄₀(OH)₂)]·6H₂O і показано, що процес дегідратації відбувається у повній відповідності до входження молекул води в координаційні сфери катіонів та аніона. Послідовність видалення води з підвищенням температури: зовнішньосферна, молекули H₂O з координаційного оточення Na, молекули води з координаційного оточення Mn, молекула конституційної H₂O зі складу аніона.

Keywords: поліоксометалат, манган, ІЧ-спектроскопія, синтез, термоліз, скануюча електронна мікроскопія, вода.

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E.S. Duvanova, S.V. Radio, G.M. Rozantsev, K.S. Yutilova*
Vasyl' Stus Donetsk National University, Vinnytsia, Ukraine
* e-mail: g.rozantsev@donnu.edu.ua

A new procedure for the preparation of sodium–manganese paratungstate was developed and used to synthesize $\text{Na}_5[\text{Mn}_{2.5}(\text{W}_{12}\text{O}_{40}(\text{OH})_2)] \cdot 36\text{H}_2\text{O}$. This procedure implies an acidity ratio represented as $Z=C(\text{H}^+)/C(\text{WO}_4^{2-})=1.00$ and a component ratio of $C_w:C_{\text{Mn}}=6:1$, which enables the synthesis of compounds to be faster, more cost-effective, and with lower energy consumption. The composition and single-phase nature of the compound was confirmed by elemental analysis and scanning electron microscopy. Furthermore, the nature of the paratungstate anion within its composition was determined by IR spectroscopy. Thermolysis of synthesized $\text{Na}_5[\text{Mn}_{2.5}(\text{W}_{12}\text{O}_{40}(\text{OH})_2)] \cdot 36\text{H}_2\text{O}$ was studied, revealing that the dehydration process proceeds in a full accordance with the entry of water molecules into the coordination spheres of cations and anions. The sequence of H_2O removal with increasing temperature is as follows: outer sphere; H_2O molecules from the Na coordination environment; H_2O molecules from the Mn coordination environment; and constitutional H_2O molecule from the anion composition.

Keywords: polyoxometalate; manganese; IR spectroscopy; synthesis; thermolysis; scanning electron microscopy; water.

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