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SYNTHESIS OF MN(II)-CONTAINING PARATUNGSTATE B FROM AQUEOUS SOLUTIONS ACIDIFIED BY ACETIC ACID

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The method of pH-potentiometric titration and mathematical simulation were used to study the equilibrium processes in aqueous solutions of the $WO_4^{2-}-CH_3COOH-H_2O$ system in the acidity range $Z=\nu(CH_3COOH)/\nu(Na_2WO_4)=0.8-1.7$ at $C_W=0.01$ mol L^{-1} and $T=298\pm0.1$ K, a constant ionic strength being maintained by sodium nitrate as a background electrolyte ($\mu(NaNO_3)=0.10$ mol L^{-1}). We developed the models of polyoxotungstate anions formation and the equilibrium transformation processes, which adequately describe experimental pH vs. Z dependences. It was found that acetic acid using to create the solution acidity that is necessary for the formation of isopoly tungstate anion contributes only to the formation of protonated paratungstate B anions $H_x[W_{12}O_{40}(OH)_2]^{(10-x)-}$ (where x=0-4). We calculated the logarithms of the concentration equilibrium constants of the polyanion formation and plotted the distribution diagrams. Double sodium-manganese(II) paratungstate B $Na_8(H_2O)_{28}Mn(H_2O)_2[H_2W_{12}O_{42}]\cdot4H_2O$ was synthesized at Z=1.00 to confirm the results of the mathematical modeling. The chemical composition of the prepared salt was established by chemical elemental analysis, thermal analysis, FTIR spectroscopy, and single crystal X-ray analysis. The stepwise process of salt dehydration was studied by means of differential thermal analysis.

Keywords: ionic equilibrium, isopoly compound, paratungstate B anion, manganese(II), differential thermal analysis, FTIR spectroscopy, single crystal X-ray analysis.

Introduction

Isopoly and heteropoly tungsten-containing compounds have found a wide application in various fields of science, technology and medicine due to the specific structure of the tungsten-oxygen framework in combination with cations of d- and f-metals [1]. Isopoly tungstates, which contain the paratungstate B anion $[W_{12}O_{40}(OH)_2]^{10-}$, are the most studied among these compounds [2]. Paratungstates of d-metals and double paratungstates of s- and d-metals are usually synthesized from acidified aqueous solutions of orthotungstate anion by the process of self-assembly or by an exchange reaction from alkali metal paratungstate dissolved in water. Thus, some of the double sodium manganese (II) paratungstates were synthesized from solution of sodium orthotungstate, where the pH value was fixed by adding the required amount of acetate buffer solution in the following way:

− $Na_2Mn_4[W_{12}O_{40}(OH)_2]\cdot30H_2O$ was prepared via self-assembly from the sodium orthotungstate in an acetate buffer solution (pH 4.44) and manganese (II) chloride [3];

− $Na_{10}Mn_5[W_{12}O_{40}(OH)_2]_2\cdot72H_2O$ was synthesized via self-assembly from a mixture of sodium orthotungstate and manganese (II) chloride (at the molar ratio of 12:1, respectively) in an acetate buffer solution (pH 4.50) [4];

− $K_2Na_4Mn[W_{12}O_{40}(OH)_2]\cdot34H_2O$ was prepared via self-assembly from an aqueous solution of sodium orthotungstate and manganese (II) sulfate (at the molar ratio of 6:1, respectively) in an acetate buffer solution (pH 4.70) [5].

Some other compounds were obtained from sodium or ammonium paratungstate solutions as follows:

− $Na_8Mn[W_{12}O_{40}(OH)_2]\cdot34H_2O$ was synthesized by the exchange reaction from a mixture of sodium paratungstate and manganese (II) chloride in an acetate buffer solution (pH 5.00) [6];

− $Na_2Mn_4[W_{12}O_{40}(OH)_2]\cdot30H_2O$ was prepared by the exchange reaction from a solution of

ammonium paratungstate in a buffer solution (pH 6.20) and manganese (II) sulfate [7].

The analysis of these synthesis procedures does not give the justification of the pH value of the acetate buffer solution, which varies in a rather wide range. Moreover, besides the $H_x[W_{12}O_{40}(OH)_2]^{(10-x)-}$, there are hepta- $HW_7O_{24}^{5-}$ and metatungstate-$[W_{12}O_{38}(OH)_2]^{6-}$ anions in this pH range [8]. The effect of pH on the ratio Mn(II):M$^+$ (M$^+$=Na$^+$, K$^+$) in synthesized salts seems unexpected. This makes it necessary to justify the acetic acid using in the composition of the acetate buffer solution for acidity creation, which would ensure the dominance of the paratungstate B anion over others in weakly acidified sodium tungstate solutions.

Experimental

Precursors

Aqueous solutions of $Na_2WO_4 \cdot 2H_2O$ (reagent grade), CH_3COOH (analytically pure), $MnCl_2 \cdot 4H_2O$ (reagent grade), $NaNO_3$ (reagent grade) in bidistilled water purified from CO_2 were used in this work. Determination of the exact concentrations of solutions was carried out according to the techniques described in the literature: Na_2WO_4 − gravimetrically (the gravimetric form of WO_3, $\delta=0.5\%$); CH_3COOH − by titration of the exact portion of $Na_2B_4O_7 \cdot 10H_2O$ (methyl red indicator, $\delta=0.5\%$); $MnCl_2$ − by direct complexometric titration in an ammonia medium (pH 9.0, eriochrome black T (ACS reagent (indicator grade), triturated 1% (w/w) in NaCl), $\delta=0.8\%$) [9]. The $NaNO_3$ solution (2 mol L^{-1}) was used to adjust the ionic strength, it was prepared by dissolving of the exact amount of pre-dried $NaNO_3$ salt.

pH-Potentiometry

Investigations of interactions in an aqueous solution of the system $WO_4^{2-}-CH_3COOH-H_2O$ were carried out by pH-potentiometric titration method in the acidity range Z=$\nu(CH_3COOH)/\nu(Na_2WO_4)$= =0.8−1.7 (here $\nu(CH_3COOH)$ and $\nu(Na_2WO_4)$ are the initial mole quantities of CH_3COOH and Na_2WO_4, respectively) at C_W=0.01 mol L^{-1} and the ionic strength adjusted by $NaNO_3$ ($\mu(NaNO_3)$= =0.10 mol L^{-1}). Initially, the solution that contains sodium tungstate Na_2WO_4 (C_W=0.05 mol L^{-1}) and acetic acid CH_3COOH (C=0.04 mol L^{-1}) and corresponds to the Z=0.8 acidity, was prepared. As far as the selected initial acidity is concerned, there are no significant changes in the state of tungsten (VI) ions in the range of Z=0−0.8, and the mixture of well-studied ortho- and hexatungstate-anions is formed. The prepared acidified solution was intensively stirred for 1 hour, and then an aliquot was taken from it, diluted to the concentration C_W=0.01 mol L^{-1} and titrated with acetic acid in the

range of Z=0.8−1.7. The ionic strength of the solution was adjusted immediately before titration by the addition of the required amount of $NaNO_3$ solution (2 mol L^{-1}). The pH values (with the accuracy of $\sigma \leq \pm 0.04$) were measured on a Hanna Instruments pH 211 ion meter in thermostated solutions at 298±0.1 K with a titration step of ΔZ=0.02. Hydrogen-ion selective glass electrode HI 1131B was served as the indicator electrode. Small temperature fluctuations were compensated by thermocompensating apparatus TDL-1000. The electrodes were calibrated with buffer solutions of potassium hydrogen phthalate (pH 4.01) and sodium tetraborate (pH 9.18). The dependences pH vs. Z obtained during titration were used for modeling the equilibria processes in the solution.

Mathematical modeling method of equilibria in solution

To create a mathematical model of equilibria chemical processes in the $WO_4^{2-}-H^+-H_2O$ system by the Newton method (quasi-Newton) using the CLINP 2.1 software, a search for an adequate reactions was carried out, which involve the mass action law and the material balance equation [10]. To give the mathematical representation of experimental data (i.e. dependences pH vs. Z), a theoretical model was formed using the most probable reactions of the isopoly and heteropoly anions formation. This model provides an effective way to accelerate the convergence of calculation and experimental results. A number of widely known and described in the literature isopoly tungstate anions were included in a set of defined equations. Then, a sequential rejection optimization of the model was carried out by including in its composition the reactions of isopoly anions formation, which improved the statistical characteristics of the model (χ^2 criterion, criterion function, and mathematical expectation) in comparison with the previously obtained model. Thus, the mathematical model that take into account all of the weightiest anions was created.

During the mathematical modeling with a 95% confidence probability, the logarithms of the concentration equilibrium constants lg K_C of polyoxotungstates anions formation were calculated:

$$12WO_4^{2-}+(14+x+2a)H^+ \leftrightarrow$$
$$\leftrightarrow H_x[W_{12}O_{40-a}(OH)_2]^{(10-x-2a)-}+(6+a)H_2O,$$

$$K_C = \frac{\left[H_xW_{12}O_{40-a}(OH)_2^{(10-x-2a)-} \right]}{\left[WO_4^{2-} \right]^{12} \left[H^+ \right]^{(14+x+2a)}}.$$

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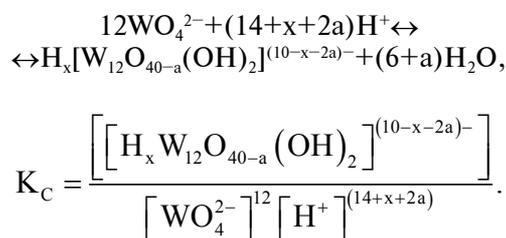
Synthetic and analytical procedures

Manganese isopoly tungstate was precipitated from a solution of the system WO_4^{2-}−CH_3COOH−H_2O with Z=1.00 by adding the Mn^{2+} solution. To this end, the CH_3COOH solution (C=0.2143 mol L^{-1}; V=27.50 mL) was added dropwise with a vigorous stirring to the Na_2WO_4 solution (C=0.2947 mol L^{-1}, V=20.00 mL) diluted with 9.28 mL of distilled water, until reaching the value of Z=1.00. Then, without stopping a vigorous stirring, the $MnCl_2$ solution (C=0.4551 mol L^{-1}; V=2.16 mL) was added dropwise to achieve the ratio C_W:C_{Mn}=6:1. As a result, a pale yellow solution was obtained, and pale yellow needle crystals were precipitated after 3 days from this solution. The crystals were separated by rigorous washing with distilled water, dried in air to achieve a constant weight and then analyzed for the content of the main components. To this end, air-dried samples were decomposed by the mixture of concentrated HCl and HNO_3, the formed yellow tungstic acid being separated and calcined at 800⁰C to the gravimetric form WO_3 (δ=0.5%). After the separation of tungsten, the solution was evaporated almost to dryness, diluted with water, and the manganese content was determined by direct complexometric titration in ammonia medium (pH 9.0, eriochrome black T, δ=0.8%). The content of sodium (σ=±0.15%) was measured by using atomic absorption spectroscopy (Saturn-3 spectrometer; air/acetylene flame, λ=589.0 nm, high-frequency electrodeless VSB-2 lamp, I=70 mA). The content of H_2O in the salts was determined by isothermal annealing of the air-dry samples weights at 500⁰C (δ=0.5%).

The differential thermal technique and spectroscopic studies

To identify the nature of anions in the synthesized salts, FTIR spectroscopic analysis of their air-dry samples was used. FTIR spectra were recorded by a FTIR spectrometer equipped with a FTIR Spectrum BXII (Perkin-Elmer) Fourier transformer in a wavenumber range of 400−4000 cm^{-1}. For this purpose, 0.0030 g of the salt was triturated with a 0.6000 g crystalline potassium bromide KBr (extra-pure grade) and compressed into thin discs. The assignment of vibrations in the FTIR spectra was carried out according to the data [11].

Differential thermal analysis was performed with a detector DTG-60H in the mode of linear temperature rise within the range of 25−600⁰C. The sample was kept in an alumina crucible without a lid.

Results and discussion

The problem of targeted synthesis of isopoly and heteropoly compounds is still not solved and it is at the stage of research, although these complex compounds have been known for a long time. The task of creating the required pH in solutions of orthotungstate anion is one of the most difficult to solve, although pH adjusting would ensure the dominance of isopoly- or heteropoly anion, which is necessary for the preparation of a salt in the solution.

The most convenient and versatile acidity value for this purpose is Z=ν(CH_3COOH)/ν(Na_2WO_4), which includes the initial concentrations of orthotungstate anion and acid, does not depend on concentration and makes it possible to easily create solutions in a wide pH range. The unpredictability of the pH value is the main obstacle during the using of a strong acid, which is highly dependent on the concentration of the solution.

The use of solutions with a predetermined value of Z=1.17, which corresponds to the dominance of the paratungstate anion formed according to the reaction in the solution:

$$12WO_4^{2-}+14H^+\leftrightarrow[W_{12}O_{40}(OH)_2]^{10-}+6H_2O,$$

$$Z=14/12=1.17,$$

made it possible to synthesize paratungstates with the majority of double-charged cations of d-metals of the IV period [12,13].

In the case of acidity Z=1.00, which corresponds to the formation of a heteropolyanion with the Anderson type structure:

$$6WO_4^{2-}+M^{n+}+6H^+\leftrightarrow[M(OH)_6W_6O_{18}]^{(6-n)-}+6H_2O,$$

the salts with this heteropolyanion were obtained only for Ni^{2+} and Cr^{3+} [14,15].

Despite the obvious advantages of the use of acidity value in preparative syntheses, the pH value of the initial solution of orthotungstate anion is more often used. In this case, the pH value varies over a wide range in this solutions, which often raises doubts about the dominance of paratungstate anion $[W_{12}O_{40}(OH)_2]^{10-}$. Thus, the synthesis of the mentioned above double paratungstates of manganese and alkali metals is carried out in solutions with a pH of 4.5 to 6.5, and the lower pH value is already more typical for meta- than for paratungstate anions. The advantage of this synthesis is the use of buffer solutions, which ensures a constant pH during the synthesis at the time of the cation addition and in overcoming the induction period, which is typically in the synthesis of tungstates. The main disadvantage

of the use of buffer solutions is the impossibility to predict the acidity in these solutions even theoretically. This is especially because the buffer solutions are usually used in a large excess.

At the same time, it is possible to adjust the acidity of the solution and provide buffer properties. The use of weak acetic acid instead of strong nitric or hydrochloric acids enables this possibility. In this case, acid protons adjust the acidity and hydrolysis of the resulting acetate anion creates a buffer solution, although with a small buffer capacity, but sufficient to maintain a constant pH.

Mathematical simulation

The mathematical simulation of complexation in Na_2WO_4 $1 \cdot 10^{-2}$ mol L^{-1} solution under the action of protons derived from CH_3COOH was carried out, since there are no systematic literature data on the effect of acetic acid on the state of tungsten (VI) ions in solution. There is one inflection in the titration curve (Fig. 1) at pH 5.92−5.25 in the zone corresponding to the para- and metatungstate anions formation, whereas two jumps are usually observed in the case of the strong acids. The elongation of the jump on the obtained pH vs. Z dependence does not exclude the possibility of the isopolyanions formation. Therefore, the starting model involves only anions and allows high-quality simulation for aqueous and aqueous-organic solutions with a nitric acid as a titrant [8].

It turned out that the starting model did not describe adequately the experimental data, which included hexatungstate-, heptatungstate-, paratungstate B-, and metatungstate-anions formed by the reactions given in Table 1. In addition, the calculated dependence did not correspond to the experimental dependence pH vs. Z (Fig. 1), and the model showed a very high value of the criterion function (i.e. criterion function) CF=9915.35 and an unsatisfactory value of the global criterion of adequacy χ^2_{exp}=1065736>>$\chi^2_{f,\alpha=0.05}$=56.94.

Table 1

Isopolyanion formation reactions in model 1

Reaction	Z
$6WO_4^{2-}+6H^+\leftrightarrow[W_6O_{20}(OH)_2]^{6-}+2H_2O$	1.00
$12WO_4^{2-}+14H^+\leftrightarrow[W_{12}O_{40}(OH)_2]^{10-}+6H_2O$	1.17
$7WO_4^{2-}+8H^+\leftrightarrow[W_7O_{24}]^{6-}+4H_2O$	1.14
$12WO_4^{2-}+15H^+\leftrightarrow H[W_{12}O_{40}(OH)_2]^{9-}+6H_2O$	1.25
$12WO_4^{2-}+18H^+\leftrightarrow[W_{12}O_{38}(OH)_2]^{6-}+8H_2O$	1.50

It should be noted that the highest differences between model 1 and experimental data are observed in the zones of hexa- and metatungstate anions

formation. At the same time, paratungstate B-anions fit well into the model 1 and can create the basis for the subsequent anions formation by adding other isopolyanions to them. The testing of a large number of possible models made it possible to select the set of reactions for the isopolytungstate anion formation and plot the refined dependence pH vs. Z (Fig. 2), which corresponds to the experimentally obtained results (Fig. 2, points).
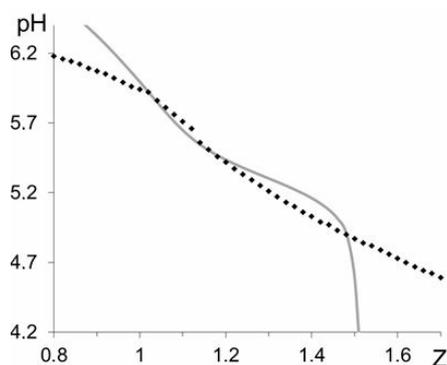
Fig. 1. Experimental (points) and calculated by CLINP 2.1 (lines) pH vs. Z dependences following from the model 1 for the $WO_4^{2-}−CH_3COOH−H_2O$ system, $C(Na_2WO_4)$=0.01 mol L^{-1}, $\mu(NaNO_3)$=0.10 mol L^{-1}
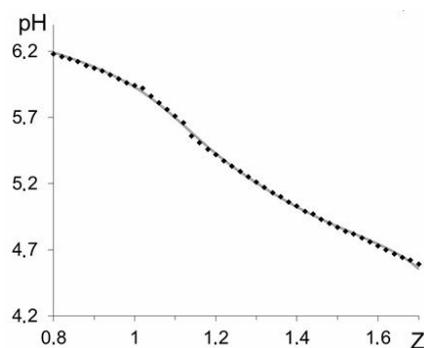
Fig. 2. Experimental (points) and calculated by CLINP 2.1 (lines) pH vs. Z dependences following from the model 2 for the $WO_4^{2-}−CH_3COOH−H_2O$ system, $C(Na_2WO_4)$=0.01 mol L^{-1}, $\mu(NaNO_3)$=0.10 mol L^{-1}

The model 2 has a low criterion function value (criterion function) CF=12.4 and is characterized by a very good global criterion of adequacy χ^2_{exp}=1.66<<$\chi^2_{f,\alpha=0.05}$=56.94. It involved isopolytungstate anions, and the formation reactions of them are given in Table. 2. The logarithms of the concentration equilibrium constants of isopolytungstate formation from an orthotungstate-anion and H^+ (Table 2) were calculated for the model 2, and the ion distribution diagram as a dependence

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Reactions and logarithms of concentrational equilibrium constants of isopolyanions in the model 2

Reactions	Z	lgK$_c$
$12WO_4^{2-}+14H^+\leftrightarrow[W_{12}O_{40}(OH)_2]^{10-}+6H_2O$	1.17	113.54
$12WO_4^{2-}+15H^+\leftrightarrow H[W_{12}O_{40}(OH)_2]^{9-}+6H_2O$	1.25	118.56
$12WO_4^{2-}+16H^+\leftrightarrow H_2[W_{12}O_{40}(OH)_2]^{8-}+6H_2O$	1.33	124.00
$12WO_4^{2-}+17H^+\leftrightarrow H_3[W_{12}O_{40}(OH)_2]^{7-}+6H_2O$	1.42	128.99
$12WO_4^{2-}+18H^+\leftrightarrow H_4[W_{12}O_{40}(OH)_2]^{6-}+6H_2O$ (or $12WO_4^{2-}+18H^+([W_{12}O_{38}(OH)_2]^{6-}+8H_2O)$	1.50	134.21

of the mole fraction on Z was plotted (Fig. 3).
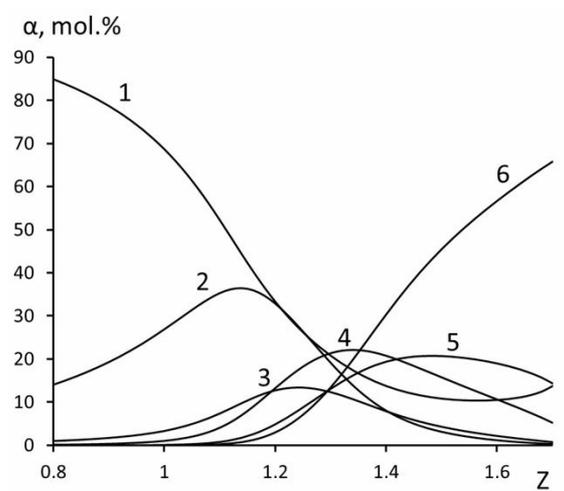
Fig. 3. Ion distribution diagram: $1 - WO_4^{2-}$;
$2 - [W_{12}O_{40}(OH)_2]^{10-}$; $3 - H[W_{12}O_{40}(OH)_2]^{9-}$;
$4 - H_2[W_{12}O_{40}(OH)_2]^{8-}$; $5 - H_3[W_{12}O_{40}(OH)_2]^{7-}$;
$6 - [W_{12}O_{38}(OH)_2]^{6-}$ (or $H_4[W_{12}O_{40}(OH)_2]^{6-}$)

The analysis of the obtained ions distribution shows that the protonated paratungstate anions are mainly formed in the studied range Z=0.8−1.6 according to the generalized reaction:

$$12WO_4^{2-}+(14+x)H^+\leftrightarrow H_x[W_{12}O_{40}(OH)_2]^{(10-x)-}+6H_2O.$$

The behavior of the ions in the solution with an acidity creating by the addition of CH_3COOH is fundamentally different from the behavior of those in solutions where the acidity was achieved by the addition of strong acid (HNO_3). In the second case, the hexatungstate anion (at low acidity), the $HW_7O_{24}^{5-}$ anion (at medium Z) and the $[W_{12}O_{38}(OH)_2]^{6-}$ anion (at high Z) exist in equilibrium with paratungstate anions. All these facts show that the presence of an acetate buffer solution markedly changes the state of isopolyanionic in the solution.

The question of the metatungstate anion formation is quite interesting and, apparently,

debatable. At Z=1.5, it is possible to form the metatungstate

$$12WO_4^{2-}+18H^+\leftrightarrow[W_{12}O_{38}(OH)_2]^{6-}+8H_2O,$$

and the tetraprotonated paratungstate anion

$$12WO_4^{2-}+18H^+\leftrightarrow H_4[W_{12}O_{40}(OH)_2]^{6-}+6H_2O.$$

The last one is supported by the value of the formation beginning at too low acidity (Z~1.00, while it is Z~1.25 in titration by nitric acid) and the inconsistency between the formation constants (about the two orders of magnitude). It is impossible to solve this question by the experimental data; therefore, both options are shown as equally possible in Table 2.

Thus, a model of polycondensation processes in solutions of orthotungstate anion acidified with acetic acid, that includes only the paratungstate anions in the range Z=0.8−1.6, was proposed. This model explains the paratungstate B salts isolation conditions with using of the acetate buffer solutions for creating and stabilizing the pH value required for the synthesis reaction. The studies showed that it is not necessary to use the buffer solutions for this, it was enough to acidify the initial monomer solution with acetic acid, adjusting the required pH in the acidity range. Probably, in the case of buffer solutions, the protonated paratungstate B anions exchanges their protons for the Mn^{2+} cation in the synthesis process, which explains a wide pH range used in the preparation of double salts [3−7].

Synthesis results

To confirm the possibility of the use of acetic acid instead of an acetate buffer solution, the double sodium-manganese(II) paratungstate B $Na_8Mn[W_{12}O_{40}(OH)_2]\cdot34H_2O$ was synthesized according to the above procedure by the self-assembly reaction in the $Mn^{2+}−WO_4^{2-}−CH_3COOH−H_2O$ system with Z=1.00. The paratungstate in work [6] was synthesized by the exchange reaction between the previously obtained sodium paratungstate B and manganese chloride in an aqueous acetate buffer with

pH 5 at T=80°C. The use of acetic acid instead of acetate buffer solution allows obtaining the same sodium paratungstate by simpler self-assembly reaction method, which is described above. The results of chemical analysis confirmed the composition of this salt, which corresponded to the formula $4Na_2O \cdot MnO \cdot 12WO_3 \cdot 35H_2O$. The results of chemical analysis were as follows: calculated (wt.%): Na_2O 6.61; MnO 1.96; WO_3 74.22; and H_2O 17.32; found (wt.%): Na_2O 6.64; MnO 1.90; WO_3 74.55; and H_2O 16.91. The anion in the synthesized polyoxotungstate was identified by FTIR spectroscopy (Fig. 4). The analysis of the registered FTIR spectrum showed that the bands in the vibration range of the tungsten-oxygen framework are similar to the examples, which are described in the literature for salts with paratungstate B anion. They are characteristic in both position and intensity and can be used to identify this anion in the composition of salts. The vibrations of the terminal groups W=O are observed in the range of more than 900 cm^{-1}, and there are stretching and deformation vibrations of linear and angular bridges W−O−W in the range from 400 to 900 cm^{-1}. Thus, the synthesized compound includes paratungstate B anion [12,13].

It should be noted that a slight difference in the content of H_2O molecules had a little impact on the structure of isopolytungstate and the single crystal X-ray analysis showed close crystallographic characteristics of salts obtained by two different methods (Table 3).

The polyhedral packing of double sodium-manganese (II) paratungstate B is shown in Fig. 5.

The structure of $Na_8Mn[W_{12}O_{40}(OH)_2] \cdot 34H_2O$ consists of one-dimensional $[Mn(H_2O)_2(W_{12}O_{40}(OH)_2)]_n^{8-}$ chains bound through $[Na_8(H_2O)_{28}]_n^{8+}$ chains into a two-dimensional network. The coordination polyhedron of the Mn^{2+} ions is a distorted octahedron (d(Mn−O) are in the range 2.147−2.215 Å) formed by four O atoms from two paratungstate B groups and is completed by two H_2O molecules (Fig. 5).

Four crystallographically independent Na^+ ions are placed in distorted octahedral coordination polyhedron formed by six O atoms from H_2O molecules and $[W_{12}O_{40}(OH)_2]^{10-}$ polyanions and form $[Na_4O_3(H_2O)_{15}]$ fragments in an edge-sharing mode. Each $[Na_4O_3(H_2O)_{15}]$ fragment is further bound via corner-sharing mode into a 1D Na−O−Na chain through [−1 0 1] direction. Adjacent $[Mn(H_2O)_2(W_{12}O_{40}(OH)_2)]_n^{8-}$ chains are bound
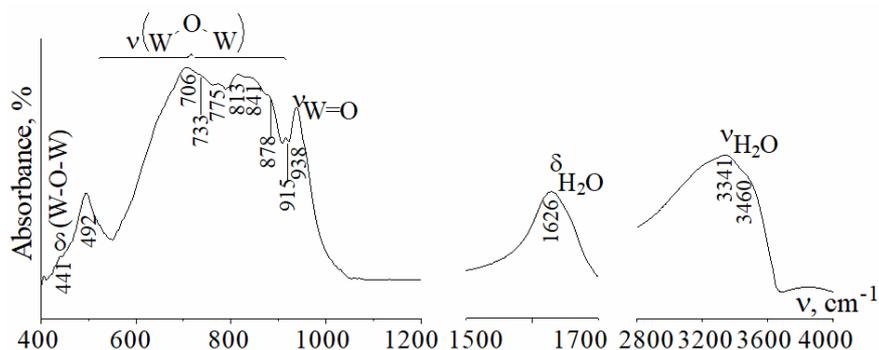
Fig. 4. FTIR spectrum of $Na_8Mn[W_{12}O_{40}(OH)_2] \cdot 34H_2O$

Table 3

Comparison of crystallographic characteristics

Parameter	$Na_8Mn[W_{12}O_{40}(OH)_2] \cdot 34H_2O$ (present research)	$Na_8Mn[W_{12}O_{40}(OH)_2] \cdot 34H_2O$ [6]
T [K]	117(2)	293
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a [Å]	12.6909(9)	12.713(3)
b [Å]	13.0905(9)	13.236(3)
c [Å]	13.1056(10)	13.241(3)
α [°]	65.327(4)	64.43(3)
β [°]	63.086(4)	62.50(3)
γ [°]	63.570(3)	63.77(3)
V [Å³]	1673.7(2)	1698.9(6)
Z	1	1

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Fig. 5. Polyhedral and ball-and-stick presentation of $Na_8Mn[W_{12}O_{40}(OH)_2]\cdot34H_2O$ structure (color codes: WO_6 octahedra are shown by light blue color, Na atoms are shown by blue balls, Mn atoms are shown by green balls, and O atoms are shown by gray balls)

together by Na−O−Na chains through sharing oxygen atoms to generate a 2D layers. Neighboring 2D layers are further extended into a 3D supramolecular network through hydrogen-bonding interactions between the coordinated H_2O molecules, terminal O atoms and uncoordinated H_2O molecules which occupied voids in the structure.

Differential thermal studies results

It is necessary to point out that the difference in the water amount is at least slight, but still affected by the parameters of the crystal lattice (Table 3), so it was interesting to see how this difference affects the dehydration process.

Almost all the salts that contain isopoly anions are polyhydric crystalline hydrates and exhibit multi-stage thermolysis. First of all, we are talking about the processes of dehydration of various types of crystalline hydrate and coordination water in the composition of these compounds. It was previously assumed that by the analogy with the structure described elsewhere [6], the synthesized double sodium-manganese (II) paratungstate B contains 4 H_2O molecules of the crystal hydrate type, 28 H_2O coordinated with cations of Na^+, 2 H_2O coordinated with Mn^{2+}, and one molecule of constitutional H_2O in the form of two OH-groups in the $[W_{12}O_{40}(OH)_2]^{10-}$ [6]. The dehydration process (Fig. 6) fully confirms the presence of coordination and constitutional water, which quite logically explains the stages of dehydration.
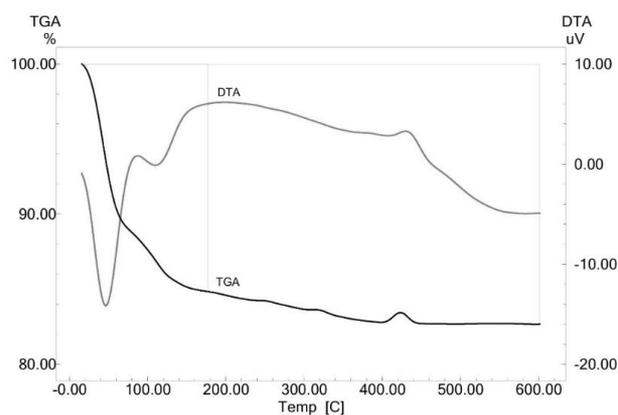
Fig. 6. Thermograms of double sodium-manganese paratungstate B (TGA − thermogravimetric analysis, and DTA − differential thermal analysis)

The analysis of the thermogram indicates a very interesting processes, which occur during the thermolysis of $Na_8(H_2O)_{28}Mn(H_2O)_2[W_{12}O_{40}(OH)_2]\cdot4H_2O$. They are accompanied not only by a sample weight decrease at the I−V, VII stages, but also by a weight increase at the VI stage. In general, the thermolysis process is consequentially presented in Table 4.

At the first five stages (40−400⁰C), based on the formula $Na_8(H_2O)_{28}Mn(H_2O)_2[W_{12}O_{40}(OH)_2]\cdot4H_2O$ derived from the single crystal X-ray analysis results,

Table 4

Stages of weight loss during the thermolysis

Stage	T,^{0}C	Weight loss (exp.), %	v(exp.), mol	Weight loss (theor.), %	v(theor.), %
I	40–105	11.9	−23.9 H_2O	11.6	−24 H_2O
II	105–200	15.0	−30.1 H_2O	14.5	−30 H_2O
III	200–270	15.5	−31.1 H_2O	15.0	−31 H_2O
IV	270–320	16.1	−32.3 H_2O	15.4	−32 H_2O
V	320–400	17.1	−34.3 H_2O	16.4	−34 H_2O
VI	400–410	16.7	+0.45 O_2	16.0	+0.50 O_2
VII	410–420	17.3	−35.5 H_2O	16.5	−35 H_2O

34 water molecules are removed and can be divided on:

− 4 outer-sphere water molecules;

− 28 water molecules coordinated with sodium cation $[Na_8(H_2O)_{28}]^{8+}$;

− 2 water molecules coordinated with the manganese cation $[Mn(H_2O)_2]^{2+}$, which are probably removed at V stage.

Then, an increase in the mass at the VI stage can be associated with the oxidation of manganese to the +4 oxidation state, which is more characteristic at this temperature together with the anion decomposition. The possible scheme of this process at 400−410^{0}C can be written as follows:

$$Mn^{2+}+[W_{12}O_{40}(OH)_2]^{10-}\rightarrow MnO(OH)_2+4W_3O_{10}^{2-}.$$
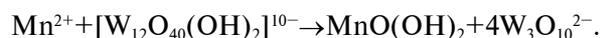
Finally, water molecules are removed during the dehydration of dihydroxooxomanganese(IV) at the VI stage. Certainly, this generalized scheme of thermolysis is hypothetical and requires further detailed study.

Conclusions

It was shown that the application of CH_3COOH instead of HNO_3 for creating the acidity of the solution, which is necessary for the isopolytungstate anions formation, leads to a simplification of the ion state, where the only protonated paratungstate B anions with different amounts of protons are formed. The use of acetic acid instead of buffer solutions allows synthesizing the paratungstate B salts in a wide range of the acidity, that was confirmed by the development of a new synthesis methodic of double sodium-manganese(II) paratungstate B $Na_8(H_2O)_{28}Mn(H_2O)_2[W_{12}O_{40}(OH)_2]\cdot 4H_2O$.

REFERENCES

1. *Bijelic A., Aureliano M., Rompel A.* Polyoxometalates as potential next-generation metallodrugs in the combat against cancer // Angew. Chem. Int. Ed. − 2019. − Vol.58. − P. 2980-2999.

2. *Jassal A.K., Mudsainiyan R.K., Shankar R.* A rational assembly of paradodecatungstate anions from clusters to morphology-controlled nanomaterials // Mater. Chem. Front. − 2021. − Vol.5. − P.1090-1125.

3. *Divalent* manganese linked tungsten-molybdenum polyoxometalates: synthesis, structure, and magnetic characteristics / Zhang X., Dou J., Wang D., Zhang Y., Zhou Y., Li R., Yan S., Ni Z., Jiang J. // Cryst. Growth Des. − 2007. − Vol.7. − No. 9. − P.1699-1705.

4. *A pure* inorganic 2-D framework based on paradodecatungstate and Mn^{2+} ions: syntheses, structure, and properties / Wu L., Yang W., Dong X., Yu C., Liu B., Yan Y., Hu H., Xue G. // J. Coord. Chem. − 2015. − Vol.68. − No. 13. − P.2324-2333.

5. *Synthesis*, crystal structure, electrochemistry and electro-catalytic properties of the manganese-containing polyoxotungstate, $[(Mn(H_2O)_3)_2(H_2W_{12}O_{42})]^{6-}$ / Teillout A.-L., de Oliveira P., Marrot J., Howell R.C., Vila N., Walcarius A., Mbomekalle I.M. // Inorganics. − 2019. − Vol.7. − Article No. 15.

6. *A new* series of polyoxometalate compounds built up of paradodecatungstate anions and transition metal/alkaline-earth metal cations / Yuan L., Qin C., Wang X., Wang E., Li Y. // Solid State Sci. − 2008. − Vol.10. − No. 8. − P.967-975.

7. *Kong Q.-J., Zhang C.-J., Chen Ya-G.* Synthesis, structure and characterization of three highly-connected 3D inorganic compounds based on paradodecatungstate-B // J. Mol. Struct. − 2010. −Vol.964. − P.82-87.

8. *Rozantsev G.M., Sazonova O.I.* Thermodynamic parameters of interconversions of isopolyanions in solutions of tungsten(VI) // Russ. J. Coord. Chem. − 2005. − Vol.31. − No. 8. − P.552-558.

9. *Schwarzenbach G., Flaschka H.* Kompleksono-metricheskoe titrovanie. − M.: Khimiya, 1970. − 360 p.

E.S. Duvanova, A.V. Popova, A.V. Rysich, S.V. Radio, G.M. Rozantsev

10. *Kholin Yu.V.* Kolichestvennyy fiziko-khimicheskiy analiz kompleksoobrazovaniya v rastvorakh i na poverkhnosti khimicheski modifitsirovannykh kremnezemov: soderzhatel'nyye modeli, matematicheskiye metody i ikh prilozheniya. − Kharkiv: Folio, 2000. − 288 p.

11. *George B.L., Aruldhas G., Botto I.L.* Vibrational spectra of sodium paratungstate 26 hydrate, $Na_{10}[H_2W_{12}O_{42}]\cdot26H_2O$ // J. Mater. Sci. Lett. − 1992. − Vol.11. − P.1421-1423.

12. *Aquapolytungstates* of d-metals in a solution with acidity Z=1.00 / Ivantsova E.S, Radio S.V., Rozantsev G.M., Shved E.N. // Voprosy Khimii i Khimicheskoi Tekhnologii. − 2018. − No. 6. − P.34-41.

13. *Crystal* structure of nickel paratungstate B $Ni_5[W_{12}O_{40}(OH)_2]\cdot37H_2O$ / Radio S.V., Rozantsev G.M., Baumer V.N., Shishkin O.V. // J. Struct. Chem. − 2011. − Vol.52. − P.111-117.

14. *Synthesis* and crystal structure of potassium−nickel heteropoly hexatungstonickelate (II) $K_3Ni_{0,5}[Ni(OH)_6W_6O_{18}]\cdot12H_2O$ with Anderson-type anion and potassium−nickel paratungstate B $K_6Ni_2[W_{12}O_{40}(OH)_2]\cdot22H_2O$ / Gumerova N.I., Kasyanova K.V., Rozantsev G.M., Baumer V.N., Radio S.V. // J. Cluster Sci. − 2015. − Vol.26. − No. 4. − P.1171-1186.

15. *Direct* single- and double-side triol-functionalization of the mixed type Anderson polyoxotungstate $[Cr(OH)_3W_6O_{21}]^{6-}$ / Gumerova N.I., Fraile T.C., Roller A., Giester G., Pascual-Borras M., Ohlin A., Rompel A. // Inorg. Chem. − 2019. − Vol.58. − No. 1. − P.106-113.

СИНТЕЗ MN(II)-ВМІСНОГО ПАРАВОЛЬФРАМАТУ Б З ВОДНИХ РОЗЧИНІВ, ПІДКИСЛЕНИХ ОЦТОВОЮ КИСЛОТОЮ

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Методами pH-потенціометричного титрування та математичного моделювання досліджено взаємодію у водному розчині системи $WO_4^{2-}-CH_3COOH-H_2O$ в інтервалі кислотності Z=ν(CH₃COOH)/ν(Na₂WO₄)=0,8−1,7 при C_W=0,01 моль/л і T=298±0,1 K, з фоновим електролітом натрій нітратом μ(NaNO₃)=0,10 моль/л. Запропоновано моделі рівноважних процесів утворення і перетворення поліоксовольфрамат-аніонів, які адекватно описують експериментальні залежності pH=f(Z). Встановлено, що використання оцтової кислоти при створенні необхідної для утворення ізополівольфрамат-аніона кислотності розчину приводить до утворення в розчині тільки гідропаравольфрамат Б аніонів з різним ступенем протонування $[H_xW_{12}O_{40}(OH)_2]^{(10-x)-}$ (x=0−4). Розраховано логарифми концентраційних констант рівноваги реакцій утворення поліаніонів та побудовано діаграми розподілу. Для підтвердження математичних моделей рівноважних процесів при Z=1,00, синтезований подвійний паравольфрамат Б натрію-мангану(II) $Na_8(H_2O)_{28}Mn(H_2O)_2[H_2W_{12}O_{42}]\cdot4H_2O$. Склад виділеної солі був встановлений за допомогою хімічного елементного аналізу, диференціального термічного аналізу, ІЧ-спектроскопії та монокристального рентгеноструктурного аналізу. За допомогою диференціального термічного аналізу вивчено поетапний процес дегідратації солі.

SYNTHESIS OF MN(II)-CONTAINING PARATUNGSTATE B FROM AQUEOUS SOLUTIONS ACIDIFIED BY ACETIC ACID

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The method of pH-potentiometric titration and mathematical simulation were used to study the equilibrium processes in aqueous solutions of the $WO_4^{2-}-CH_3COOH-H_2O$ system in the acidity range Z=ν(CH₃COOH)/ν(Na₂WO₄)=0.8−1.7 at C_W=0.01 mol L⁻¹ and T=298±0.1 K, a constant ionic strength being maintained by sodium nitrate as a background electrolyte (μ(NaNO₃)=0.10 mol L⁻¹). We developed the models of polyoxotungstate anions formation and the equilibrium transformation processes, which adequately describe experimental pH vs. Z dependences. It was found that acetic acid using to create the solution acidity that is necessary for the formation of isopoly tungstate anion contributes only to the formation of protonated paratungstate B anions $H_x[W_{12}O_{40}(OH)_2]^{(10-x)-}$ (where x=0−4). We calculated the logarithms of the concentration equilibrium constants of the polyanion formation and plotted the distribution diagrams. Double sodium-manganese(II) paratungstate B $Na_8(H_2O)_{28}Mn(H_2O)_2[H_2W_{12}O_{42}]\cdot4H_2O$ was synthesized at Z=1.00 to confirm the results of the mathematical modeling. The chemical composition of the prepared salt was established by chemical elemental analysis, thermal analysis, FTIR spectroscopy, and single crystal X-ray analysis. The stepwise process of salt dehydration was studied by means of differential thermal analysis.

REFERENCES

1. Bijelic A, Aureliano M, Rompel A. Polyoxometalates as potential next-generation metallodrugs in the combat against cancer. *Angew Chem Int Ed.* 2019; 58: 2980-2999. doi: 10.1002/anie.201803868.

2. Jassal AK, Mudsainiyan RK, Shankar R. A rational assembly of paradodecatungstate anions from clusters to morphology-controlled nanomaterials. *Mater Chem Front.* 2021; 5: 1090-1125. doi: 10.1039/D0QM00646G.

3. Zhang X, Dou J, Wang D, Zhang Y, Zhou Y, Li R, et al. Divalent manganese linked tungsten−molybdenum polyoxometalates: synthesis, structure, and magnetic characteristics. *Cryst Growth Des.* 2007; 7: 1699-1705. doi: 10.1021/cg060723f.

4. Wu L, Yang W, Dong X, Yu C, Liu B, Yan Y, et al. A pure inorganic 2-D framework based on paradodecatungstate and Mn²⁺ ions: syntheses, structure, and properties. *J Coord Chem.* 2015; 68: 2324-2333. doi: 10.1080/00958972.2015.1046851.

5. Teillout AL, de Oliveira P, Marrot J, Howell RC, Vila N, Walcarius A, et al. Synthesis, crystal structure, electrochemistry and electro-catalytic properties of the manganese-containing polyoxotungstate, $[(Mn(H_2O)_3)_2(H_2W_{12}O_{42})]^{6-}$. *Inorganics.* 2019; 7: 15. doi: 10.3390/inorganics7020015.

6. Yuan L, Qin C, Wang X, Wang E, Li Y. A new series of polyoxometalate compounds built up of paradodecatungstate anions and transition metal/alkaline-earth metal cations. *Solid State Sci.* 2008; 10: 967-975.
doi: 10.1016/j.solidstatesciences.2007.12.011.

7. Kong QJ, Zhang CJ, Chen YG. Synthesis, structure and characterization of three highly-connected 3D inorganic compounds based on paradodecatungstate-B. *J Mol Struct.* 2010; 964: 82-87. doi: 10.1016/j.molstruc.2009.11.015.

8. Rozantsev GM, Sazonova OI. Thermodynamic parameters of interconversions of isopolyanions in solutions of tungsten(VI). *Russ J Coord Chem.* 2005; 31: 552-558.
doi: 10.1007/s11173-005-0135-x.

9. Schwarzenbach G, Flaschka H. *Kompleksonometricheskoe titrovanie* [Complexometric titrations]. Moscow: Khimiya; 1970. 360 p. (*in Russian*).

10. Kholin YV. *Kolichestvennyy fiziko-khimicheskiy analiz kompleksoobrazovaniya v rastvorakh i na poverkhnosti khimicheski modifitsirovannykh kremnezemov: soderzhatel'nyye modeli, matematicheskiye metody i ikh prilozheniya* [Quantitative physicochemical analysis of complex formation in solutions and on chemically modified silicas: content models, mathematical methods, and their applications]. Kharkiv: Folio; 2000. 288 p. (*in Russian*).

11. George BL, Aruldhas G, Botto IL. Vibrational spectra of sodium paratungstate 26 hydrate, $Na_{10}[H_2W_{12}O_{42}]\cdot26H_2O$. *J Mater Sci Lett.* 1992; 11: 1421-1423. doi: 10.1007/BF00729648.

12. Ivantsova ES, Radio SV, Rozantsev GM, Shved EN. Aquapolytungstates of d-metals in a solution with acidity Z=1.00. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2018; (6): 34-41.
doi: 10.32434/0321-4095-2018-121-6-34-41.

13. Radio SV, Rozantsev GM, Baumer VN, Shishkin OV. Crystal structure of nickel paratungstate B $Ni_5[W_{12}O_{40}(OH)_2]\cdot37H_2O$. *J Struct Chem.* 2011; 52: 111-117.
doi: 10.1134/S002247661101015X.

14. Gumerova NI, Kasyanova KV, Rozantsev GM, Baumer VN, Radio SV. Synthesis and crystal structure of potassium−nickel heteropoly hexatungstonickelate (II) $K_3Ni_{0.5}[Ni(OH)_6W_6O_{18}]\cdot12H_2O$ with Anderson-type anion and potassium−nickel paratungstate B $K_6Ni_2[W_{12}O_{40}(OH)_2]\cdot22H_2O$. *J Cluster Sci.* 2015; 26: 1171-1186.
doi: 10.1007/s10876-014-0805-2.

15. Gumerova NI, Fraile TC, Roller A, Giester G, Pascual-Borras M, Ohlin A, et al. Direct single- and double-side triol-functionalization of the mixed type Anderson polyoxotungstate $[Cr(OH)_3W_6O_{21}]^{6-}$. *Inorg Chem.* 2019; 58: 106-113.
doi: 10.1021/acs.inorgchem.8b01740.