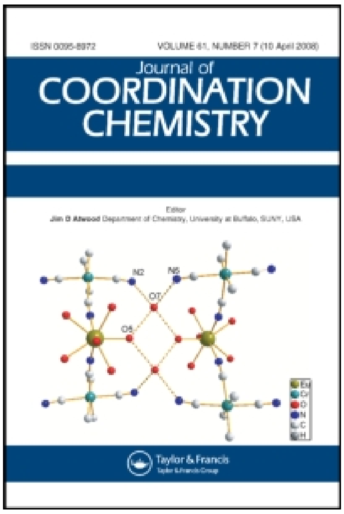

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Equilibrium in the acidified aqueous solutions of tungstate anion: synthesis of Co(II) isopolytungstates. Crystal structure of Co(II) paratungstate B $Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O$

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The system of Na_2WO_4–HNO_3–KNO_3–H_2O was investigated by means of single-point pH-potentiometric titration, and subsequent mathematical modeling of the equilibrium processes revealed that hydroheptatungstate anion $HW_7O_{24}^{5-}$ transforms into protonated forms of paratungstate B anion $H_xW_{12}O_{40}(OH)_2^{10-}$. The mathematical modeling data were used to create a procedure for the synthesis of Co(II) isopolytungstates. Chemical and spectroscopic analyses of the products isolated from the systems of Na_2WO_4–HNO_3–$Co(NO_3)_2$–H_2O with different acidity allowed the determination of the conditions of Co(II) paratungstate B formation. The structure of the cobalt paratungstate B $Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O$ was confirmed by single-crystal X-ray diffraction analysis.

Keywords: Isopolytungstate; Paratungstate B; Crystal structure; Cobalt(II)

1. Introduction

Polyoxotungstates of Co(II) have attracted much interest due to its potential use in complex catalytic systems [1, 2] and in medicine [3]. Isopolytungstate anion formation can be described by the following equation:

$$nWO_4^{2-} + mH^+ \rightleftarrows [H_{m-2k}W_nO_{4n-k}]^{(2n-m)-} + kH_2O$$

In this system, the ratio $m:n = Z$ determines the formation of anions with different composition. Thus, at $Z = 1.00$ $[W_6O_{20}(OH)_2]^{6-}$ forms; at $Z = 1.14$, $[W_7O_{24}]^{6-}$; $Z = 1.17$, $[W_{12}O_{40}(OH)_2]^{10-}$; $Z = 1.29$, $[HW_7O_{24}]^{5-}$; $Z = 1.50$, $[W_{12}O_{38}(OH)_2]^{6-}$; and $Z = 1.60$, $[W_{10}O_{32}]^{4-}$ [4, 5]. The presence of *d*-element cations in the system can lead to the formation of isopoly and heteropolytungstates of different structural

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types: $[M^{k+}O_6W_6O_{18}]^{(12-k)-}$ or $[M^{k+}(OH)_6W_6O_{18}]^{(6-k)-}$ (Anderson–Evans type); $[M^{k+}W_{12}O_{40}]^{(8-k)-}$ (Keggin type); and $[M^{k+}W_{11}O_{39}]^{(12-k)-}$ (lacunar derivatives of Keggin-type structures) [4, 6], etc.

A limited number of Co(II) isopolytungstates have been structurally characterized. They are: heteropoly tungstocobaltates of Keggin-type structure $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ [1] and $[Co(2,2'\text{–bipy})_3]_2H_2[CoW_{12}O_{40}] \cdot 9.5H_2O$ [7]; paratungstates $[Co_4Na(H_2O)_{21}][H(H_2W_{12}O_{42})] \cdot 18H_2O$ and $[Co_5(H_2O)_{22}][H_2W_{12}O_{42}] \cdot 12H_2O$ [8], $K_6[Co(H_2O)_4]_2[H_2W_{12}O_{42}] \cdot 14H_2O$ [9]; lacunar polyoxometallates of 11th row $(NH_4)_9K[(CoO_4)W_{11}O_{31}(O_2)_4] \cdot 5H_2O$ [10].

Recently, Sun *et al.* [11] reported a structural investigation of double cobalt–sodium paratungstate B $Na_6[\{Co(H_2O)_3\}\{Co(H_2O)_4\}(H_2W_{12}O_{42})] \cdot 29H_2O$ that was prepared by an exchange reaction in the solution of sodium paratungstate B $Na_{10}[H_2W_{12}O_{42}] \cdot 20H_2O$ and $CoCl_2 \cdot 6H_2O$, in acetic buffer at pH = 6. Sun *et al.* [11] also noted that if an acidified solution of $Na_2WO_4 \cdot 2H_2O$ was used instead of sodium paratungstate B, then the formation of the acidic cobalt–sodium paratungstate B $(H_3O^+)_3[\{Na(H_2O)_4\}\{Co(H_2O)_4\}_3(H_2W_{12}O_{42})] \cdot 24.5H_2O$ takes place.

Indeed, it seems purposeful to investigate the possibility of the preparation of Co(II) isopolytungstate from the acidified aqueous solutions of sodium tungstate. First of all, such investigation should rely on the state of the tungstate anions in aqueous solutions that establishes not only immediately after the addition of acid, but also after 60 min time needed for solid-phase synthesis.

In this work, we conducted pH-potentiometric studies of equilibria in tungstate solutions and analyses of the solid phases that were isolated from the solutions with different acidity Z. The information provides a means for creating new, and the correction of the existing methods for known, Co(II) polyoxotungstates.

2. Experimental

2.1. *pH-potentiometric studies*

Investigation of interactions in aqueous solutions of sodium tungstate were carried out by pH-potentiometric titration in the region of acidity $Z = \nu(H^+)/\nu(WO_4^{2-}) = 0.0$–2.5 using different initial concentrations of sodium tungstate (C_W) and different ionic strengths (μ): $C_W = 1\,\text{mmol L}^{-1}$ ($\mu = 25\,\text{mmol L}^{-1}$); $C_W = 5\,\text{mmol L}^{-1}$ ($\mu = 250\,\text{mmol L}^{-1}$); and $C_W = 10\,\text{mmol L}^{-1}$ ($\mu = 500\,\text{mmol L}^{-1}$). Ionic strength was created by the addition of $2\,\text{mol L}^{-1}$ of potassium nitrate.

The pH values (accuracy $\delta \leq \pm 0.04$) were obtained using I-160 (ZIP, Belarus) ionomer at 298.0 ± 0.1 K, step $\Delta Z = 0.05$–0.10. Indicator electrode was hydrogen-ion selective glass electrode ESL 63–07 Sr (Belarus) with isopotential point $pH_i = 7.00$ and $E_i = -25 \pm 10$ mV, auxiliary electrode EVL-1M3 was a silver chloride electrode (Ag/AgCl, sol. KCl, saturated) with the potential of 202 ± 2 mV, according to the standard hydrogen electrode. Small temperature fluctuations were compensated by thermocompensating apparatus (TCA 7.1, Belarus). Calibration and preciseness of the readings were controlled by potassium tetraoxalate: $KH_3C_4O_8 \cdot 2H_2O$ (pH = 1.68), potassium hydrophthalate: $KC_8H_5O_4$ (pH = 4.01), and sodium tetraborate: $Na_2B_4O_7 \cdot 10H_2O$ (pH = 9.18) standard buffer solutions.

2.2. *Synthetic and analytical procedures*

To prepare Co(II) polyoxotungstates, we used aqueous solutions of $Na_2WO_4 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and HNO_3 (all reagent grade). The precise concentration of solutions was determined by chemical analysis: W contents, gravimetrically (gravimetric form WO_3, $\delta \leq \pm 0.5\%$); Co contents by direct complexonometry (pH = 6, murexide indicator, $\delta \leq \pm 0.8\%$); HNO_3 concentration by the titration of standard $Na_2B_4O_7 \cdot 10H_2O$ solution ($\delta \leq \pm 0.5\%$).

For the preparation of polyoxotungstates, solutions of sodium tungstate were acidified with HNO_3 solution until the desired Z was reached. Then, Co(II) nitrate solution was added dropwise with vigorous stirring until the desired $Y = \nu(\mathrm{W})/\nu(\mathrm{Co})$ was reached. If crystalline mixtures were formed, different colors of the target crystalline phases were separated by rigorous washing with hot water. If mixtures of crystalline and amorphous species were formed, then they were separated by rigorous washing out of the amorphous powder from the crystalline phase. Moreover, pH control was conducted during all the acidification steps, before the addition of Co(II) and after the isolation of solid phase. The composition of the solid phases was determined as described below.

A 150 mg sample of each cobalt salt obtained was refluxed in 20 mL of 3 : 1 v/v mixture of HNO_3 (70 wt%) and HCl (36 wt%) and then evaporated using a water bath. The wet residue was diluted with 70 mL of water and concentrated to *ca* 40–50 mL by evaporation on the water bath. The solid phase, $WO_3 \cdot xH_2O$, was filtered, washed with 3% aqueous solution of HNO_3, dried and, finally, annealed at 800°C until constant mass was reached (gravimetric form WO_3, $\delta \leq \pm 0.5\%$).

The sodium content in the filtrate was determined by atomic absorption spectroscopy using a Saturn-3 spectrometer. The Acetylene–air flame with analytical line 589 nm was used, and the source of resonance irradiation was an electrodeless high-frequency lamp VSB-2 ($I = 70$ mA).

The contents of cobalt in the filtrate were determined by direct complexonometric titration. First, the pH 5.5–6.0 was created by the addition of 10% aqueous ammonia. Then, the obtained solution was titrated by Trilon B until the color of murexide changed from yellow to violet ($\delta \leq \pm 0.8\%$). The water content in Co(II) polyoxotungstates was determined gravimetrically by the annealing of dry samples at 500°C ($\delta \leq \pm 0.5\%$).

To identify the anions in the synthesized salts, we used Fourier transform infrared (FT-IR) spectra recorded in KBr pellets on a Spectrum BXII (Perkin Elmer) spectrometer in the range of $\bar{\nu} = 400$–$4000\ \mathrm{cm}^{-1}$. The contents of the sample in KBr matrix was 0.5 wt%.

2.2.1. Amorphous cobalt tungstate $CoWO_4 \cdot 4H_2O$ (system with acidity $Z = 0.00$). Anal. Calcd for $CoWO_4 \cdot 4H_2O$: CoO, 19.78; WO_3, 61.20; and H_2O, 19.02. Found: CoO, 19.55; WO_3, 61.27; and H_2O, 18.92. FT-IR (KBr): ν(W–O–W) 587 m, 715 sh, 839s, 910 m; $\delta(H_2O)$ 1630 m; and $\nu(H_2O)$ 3395s br cm^{-1}.

2.2.2. Cobalt paratungstate $Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O$ (1) (system with acidity $Z = 1.00$). Anal. Calcd for $Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O$: CoO, 9.89; WO_3, 73.46; and H_2O, 16.65. Found: CoO, 9.57; WO_3, 73.18; and H_2O, 16.48. FT-IR (KBr): δ(W–O–W)

439w, ν(W–O–W) 504 m, 530 m, 712 s, 820 s, 873 s, ν(W=O) 945 s, (W–O–H) 1073 w, 1165 w, δ(H_2O) 1630 s, and ν(H_2O) 3365 s br cm^{-1}.

2.2.3. Cobalt paratungstate $Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O$ (2) (system with acidity $Z = 1.17$). Anal. Calcd for $Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O$: CoO, 9.75; WO_3, 72.42; and H_2O, 17.82. Found: CoO, 9.59; WO_3, 72.77; and H_2O, 17.41. FT-IR (KBr): δ(W–O–W) 439w, ν(W–O–W) 503 m, 533 m, 713 s, 814 s, 874 s, ν(W=O) 943 s, (W–O–H) 1073 w, 1163 w, δ(H_2O) 1631 s, and ν(H_2O) 3365 s br cm^{-1}.

2.2.4. Cobalt paratungstate $Co_4H_2[W_{12}O_{40}(OH)_2] \cdot 34H_2O$ (3 and 4) (system with acidity $Z = 1.29$). Anal. Calcd for $Co_4H_2[W_{12}O_{40}(OH)_2] \cdot 34H_2O$: CoO, 8.03; WO_3, 74.58; and H_2O, 17.39. Found (for **3**): CoO, 8.19; WO_3, 73.95; and H_2O, 17.25. Found (for **4**): CoO, 8.16; WO_3, 73.72; and H_2O, 17.31. FT-IR (for **3**, KBr): δ(W–O–W) 438 w, ν(W–O–W) 500 m, 530 m, 627 sh, 711 s, 750 s, 820 s, 879 s, ν(W=O) 943 s, (W–O–H) 1080 w, 1165 w, δ(H_2O) 1632 s, and ν(H_2O) 3406 s br, 3515 s cm^{-1}. FT–IR (for **4**, KBr): δ(W–O–W) 443 w, ν(W–O–W) 499 m, 528 m, 627 sh, 702 s, 750 s, 820 s, 879 s, ν(W=O) 941 s, (W–O–H) 1080 w, 1165 w, δ(H_2O) 1632 s, and ν(H_2O) 3406 s br, 3515s cm^{-1}.

2.3. *X-ray crystallography of 2*

Single-crystal X-ray diffraction analysis of **2** was acquired on an Xcalibur-3 (Oxford Diffraction) diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å, graphite monochromator) equipped with a Sapphire-3 CCD detector (ω/θ scanning in the range $2.66 \le 2\theta \le 60°$ with $-30 \le h \le 30$, $-21 \le k \le 21$, $-31 \le l \le 31$, 230,886 measured reflections). The structure was solved by direct methods using SHELX-97 [12, 13]. Structural analysis and image making were performed in WinGX [14] and Ball & Stick [15] softwares, respectively.

Crystals suitable for analysis were isolated from solution, dried in air, and then used for crystal structure determination. Part of the disordered water molecules were not located. Selected crystal parameters of **2** are summarized in table 1.

3. Results and discussion

3.1. *pH-Potentiometric analysis of acidified aqueous solutions of WO_4^{2-}*

To obtain information about the particles present in solutions of sodium tungstate at different acidities, single-point pH-potentiometric titration was carried out at 298 ± 0.1 K. Titration data were allowed to build pH = *f*(*Z*) dependences (figure 1) for different time intervals from the beginning of interaction. Since pH of the system changed gradually in time, figure 1 contains only initial (immediately after addition) and final (60 min after addition) pH = *f*(*Z*) dependences for simplicity. Based on the titration results, mathematical modeling using quasi-Newton method was carried out by CLINP 2.1 software [16, 17].

The target goal of mathematical modeling for the chemical processes in the system WO_4^{2-}–H^+–H_2O was to successively find such a model that adequately describes

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

Empirical formula	$Co_5H_{76}O_{79}W_{12}$
Formula weight	3841.46
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimnensions (Å, °)	
a	21.9473(15)
b	14.9505(14)
c	22.2149(9)
β	107.396(5)
Volume (Å^3), Z	6955.8(9), 4
Calculated density (g cm^{-3})	3.668
Absorption coefficient (mm^{-1})	21.039
$F(000)$	6924
Reflections collected	20,233
Independent reflections	14,434 [$R(\text{int}) = 0.052$]
Final R indices [$I > 2\sigma(I)$]	$R_F = 0.0375$, $wR_2 = 0.0862$ (for the observed reflections) $R_F = 0.0597$, $wR_2 = 0.0927$ (for all independent reflections)
S	1.001

physico-chemical measurements in a material balance equation. First, the set of the most probable chemical reactions was created, and then by sequential exclusion only those reactions that enhanced (or diminished) the calculated criterial parameters (compared with precedent calculations) were left in the model. The main parameter was the value of F, that is the sum of squares of deviations between calculated and experimental values of pH along the entire titration curve:

$$F = \sum_{k=1}^{n} \left(\Delta \mathrm{pH}_k\right)^2 = \sum_{k=1}^{n} \left(\mathrm{pH}_k{}^{(\mathrm{calc})} - \mathrm{pH}_k^{(\exp)}\right)^2$$

where n is the number of points in the series of interest, $k = 1, 2, \ldots, n$

The calculated model was considered to be successful if the calculated values of pH deviated from he experimental values by ±0.12 in each titration point. The result of mathematical modeling was the determination of concentration formation constants ($\log K_c$) of individual isopolytungstate anions in the solution (table 2).

Calculation of formation constants allowed us to build diagrams of the distribution of different ionic forms related to acidity Z and the time of solution's maturation period (figure 1).

Detailed analysis of these relationships indicates that in the region of acidity $Z = 1.0$–1.6 increase of pH occurs. According to the modeling results, such an increase can be explained by the transformation of hydroheptatungstate anion into the protonated forms of paratungstate B:

$$12HW_7O_{24}^{5-} + 10H_2 \leftrightarrows 7H_2W_{12}O_{40}(OH)_2^{8-} + 4OH^-$$

$$12HW_7O_{24}^{5-} + 17H_2O \leftrightarrows 7H_3W_{12}O_{40}(OH)_2^{7-} + 11OH^-$$

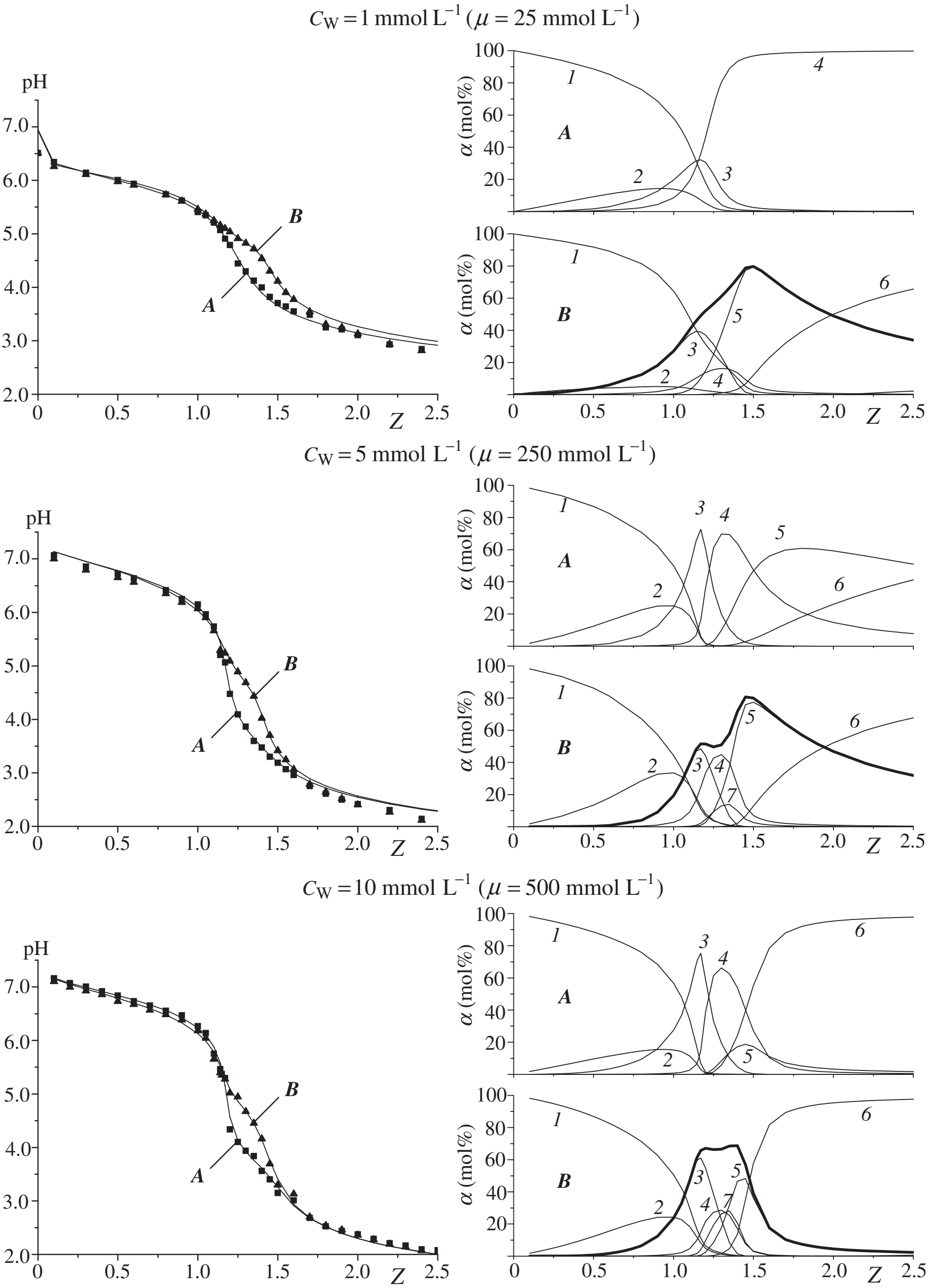

Figure 1. (left) Experimental (■, ▲) and calculated (—) (by CLINP 2.1) pH = *f*(*Z*) dependences for the system $WO_4^{2-}-H^+-H_2O$ at different concentrations. (right) Calculated diagrams of IPTA distribution α, mol.% = $\varphi(Z)$: **1**, WO_4^{2-}; **2**, $W_6O_{20}(OH)_2^{6-}$; **3**, $W_{12}O_{40}(OH)_2^{10-}$; **4**, $HW_7O_{24}^{5-}$; **5**, $H_3W_{12}O_{40}(OH)_2^{7-}$; **6**, $W_{12}O_{38}(OH)_2^{6-}$; **7**, $H_2W_{12}O_{40}(OH)_2^{8-}$; bold line, overall quantity of paratungstate anions $H_xW_{12}O_{40}(OH)_2^{(10-x)^-}$.

Curves **A** are for solutions immediately after mixing and **B**, 60 min after mixing.

Table 2. Concentration constants of the formation of isopolytungstate anions.

	$\log K_c$ (*S*)[a] of particle formation					
	$C_W = 0.001\,\mathrm{mol\,L^{-1}}$ ($\mu = 0.025\,\mathrm{mol\,L^{-1}}$)		$C_W = 0.005\,\mathrm{mol\,L^{-1}}$ ($\mu = 0.25\,\mathrm{mol\,L^{-1}}$)		$C_W = 0.01\,\mathrm{mol\,L^{-1}}$ ($\mu = 0.50\,\mathrm{mol\,L^{-1}}$)	
Anions	0 min	60 min	0 min	60 min	0 min	60 min
$W_6O_{20}(OH)_2^{6-}$	51.39 (0.37)	51.09 (1.28)	52.82 (0.33)	52.82 (0.27)	51.49 (0.25)	51.37 (0.17)
$HW_7O_{24}^{5-}$	71.38 (0.25)	71.31 (0.77)	72.94 (0.27)	73.18 (0.25)	71.82 (0.19)	71.49 (0.20)
$W_{12}O_{40}(OH)_2^{10-}$	118.33 (0.45)	118.88 (0.59)	121.43 (0.44)	120.94 (0.48)	119.20 (0.30)	118.31 (0.27)
$H_2W_{12}O_{40}(OH)_2^{8-}$	–	–	–	130.17 (1.06)	–	127.73 (0.41)
$H_3W_{12}O_{40}(OH)_2^{7-}$	–	133.60 (0.52)	132.63 (0.50)	135.05 (0.42)	130.61 (0.48)	132.24 (0.27)
$W_{12}O_{38}(OH)_2^{6-}$	–	136.60 (0.90)	134.82 (0.30)	137.67 (0.40)	134.37 (0.35)	135.85 (0.28)
F	0.105	0.207	0.236	0.331	0.182	0.148
F/*n*	0.004	0.007	0.008	0.012	0.006	0.004

[a] *S* denotes a mean square deviation.

In this case, $HW_7O_{24}^{5-}$ almost disappears from solution, and the contents of paratungstates $H_xW_{12}O_{40}(OH)_2^{(10-x)-}$ increase dramatically resulting in an increase in the pH. This is what can be seen in the distribution diagrams that describe the state of ions 60 min after the initial solution mixing (figure 1). Therefore, this might complicate the prepartion of heptatungstate, and at the same time paratungstates can be obtained in a relatively wide *Z* range.

To successfully prepare Co(II) isopolytungstates, we took into consideration the results obtained during the investigation of the processes in acidified solutions of sodium tungstate, namely changes in the isopolytungstate anions distribution diagrams depending on the acidity *Z* and the time of maturation. To obtain cobalt(II) isopolytungstates, the needed acidity *Z* was created by nitric acid in 0.1 or 0.01 mol L^{-1} solutions of sodium tungstate, and then cobalt nitrate was added dropwise with vigorous stirring until the desired $Y = \nu(W)/\nu(Co)$ was reached.

3.2. *System with acidity Z = 0.00*

First of all, violet amorphous cobalt tungstate $CoWO_4 \cdot 4H_2O$ can be isolated from 0.1 mol L^{-1} solution of sodium tungstate at pH = 8.24 and *Y* = 0.67. Investigation of thermolysis products by X-ray diffraction analysis showed that the product of annealing at 500°C is a pure $CoWO_4$ phase (JCPDS 15–867).

3.3. *System with acidity Z = 0.50*

After the addition of a small amount of cobalt nitrate (*Y* = 26) to the acidified 0.1 mol L^{-1} solution of sodium tungstate (*Z* = 0.50, pH = 7.6), precipitation was not observed, but later white crystals of sodium paratungstate $Na_{10}[W_{12}O_{40}(OH)_2] \cdot 21H_2O$ appeared.

When the amount of cobalt nitrate was increased ($Y = 6.65-1.33$), then the violet mixed precipitation of $16CoWO_4 \cdot 4H_2O + Na_{10}[W_{12}O_{40}(OH)_2] \cdot 32H_2O$ appeared. It is interesting to note that if the same acidified solution of sodium tungstate was first matured for 2 months, and then the same amount of cobalt nitrate ($Y = 6.65$–1.33) was added, the pink–violet precipitation mixture contained also cobalt paratungstate: $6Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O + 70CoWO_4 \cdot 4H_2O + Na_{10}[W_{12}O_{40}(OH)_2] \cdot 32H_2O$, correlating well with the material balance equation and supported by elemental analysis.

3.4. *System with acidity Z = 0.75*

When cobalt nitrate was added to the acidified $0.1\,mol\,L^{-1}$ solution of sodium tungstate ($pH = 7.35$) till $Y = 4.43$, the mixed pink precipitation was $13CoWO_4 \cdot 4H_2O + Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O + Na_{10}[W_{12}O_{40}(OH)_2] \cdot 32H_2O$. When the amount of cobalt nitrate was increased ($Y = 2.26$) and the precipitation was left to stir for 1 day, then the pink precipitate contained cobalt tungstate and paratungstate B $6CoWO_4 \cdot 4H_2O + Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O$.

3.5. *Systems with acidity Z = 1.00*

At this acidity at $Y = 2.66$ and 1.33, sodium tungstate solutions (0.1 mol, $pH = 6.67$) give the mixed pink precipitate of cobalt tungtate and paratungstate B of cobalt and sodium ($3.5CoWO_4 \cdot 4H_2O + 1.5Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O + Na_{10}[W_{12}O_{40}(OH)_2] \cdot 21H_2O$). Moreover, at $Y = 1.33$, the amount of sodium paratungstate B decreases.

If the same acidified solution of sodium tungstate was first matured for 2 months ($pH = 6.98$), and only then cobalt nitrate was added till $Y = 1.33$, the precipitate contained cobalt tungstate and paratungstate $2CoWO_4 \cdot 4H_2O + Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O$ only and sodium paratungstate was absent.

If acidified $0.01\,mol\,L^{-1}$ solution of sodium tungstate is used, then at $Y = 1.33$, crystallization of only $Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O$ (**1**) occurs and its composition is the same as described [8].

Thus, the decrease of Y leads to the decrease of sodium paratungstate content in precipitation, and the latter disappears completely if the solutions were matured before the addition of Co(II). Decrease of the initial concentration of sodium tungstate from 0.1 to $0.01\,mol\,L^{-1}$ leads to the predominant formation of cobalt paratungstate B $Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O$.

3.6. *Systems with acidity Z = 1.17*

At $Z = 1.17$ and $Y = 3.33$, sodium tungstate solution (0.1 mol, $pH = 5.15$) gives orange–red precipitate that was matured under the mother liquor for 10 days. The results of chemical analysis suggest that the obtained solid is a mixture of neutral and acidic cobalt paratungstate B $5Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O + 2Co_4H_2[W_{12}O_{40}(OH)_2] \cdot 34H_2O$. Interestingly, the increase in Co(II) ($Y = 1.60$) does not change the qualitative composition of the precipitation: $5Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O + 2Co_4H_2[W_{12}O_{40}(OH)_2] \cdot 20H_2O$.

When $0.01\,\mathrm{mol\,L^{-1}}$ solution of sodium tungstate was used ($Z = 1.17$, $Y = 2.66$) and the orange–red precipitate that appeared after Co(II) addition was matured for 40 days under the mother liquor, the new phase was solely cobalt paratungstate $Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O$ (**2**), and its hydrate composition was different from the one described in [8].

Therefore, we have shown that the utilization of initial solutions of sodium tungstate with concentration $C_W = 0.01\,\mathrm{mol\,L^{-1}}$ instead of $0.1\,\mathrm{mol\,L^{-1}}$ led to the elimination of acidic paratungstate formation. As a result, pure cobalt paratungstate B with different cation and anion sub-lattice structures was isolated.

As in the similar structure [8] that differs from **2** by the content of crystallized water, one can observe clusters of tungstate octahedra being surrounded by cobalt octahedra and water. The structure of cluster in **2** is shown in figure 2.

The W–O distances lie within the limits of 1.712–2.348 Å, and "theoretically right" angles in the tungsten octahedra are within 70.54–104.37°, indicating a significant distortion of these octahedra. Variation of the respective Co–O distances and O–Co–O angles is substantially smaller. Figures 3 and 4 show the projection of the structure of **2**. Cobalt octahedra serve as bridges and combine tungsten clusters into complex 3-D structures, similar to the structure described [8]. But, compared to the latter, cobalt octahedra are packed more regularly, located either in the crystallographic planes (1 0 0) or in the channels along the direction (1 0 0). As a result, the structure possesses some voids along (1 0 0) that contain only water molecules (figure 4), and some of them are disordered (atoms O73–O82).

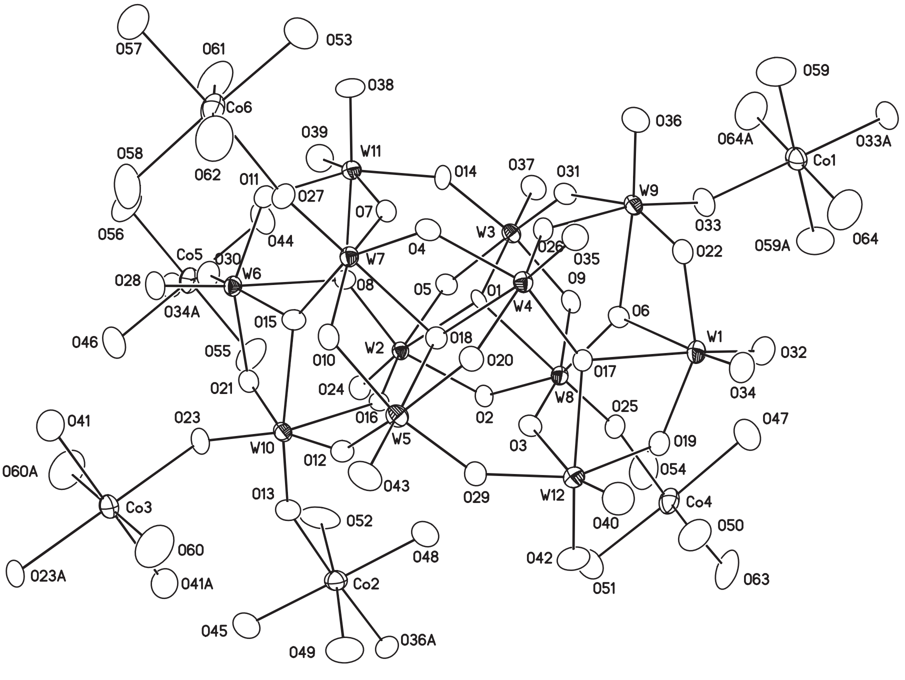

Figure 2. The structure of the cluster in **2**. Symmetry equivalent atoms are marked with *A*.

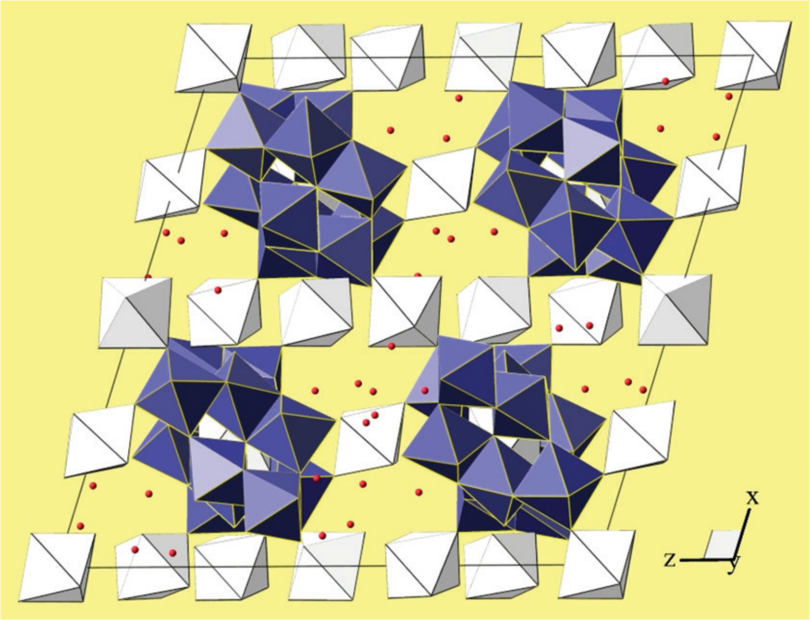

Figure 3. Projection of the structure of **2** along *y*-axis.

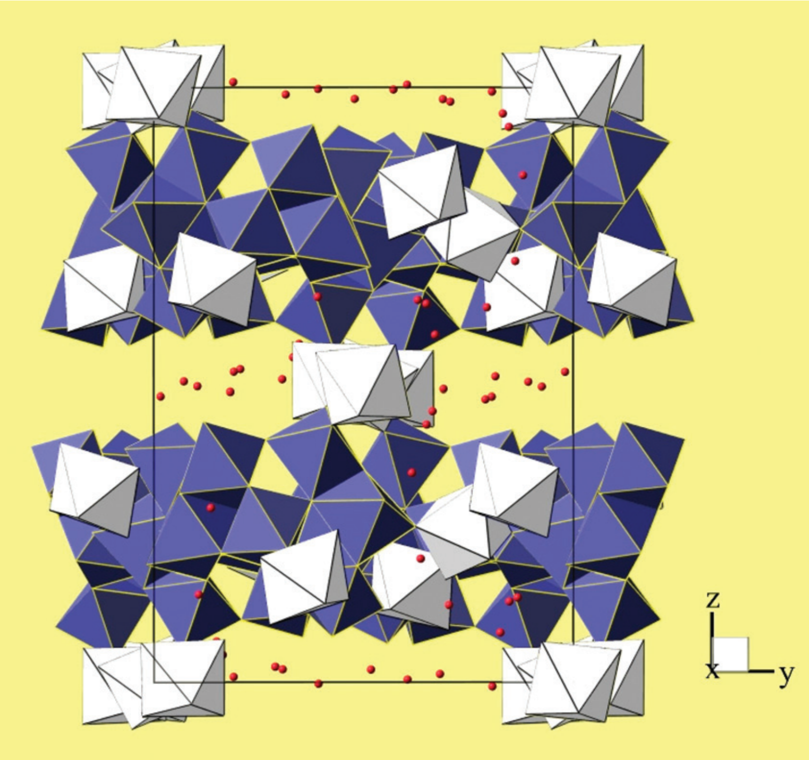

Figure 4. Projection of the structure of **2** along *x*-axis.

3.7. *System with acidity $Z = 1.29$*

At $Z = 1.29$ and $Y = 1.87$, red precipitate is formed from 0.1 mol L^{-1} solution of sodium tungstate. The maturation of this precipitate under the mother liquor for 2 weeks (phase **3**) and 3 weeks (phase **4**) does not lead to changes in the quantitative composition of the solids. The isolated phases can be related to the acidic cobalt paratungstates $Co_4H_2[W_{12}O_{40}(OH)_2] \cdot 34H_2O$.

3.8. *Systems with acidity $1.35 < Z < 2.00$*

The addition of cobalt nitrate to the 0.1 mol L^{-1} solution of sodium tungstate with acidity $Z > 1.35$ does not lead to the formation of precipitate. The addition of acetone (till *ca* 50% v/v) to these systems leads to the formation of red glassy phase that is stable in the mother liquor. In open air, the isolated phase is extremely hygroscopic that makes chemical analysis and precise molecular formula determination difficult.

4. Conclusions

The conditions for the successful preparation of neutral Co(II) paratungstates ($Co_5[W_{12}O_{40}(OH)_2] \cdot 34H_2O$ and $Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O$), and an acidic ($Co_4H_2[W_{12}O_{40}(OH)_2] \cdot 34H_2O$) Co(II) paratungstate were optimized. The most suitable systems for the successful synthesis of the compounds with paratungstate B anion $W_{12}O_{40}(OH)_2^{10-}$ appear to be those with $Z = 1.00$–1.25. Structural investigation of Co(II) paratungstate B $Co_5[W_{12}O_{40}(OH)_2] \cdot 37H_2O$ by single-crystal X-ray diffraction analysis revealed the formation of cluster.

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Supplementary material

Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and isotropic displacement parameters were deposited at Fachinformationszentrum Karlsruhe under depository number CSD No. 421297. These data can be obtained from FIZ *via* http://www.fiz–karlsruhe.de/obtaining_crystal_structure_data.html

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