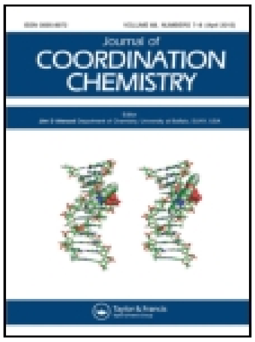

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Phase formation in the system Co^{2+}–$WO_4{}^{2-}$–H^+–C_3H_7ON–H_2O. Synthesis, crystal structure, and characterization of cobalt(II) decatungstate $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]$

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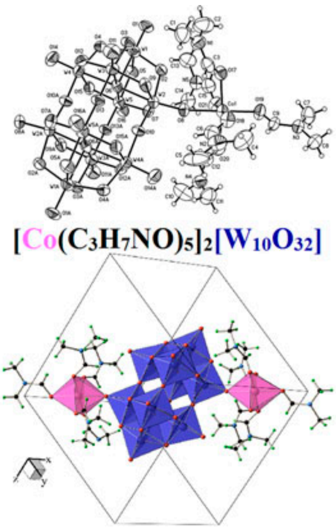

The phase formation processes of isopolytungstates in the system~~s~~ Co^{2+}–WO_4^{2-}–H^+–DMF–H_2O (DMF-dimethylformamide) with different acidities ($Z = \nu(H^+)/\nu(WO_4^{2-}) = 1.14$–$1.60$) have been studied. It was found that only cobalt(II) hepta-, para-, and decatungstates could be isolated from aqueous DMF solutions. The chemical and FTIR spectroscopic analysis of the products isolated from the system allowed determination of conditions of Co(II) decatungstate formation. Cobalt(II)

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decatungstate, $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]$, was characterized by elemental and EDX spectral analysis, SEM, FTIR spectroscopy, thermal analysis, single-crystal X-ray diffraction, and by UV–vis spectroscopy analysis.

Keywords: Isopolytungstates; Decatungstate; Aqueous dimethylformamide solution; Cobalt(II); Crystal structure

1. Introduction

Polyoxometalates (POMs) represent a special class of coordination compounds containing nanosized metal-oxide anions. Compounds with polyoxometalate anions (POMAs) attract interest not only due to their molecular and electronic structure, but also because of their properties that make it possible to use them in various fields such as photochemistry, analytical chemistry, catalysis, biology, and medicine [1].

The formation of various POMAs depends on pH, temperature, the initial concentration of d-metal (V–VI group) salt solution, and polarity of the solvent [2, 3]. POMs are mainly synthesized from aqueous solutions, whereas there is less information about synthesis and properties of POMs obtained from aqueous organic solutions. Dimethylformamide (DMF) is one of the most common solvents used in organic synthesis, where POMs are used as catalysts. That is why study of interactions in systems based on mixtures of water and DMF is an important step for establishing a systematic relationship between the composition of a combined medium and the state of POMAs in it. Also, it is interesting to study the influence of organic and inorganic cations on the structure of isolated isopolytungstates (IPTs).

Previous study of isopolytungstate anions (IPTAs) in aqueous DMF medium [4] showed that in strongly acidified ($Z = \nu(H^+)/\nu(WO_4^{2-}) = 1.60$) aqueous DMF solutions, heptatungstate anions $H_xW_7O_{24}{}^{(6-x)-}$ ($x = 0$–1) and decatungstate anions $W_{10}O_{32}^{4-}$ dominate. Only cobalt(II) paratungstate B could be isolated from aqueous solutions of orthotungstate anion, acidified to $Z = 1.00$–1.29, and the addition of cobalt(II) nitrate to the solutions with $1.35 < Z < 2.00$ generally does not lead to the formation of cobalt IPTs [5]. The salt with decatungstate anion $[Co(NH_3)_5Cl]_2[W_{10}O_{32}]\cdot 4H_2O$ was synthesized from the aqueous solution of sodium tungstate, acidified to pH 2.2–2.4 ($Z > 1.60$), by addition of $[Co(NH_3)_5Cl]Cl_2$, containing Co(III) [6]. Unlike aqueous solutions, no data about the formation of cobalt (II) salts with IPTAs from aqueous organic solutions have been found in the literature.

In this article, we studied the phase formation in acidified solutions of orthotungstate anion in the presence of cobalt(II) cations in a mixed aqueous DMF (40% v/v) solution that made it possible to establish the conditions of formation of cobalt(II) IPTs and synthesize for the first time a cobalt(II) decatungstate $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]$.

2. Experimental

2.1. *Synthetic and analytical procedures*

Aqueous solutions of $Na_2WO_4\cdot 2H_2O$, $Co(NO_3)_2$, HCl, as well as DMF (all reagent grade) were used for the preparation of Co(II) polyoxotungstates. The precise concentrations were defined through chemical analysis: W contents – gravimetrically (gravimetrical form of WO_3, $\delta \le \pm 0.5\%$); Co contents – using a direct complexometric titration ($\delta \le \pm 0.8\%$); HCl concentration – through titration of a weighed portion of sodium tetraborate $Na_2B_4O_7 \cdot 10H_2O$ ($\delta \le \pm 0.5\%$).

The model of IPTAs state in aqueous DMF medium has been described in the previous study [4]. It consisted of $W_6O_{20}(OH)_2^{6-}$, $W_{12}O_{40}(OH)_2^{10-}$, $W_7O_{24}^{6-}$, $HW_7O_{24}^{5-}$, $H_nW_{12}O_{40}(OH)_2^{(10-n)-}$, and $W_{10}O_{32}^{4-}$ for solutions with 40% (v/v) DMF. We decided to investigate the phase formation in solutions with acidities of these IPTAs domination: $Z = 1.14$, 1.17, 1.29, 1.42, 1.60. Moreover, the acidity $Z = 1.50$ was also used as working one, at which formation of $W_{12}O_{38}(OH)_2^{6-}$ theoretically occurs in aqueous solutions.

The salts were obtained by the standard technique [4–9]. So in order to synthesize an IPT in sodium tungstate solution with 40% (v/v) DMF, an appropriate acidity Z was created by dropwise addition of HCl solution under vigorous stirring. Then cobalt(II) nitrate solution was added with continuous stirring until the stoichiometric ratio of W and Co $Y = \nu(WO_4^{2-}) : \nu(Co^{2+})$ was reached in the reaction of IPT formation. For example, the solution of 40.00 mL of DMF, 2.90 mL of distilled water, 20.00 mL of sodium tungstate solution ($C_W = 500$ mmol L^{-1}) was acidified by HCl to $Z = 1.14$ ($C_{HCl} = 500$ mmol L^{-1}, $V = 22.80$ mL) and an aqueous solution of cobalt(II) nitrate was added ($Y = 7 : 3 = 2.33$ according to the reaction $3Co^{2+} + 7\ WO_4^{2-} + 8H^+ \leftrightarrows Co_3W_7O_{24}\downarrow + 4H_2O$, $C_{Co} = 300$ mmol L^{-1}, $V = 14.30$ mL), so, the final volume of the solution reached 100 mL. pH was controlled at all stages during the synthesis. The obtained residue was separated, washed with cold water, air-dried to constant weight, and analyzed for the major components as described below.

Weighed amount of salt (120 mg) was refluxed by mixture of 15 mL HCl (36 wt.%) and 5 mL HNO_3 (63 wt.%), boiled down on a bain-marie to “wet residue” and then 70 mL of distilled water was added to the residue, after that it was concentrated to 50 mL being boiled down on a bain-marie. The final residue, $WO_3 \cdot xH_2O$, was filtered and flushed out with 3% solution of HNO_3 and then dried and calcined at 800 °C to constant weight (gravimetric form WO_3, $\delta \le \pm 0.5\%$).

In the filtrate, which remained after separation of $WO_3 \cdot xH_2O$, the contents of sodium and cobalt were determined. The sodium content was determined by atomic absorption spectrometer Saturn-3 in air-acetylene flame with analytical line of 589.6 nm, using a high-frequency electrodeless lamp VSB-2 as a source of resonance radiation (current $I = 70$ mA).

The cobalt(II) content in the filtrate was determined by the method of direct complexometric titration. For this, pH 5.5–6.0 was fixed by addition of 10% aqueous solution of ammonium chloride, and the resulting solution was titrated with Trilon B until murexide changed from yellow to violet ($\delta \le \pm 0.8\%$).

The content of water and DMF was determined by mass loss of air-dried samples at 500 °C ($\delta \le \pm 0.5\%$). Salts synthesized within acidity range from 1.14 to 1.50 contained in the solvation shell only water, but the crystalline salt, obtained at acidity $Z = 1.60$ – only DMF. In the latter case, the absence of water was qualitatively confirmed by Fischer method.

In order to identify anion in the synthesized salts, FTIR spectra were recorded for air-dried samples in KBr using the FTIR Spectrum BXII (“Perkin-Elmer”) from 400 to 4000 cm^{-1} (content of the sample in KBr matrix was 0.5 wt.%).

The electronic spectrum of cobalt(II) decatungstate salt (**1**) in water was recorded using the double-beam spectrophotometer SF-2000 from $\lambda = 200$–1000 nm. The solution was placed in a quartz cuvette with absorbing layer thickness of 10 mm, and the spectrum was recorded against distilled water.

X-ray diffraction study was performed using single-crystal diffractometer “Xcalibur-3” (“Oxford Diffraction”) (MoK_α-radiation, $\lambda = 0.71073$ Å, graphite monochromator, CCD-detector “Sapphire-3,” ω/θ-scanning in the interval $5.58 \le \theta \le 60.0°$ with $13 \le h \le 15$, $-16 \le k \le 17$, $-19 \le l \le 19$, 19,204 measured reflections. Interpretation and elaboration of the structure was made using SHELX-97 [10]. The hydrogens were located geometrically and refined using a riding model. For structural analysis and figure creation, WinGX [11] and Ball&Stick [12] programs were used.

Diffractometer DRON-3, CuKα-radiation, Ni-filter, scanning within the angle range $6° \le 2\theta \le 66$ was used for X-ray powder diffraction analysis.

The study of the surface morphology of the triturated sample of **1** was carried by scanning (raster) electron microscopy; X-ray microanalysis was carried out using a complex analytical scanning electron microscope JSM 6490 LV (JEOL) and energy dispersive X-ray spectrometer INCA PentaFETx3 (OXFORD Instruments).

Thermal analysis was performed on a Q 1500 derivatograph in a mode of linear increase of temperature from 20 to 800 °C (the rate of temperature increase −5 °C min^{-1}; ceramic crucible without cap).

3. Results and discussion

3.1. *Systems with acidity* Z = *1.14–1.17*

Adding cobalt(II) nitrate to aqueous DMF solutions acidified to the necessary Z values immediately led to the formation of pink-purple precipitates: the higher the acidity of the initial solution, the less was the mass of precipitate.

After addition of cobalt(II) nitrate ($Y = 2.33$) to the solution with $Z = 1.14$ (the reaction, $3Co^{2+} + 7\ WO_4^{2-} + 8H^+ \leftrightarrows Co_3W_7O_{24}\downarrow + 4H_2O$) pH immediately dropped from 7.33 to 5.76 and two-phase sample was obtained. It consisted of the powder (**a**) and eventually solidifying oil (**b**), both of which had the same composition $Co_3W_7O_{24}\cdot 23H_2O$ (Anal. Calcd: CoO, 9.93; WO_3, 71.64; and H_2O, 18.43. Found: CoO, 9.54; WO_3, 72.02; and H_2O, 18.44). Based on FTIR spectroscopic analysis, the anion in the salts was classified as heptatungstate anion, and the absorbance bands in FTIR spectra [figure 1(a) and (b)] turned out to be characteristic both in position and intensity [13].

Although the acidity $Z = 1.17$ points to domination of paratungstate B anion in the solution, we have not managed to obtain an appropriate salt by the reaction $5Co^{2+} + 12\ WO_4^{2-} + 14\ H^+ \leftrightarrows Co_5W_{12}O_{40}(OH)_2\downarrow + 6\ H_2O$ ($Y = 2.4$). The presence of DMF in the solution leads to decrease of the polarity of the medium compared to the aqueous solution that appears to stabilize the particles with lower charge and shifts the interconversion equilibrium between IPTAs toward formation of heptatungstate anion: $7W_{12}O_{40}(OH)_2^{10-} \leftrightarrows 12W_7O_{24}^{6-} + 2H^+ + 6H_2O$. Like in the case with acidity 1.14, a two-phase precipitate with identical phase composition was obtained: $Co_3W_7O_{24}\cdot 21H_2O$ (Anal. Calcd: CoO, 10.10; WO_3, 72.90; and H_2O, 17.00. Found: CoO, 9.94; WO_3, 73.02; and H_2O, 16.94); the anion in its structure was identified by FTIR spectroscopy (FTIR spectra on [figure 1(c) and (d)]; during this synthesis, pH lowered from 6.97 to 5.72.

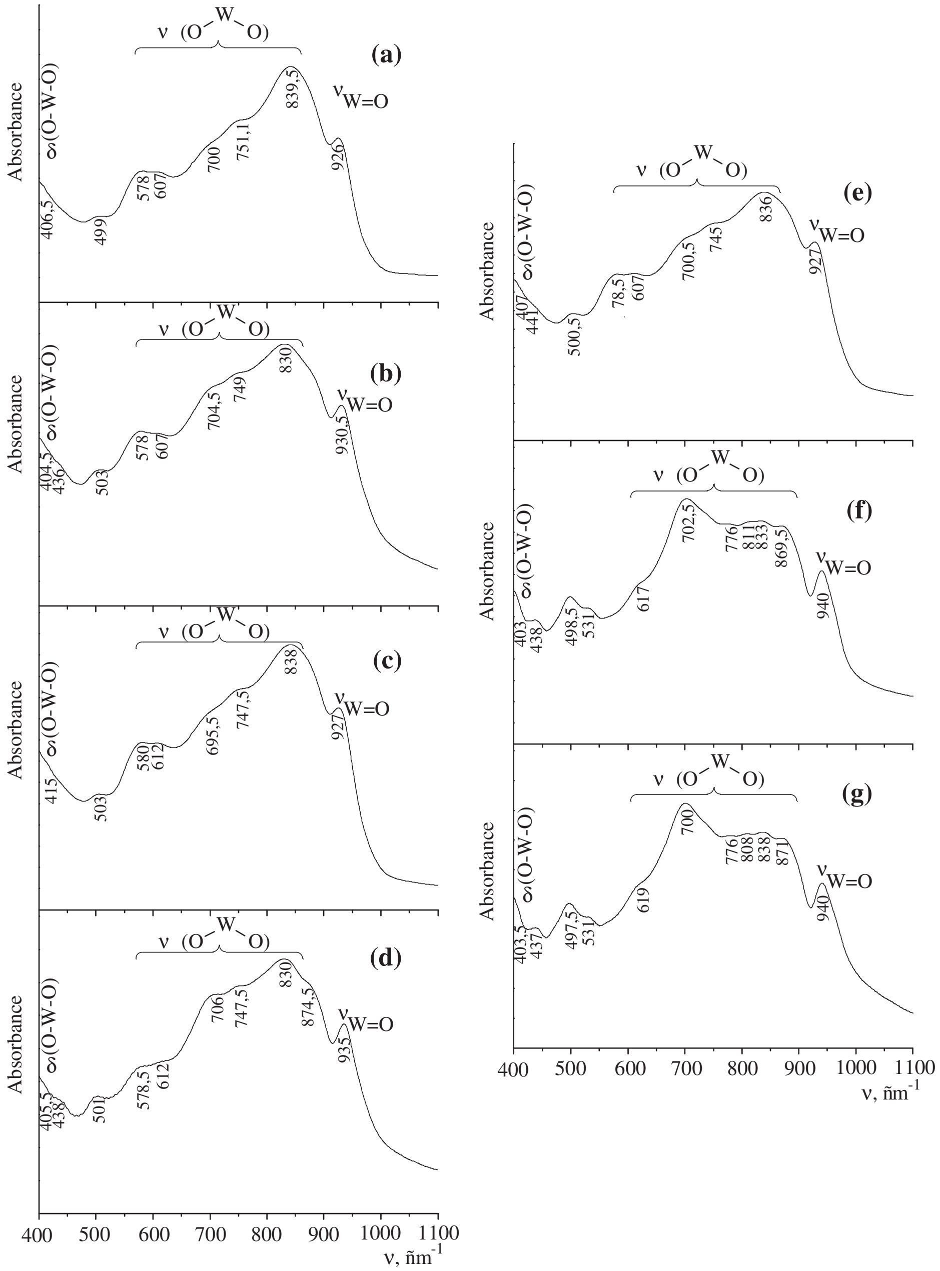

Figure 1. FTIR spectra of the salts synthesized at $Z = 1.14$ [(a), (b)], $Z = 1.17$ [(c), (d)], $Z = 1.29$ (e), $Z = 1.42$ (f), 1.50 (g).

After addition of cobalt(II) nitrate ($Y = 2.8$) to aqueous DMF solution of sodium tungstate ($C_W = 0.1$ mol L^{-1}), acidified to $Z = 1.29$ (pH 5.75), the reaction $5Co^{2+} + 14 WO_4^{2-} + 18H^+ \leftrightarrows Co_5[HW_7O_{24}]_2\downarrow + 8H_2O$ took place and a strawberry-colored single-phase cobalt heptatungstate $Co_3W_7O_{24}\cdot19H_2O$ precipitated instead of the expected cobalt(II) hydroheptatungstate [Anal. Calcd: CoO, 10.26; WO_3, 74.10; and H_2O, 15.64. Found: CoO, 9.94; WO_3, 74.42; and H_2O, 15.45; FTIR spectrum is shown in figure 1(e)]. Obtaining heptatungstate anion instead of hydroheptatungstate anion can be explained by the exchange reaction $3Co^{2+} + HW_7O_{24}^{5-} = Co_3W_7O_{24} + H^+$, accompanied by the decrease in pH from 5.75 to 5.61.

Small quantities of sediments were formed after addition of cobalt(II) nitrate to the aqueous DMF solutions of sodium tungstate acidified to $Z = 1.42$ and 1.50. In both cases, acidic cobalt(II) paratungstates B $Co_3H_4[W_{12}O_{40}(OH)_2]\cdot11H_2O$ ($Z = 1.42$; Anal. Calcd: CoO, 6.90; WO_3, 85.36; and H_2O, 7.74. Found: CoO, 7.24; WO_3, 84.52; and H_2O, 8.20) and $Co_3H_4[W_{12}O_{40}(OH)_2]\cdot10H_2O$ ($Z = 1.50$; Anal. Calcd: CoO, 6.94; WO_3, 85.84; and H_2O, 7.22. Found: CoO, 6.82; WO_3, 86.12; and H_2O, 7.05) precipitated. Theoretically, protonated paratungstate B anions $H_3[W_{12}O_{40}(OH)_2]^{7-}$ and $H_4[W_{12}O_{40}(OH)_2]^{6-}$ are formed in aqueous solutions at acidities 1.42 and 1.50 correspondingly. It was shown [4] that formation of protonated forms of paratungstate B anion together with Keggin metatungstate anion $[W_{12}O_{38}(OH)_2]^{6-}$ and decatungstate anion could also occur in aqueous DMF medium. Formation of cobalt(II) paratungstate B can be explained by its lower solubility compared to meta- and deca-forms as well as by shift in the interconversion equilibria of IPTAs toward formation of acidic paratungstate B anions:

$$W_{12}O_{38}(OH)_2^{6-} + 2H_2O \leftrightarrows H_4W_{12}O_{40}(OH)_2^{6-};$$

$$12W_{10}O_{32}^{4-} + 36H_2O \leftrightarrows 10H_4W_{12}O_{40}(OH)_2^{6-} + 12H^+.$$

The hydrolyses of decatungstate or metatungstate anions were considered as the ways of obtaining salts with paratungstate B anions [14, 15]. The results of the present work confirm the viability of such synthetic approaches.

There are bands within the area of 400–1000 cm^{-1} on FTIR spectra of $Co_3H_4[W_{12}O_{40}(OH)_2]\cdot nH_2O$ ($n = 10$–11), which stand for vibrations in the frame O–W–O of paratungstate B anion, while there are no bands for DMF; this means that the obtained salts have a hydrate shell only [figure 1(f) and (g)].

When the mother solutions, obtained after separation of cobalt(II) salts, were boiled down to 80 mL, their color changed from pink to brown. That can be explained by the change in cobalt oxidation to +3, and the reaction was accompanied by immediate precipitation of slight quantities of amorphous gray residue (its exact composition could not be identified), and red crystals of cobalt(II) form after a period of time.

The method of synthesis was just as described above: firstly, the initial orthotungstate aqueous DMF solution was acidified to different Z values and then cobalt(II) nitrate was added. That is the way of establishing the relations between the state of IPTAs in solution and solid. Another route of synthesis cobalt IPTs could be proposed, for example, dissolution of tetrabutylammonium IPT in aqueous DMF solution and addition of cobalt(II) nitrate after that. However, as reported earlier [4], DMF affects the equilibria between the IPTA. So it is hard to obtain the same IPTA in the salt composition after dissolution of it and precipitation with another cation. As a consequence, this method could result in a mixture of IPTs, for instance, a mixture of deca- and hexatungstates from the initial tetrabutylammonium decatungstate.

3.2. *System with acidity Z = 1.60*

A stoichiometric amount of cobalt(II) nitrate (*Y* = 5.0) was added to the aqueous DMF solution of Na_2WO_4, acidified to 1.60 (pH 3.16), according to the reaction $2\ Co^{2+} + 10\ WO_4^{2-} + 16\ H^+ \leftrightarrows Co_2W_{10}O_{32} + 8\ H_2O$, as a result, the solution became pink, pH decreased to 3.04, but nothing precipitated. Even a month after preparation of the solution, no residue formed. Therefore, the solution was concentrated by evaporation on a bain-marie from 100 to 50 mL. As a result, the color of the solution became purple and a small amount of a light pink sediment precipitated. The composition of this phase represents no interest, since it does not contain tungsten. Its FTIR spectrum contains only the following bands: 1385, 1632, 1655, 3468 cm^{-1} that points to the formation of cobalt(II) nitrate hydrate residue as a result of decrease in its solubility in aqueous DMF mixture.

When the remaining mother solution was evaporated to 45 mL, it turned blue as a result of the formation of the Keggin anion $[CoW_{12}O_{40}]^{6-}$ in solution, in which the Co(II) ion occupies a central tetrahedral cavity [16]. Pink-red transparent crystals of $Co_2[W_{10}O_{32}]\cdot10C_3H_7NO$ (**1**) formed in the solution a month later (Anal. Calcd: CoO, 4.68; WO_3, 72.47; and C_3H_7ON, 22.85. Found: CoO, 5.01; WO_3, 71.97; and C_3H_7ON, 22.78). Vibrations 591, 689, 801, 890, 944, 959 in the FTIR spectrum (**1**) (figure 2) confirm the presence of decatungstate anion in the salt. **1** in the system Co^{2+}–WO_4^{2-}–H^+–DMF–H_2O with various acidities is the only one that contains DMF instead of water in its solvation shell. This is indicated by the absence of absorbance bands typical of H_2O (~1630, 3400 cm^{-1}) and the presence of absorbance bands typical of DMF (~1650, 3415, 3540 cm^{-1}) in the FTIR spectrum of cobalt(II) decatungstate. The absence of water was also qualitatively confirmed by Fischer method.

Solutions containing decatungstate anion give an absorption spectrum with maximum values at 320–325 nm [17]. Interestingly, decatungstate is the only IPTA, which produces a signal in the near ultraviolet region that is caused by its structure; $W_{10}O_{32}^{4-}$ is formed by two lacunar blocks W_5O_{18}, connected through almost linear bridges W–O–W (175°). There is a band at 325 nm in the absorption spectrum of the aqueous solution **1** ($C_{(\mathbf{1})}$ = 0.5 mmol L^{-1}), which together with FTIR spectroscopy also confirms the presence of decatungstate anion in the salt.

SEM-pictures of triturated **1** (figure 3) show the absence of zones with different surface morphology. Magnification (20,000 times) shows that the salt surface consists of spherical

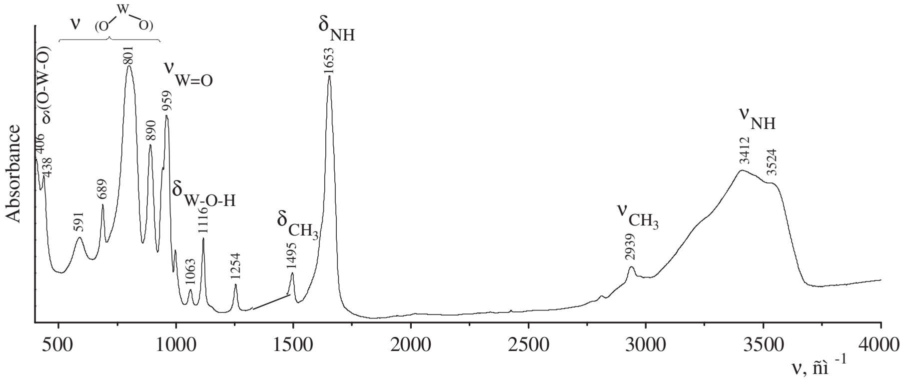

Figure 2. FTIR spectrum of $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]$ (**1**).

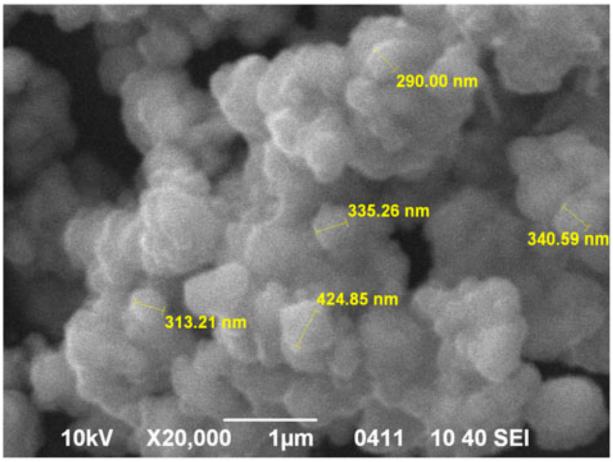

Figure 3. SEM image of the surface of triturated sample of **1** (×20,000 times).

grains with blurred indistinct edges whose size is in the range of 290–425 nm. The results of EDX, conducted in different areas (discrete points) of the sample (figure 4), indicate the maintenance of the molar ratio Co : $W = 1 : 5$ (table 1), thus showing the formation of a single-phase sample.

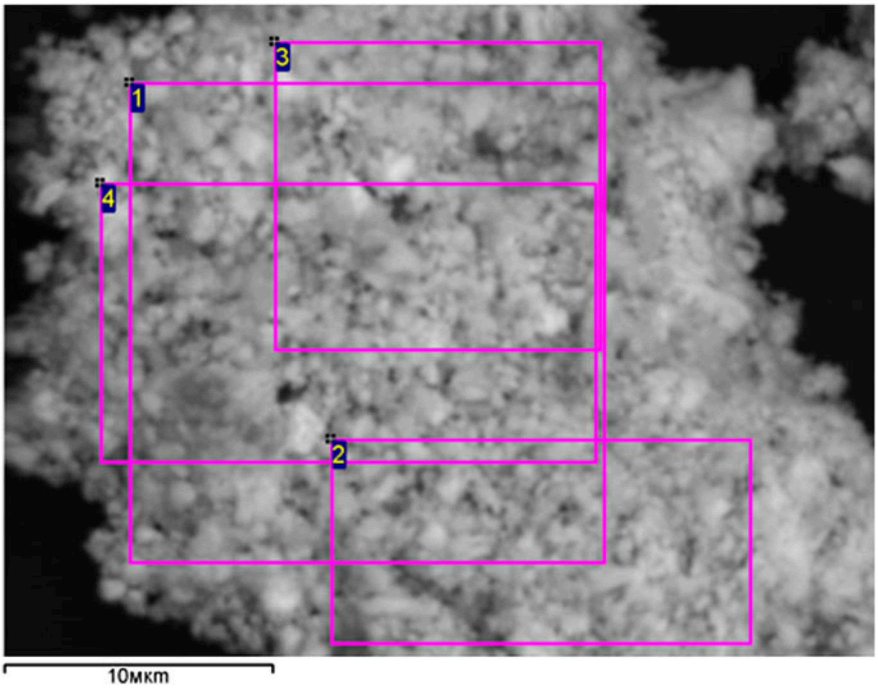

Figure 4. SEM images of the morphology of triturated **1**.
Note: EDX analysis was made in zones indicated (see table 1).

Table 1. Atomic ratio of Co and W in different surface zones of triturated **1**.

W, at. (%)	Zones 1	2	3	4	Average	$\nu_{Co} : \nu_W$ Exp.	Theor.
Co	5.70	5.07	5.61	5.16	5.39	1	1
W	28.50	25.53	27.05	25.26	26.59	4.93	5

The main crystallographic data of X-ray analysis of $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]$, obtained during analysis of the single crystal with dimensions 0.15 × 0.10 × 0.003 mm^3, are given in table 2.

Centrosymmetric $W_{10}O_{32}^{4-}$ in the structure has a typical structure, in which two “square pyramids” consisting of five distorted octahedra WO_6 – lacunar derivatives of the Lindqvist structure – are connected through “bases” at the expense of the common vertices of four octahedra (figure 5). Basic geometric characteristics of structure **1** – bond distances and angles – are given in Supplementary Material (tables S1 and S2).

Coordination of cobalt is an octahedron (Co–O distances of 2.048–2.107 Å), one of the vertices is O (8) of the anion, while the other vertices are occupied by carbonyl oxygens of five DMF molecules. Octahedral CoO_6 is distorted as indicated by both bond angles (theoretically right bond angles O–Co–O vary within 84.8°–95.4° (average −89.975°) and the angles in the theoretically linear fragments vary from 170.7° to 177.7° (average −174.933°)). One octahedron and half of the anion represent a symmetrically independent part of the structure; therefore, the basic structural unit of the complex anion is $W_{10}O_{32}^{4-}$ and two cation polyhedra $Co(C_3H_7NO)_5^{2+}$. A structural unit $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]$ occupies the center of symmetry $\left[\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\right]\right]$ in the elementary cell (figure 6) and is extended along the direction $[11\bar{1}]$, while interactions between the neighboring complex units are van der Waals forces (table 3).

Table 2. Crystallographic data and structure refinement parameters of **1**.

Empirical formula	$C_{30}H_{70}Co_2N_{10}O_{42}W_{10}$
Formula weight	3199.32
Crystal system	Triclinic
Space group	*P-1*
T (K)	293 (2)
Wavelength (Å)	0.71073
a (Å)	11.2239(7)
b (Å)	12.2221(10)
c (Å)	13.9184(8)
α (°)	71.380 (6)
β (°)	89.506(5)
γ (°)	72.144(6)
Volume (Å^3)	1713.8(2)
Z	1
Calculated density (g cm^{-3})	3.100
Absorption coefficient (mm^{-1})	17.270
F(0 0 0)	1450
Total reflections	19,204
Independent reflections	9566 [R(int) = 0.055]
Final R indices [$I_{hkl} > 2\sigma(I)$]	$R_F = 0.0488$, $wR_2 = 0.0940$ (for the observed reflections) $R_F = 0.0694$, $wR_2 = 0.1036$ (for all independent reflections)
S	0.983

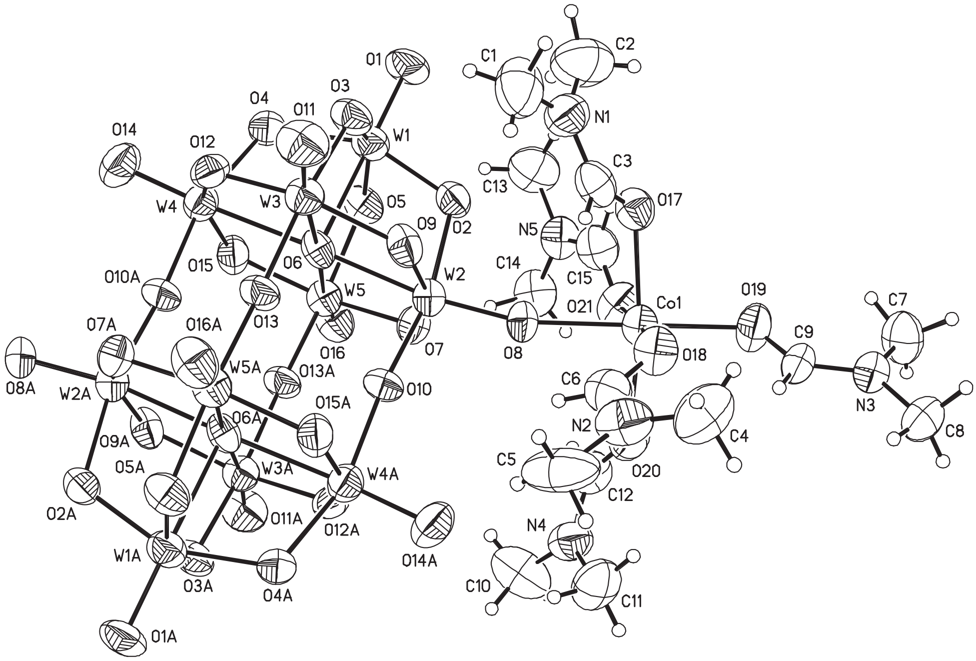

Figure 5. Main structural unit of **1**.
Note: Symmetry equivalent atoms are marked with "A."

Two lacunar derivatives from Lindquist structure units W_5O_{18} in the centrosymmetrical decatungstate anion $W_{10}O_{32}^{4-}$ are bonded mirror-symmetrically through common tops of four oxygens with formation of an octahedral space. The polyanion contains four different groups of oxygens: 10 terminal O atoms (O_t = O(1), O(8), O(11), O(14), O(16), and their symmetry equivalents), 16 O atoms (O_b = O(2)–O(5), O(7), O(9), O(12), O(15) and their symmetry equivalents) each bridging two W ions to each other through edges of octahedra, 4 O atoms (O_e = O(10), O(13), O(10A), O(13A)) bridging two W ions through corners of octahedra, and 2 O atoms (O_c = O(6), O(6A)) each coordinated to five W ions. The W–O distances within the polyanion are W–O_t = 1.710–1.743 Å, W–O_b = 1.897–1.979 Å, W–O_e = 1.851–1.927 Å, and W–O_c = 2.232–2.354 Å.

Octahedra WO_6 in $W_{10}O_{32}^{4-}$ are significantly distorted, indicated by both bond angles (theoretically right bond angles O–W–O vary within 74.3–104.2° and the angles in linear fragments vary from 152.2° to 179.0°).

Analyzing the structural data of bond distances and values of bond angles in the compounds with decatungstate anion (table 4), it can be concluded that the composition of the cationic sublattice, presence of coordination of the cation to the anion through the terminal oxygens (**1**, $[Ba(H_2O)_2(C_3H_7NO)_3]_2–[W_{10}O_{32}]{\bullet}(C_3H_7NO)_2$ [4]), or absence of covalent bonds between the cation and the anion ($[Co(NH_3)_5Cl]_2–[W_{10}O_{32}]\cdot 4H_2O$ [6], $[HN(C_4H_9)_3]_4W_{10}O_{32}$ [7], $[Cu(phen)_2]_4[W_{10}O_{32}]$ [8], $[C_5H_5\,N(C_{16}H_{33})]_4[W_{10}O_{32}]$ [9]), as well as the presence ([4, 6]) or absence ([7–9]) of solvate sphere almost does not influence the values of bond distances W–O and bond angles O–W–O in the $W_{10}O_{32}^{4-}$ anion.

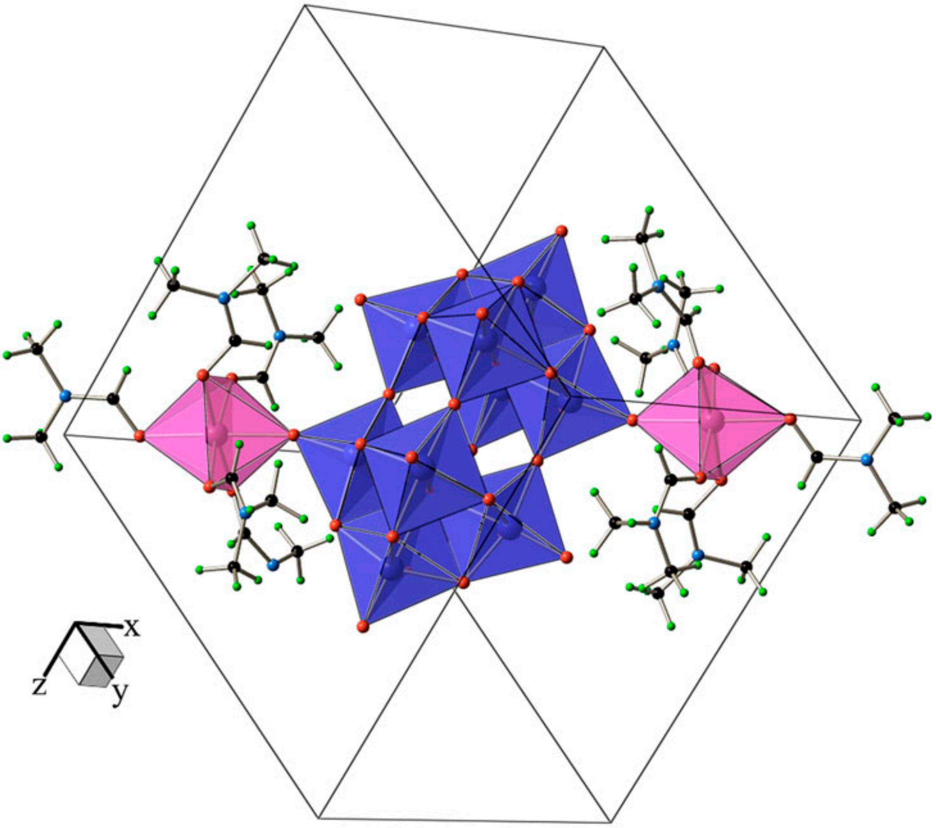

Figure 6. Projection of the structure of **1** along the [0 1 0] direction.
Notes: Color codes: {CoO_6}, magenta polyhedron; {WO_6}, blue octahedron; C (black), N (blue), H (green), and O (red) are shown with thick sticks (see http://dx.doi.org/10.1080/00958972.2015.1090563 for color version).

During thermolysis of **1**, a thermogram fixes several temperature ranges of mass loss caused by desolvation: 135–165 °C (2 DMF molecules), 212–331 °C (7 DMF molecules), 417-451 °C (1 DMF molecule); they are accompanied by endo-effects on DTA curve at $T = 158$, 266, and 444 °C, respectively (figure 7). As a result of complete desolvation, decomposition of **1** occurs and WO_3 and $CoWO_4$ are formed, which reflexes are fixed on the radiograph of product thermolysis [figure 8(a)–(c)] [18].

Table 3. Selected lengths of short contacts in **1**.

	d (Å)		*d* (Å)
O(17)···H(8B)	2.432	O(1)···H(4C)	2.661
C(12)···O(21)	3.125	O(1)···H(8A)	2.459
O(5)···H(13C)	2.651	O(15)···H(1A)	2.672
O(16)···H(13C)	2.633	O(11)···H(3A)	2.562
O(20)···H(14A)	2.542	O(11)···C(4)	3.186
O(21)···C(12)	3.125	O(11)···C(6)	3.203

Table 4. Comparison of the structural parameters of decatungstate anion in compounds with different cations.

Parameter	$[Co(C_3H_7NO)_5]_2$–$[W_{10}O_{32}]$ (**1**)	$[Ba(H_2O)_2(C_3H_7NO)_3]_2$–$[W_{10}O_{32}]$•$(C_3H_7NO)_2$ [4]	$[Co(NH_3)_5Cl]_2$–$[W_{10}O_{32}]\cdot 4H_2O$ [6]
W–O_t	1.710–1.743 Å	1.696–1.715 Å	1.686–1.710 Å
W–O_b	1.897–1.979 Å	1.895–1.955 Å	1.883–1.998 Å
W–O_e	1.851–1.927 Å	1.881–1.908 Å	1.863–1.923 Å
W–O_c	2.232–2.354 Å	2.272–2.337 Å	2.282–2.341 Å
Angle O–	74.3°–104.2°	75.12°–104.34°	75.2°–106.7°
W–O	152.2°–179.0°	151.28°–178.81°	151.6°–177.7°

Parameter	$[HN(C_4H_9)_3]_4W_{10}O_{32}$ [15]	$[Cu(phen)_2]_4[W_{10}O_{32}]$ [16]	$[C_5H_5N(C_{16}H_{33})]_4[W_{10}O_{32}]$ [17]
W–O_t	1.68–1.76 Å	1.664–1.708 Å	1.686–1.701 Å
W–O_b	1.86–2.01 Å	1.875–1.949 Å	1.893–1.972 Å
W–O_e	1.88–1.94 Å	1.855–1.924 Å	1.874–1.910 Å
W–O_c	2.28–2.34 Å	2.243–2.329 Å	2.276–2.340 Å
Angle O–	Not given	72.9°–104.8°	75.11°–104.89°
W–O	Not given	152.8°–179.8°	152.63°–178.75°

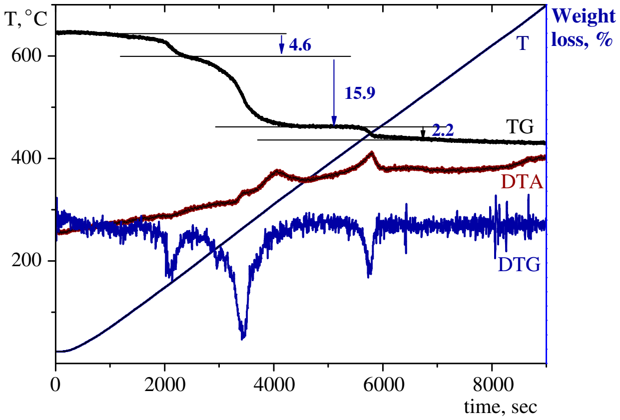

Figure 7. Thermal decomposition of **1**.
Notes: Curves: *T* – temperature, TG – thermogravimetric, DTG – differential thermogravimetric, DTA – differential thermal analysis.

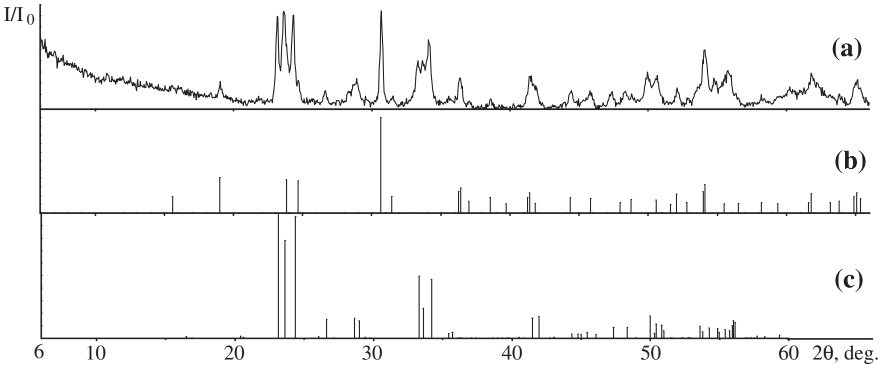

Figure 8. Powder X-ray diffraction patterns of thermolysis products of **1** (2 h at 550 °C) (a); $CoWO_4$ (ICDD PDF 01-072-0479) (b); WO_3 (ICDD PDF 01-072-1465) (c).

4. Conclusion

A study of phase formation in the system Co^{2+}–WO_4^{2-}–H^+–DMF–H_2O shows that at low acidities (1.14–1.29) in aqueous DMF solutions only cobalt(II) heptatungstate is deposited, at acidities 1.42–1.50 acidic cobalt(II) paratungstate B precipitates, while at higher acidity ($Z = 1.60$), in contrast to an aqueous medium, cobalt(II) decatungstate forms. A structural study of $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]$ revealed the following results: triclinic, *P-1*, $a = 11.2239(7)$ Å, $b = 12.2221(10)$ Å, $c = 13.9184(8)$ Å, 71.380 (6)°, $\beta = 89.506(5)°$, $\gamma = 72.144(6)°$, $V = 1713.8(2)$ Å^3. Centrosymmetric anion $W_{10}O_{32}^{4-}$ in **1** has a typical structure, in which two "square pyramids" consisting of five distorted WO_6 octahedra are connected through "bases" by means of the common vertices of four octahedra. Comparison of the structural data in different compounds with decatungstate anion led to the conclusion that the composition of the cationic sublattice, presence of coordination of the cation to the anion through the terminal oxygens or absence of covalent bonds between the cation and the anion, as well as presence or absence of solvate sphere almost does not affect the values of bond distances W–O and angles O–W–O in the $W_{10}O_{32}^{4-}$ anion.

Desolvation of **1** begins at 135 °C and completes at 444 °C with decomposition of the salt to tungsten(VI) oxide and cobalt(II) orthotungstate. SEM-analysis shows that the salt surface after trituration consists of spherical nanosized grains.

Supplementary material

Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters were deposited at the Cambridge Crystallographic Data Center under depository number CCDC 1035468 and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Basic geometric characteristics of the structure (**1**) – bond distances and angles – are given in table S1 and table S2.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

The supplemental data for this paper is available online at http://dx.doi.org/10.1080/00958972.2015.1090563.

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