

SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Synthesis and Thermal Dehydration of Hexaaquarhodium(III) Phosphates

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Abstract—Complex salts $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4$ (**I**) and $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4 \cdot \text{H}_2\text{O}$ (**II**) were obtained. Dehydration processes of compounds **I** and **II** were studied by thermogravimetry and differential scanning calorimetry. The heat effect for the loss of 0.82 ± 0.01 H_2O (hydration) molecule was found to be 54 ± 1 kJ/mol, while that for the loss of coordinated H_2O is 47 ± 1 kJ/mol (for **I**) and 43 ± 1 kJ/mol (for **II**). The solid phases of dehydration products were studied by X-ray powder diffraction, IR and ^{31}P MAS NMR spectroscopy, and they were found to be polymers.

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There is no information in the literature on the dehydration of platinum metal aqua complexes in spite of the fact that aqua ions of all these metals, except osmium, were found to exist in solutions. This is likely to be caused by the difficulties of isolation of these cations into solid phase as simple salts with inorganic acid anions.

The complex salts of stoichiometry $[\text{M}(\text{H}_2\text{O})_6]\text{A}$ and $[\text{M}(\text{H}_2\text{O})_6]\text{A} \cdot x\text{H}_2\text{O}$, where A is an anion of a strong acid, represent good models to answer the question on the difference in the behavior of hydration and coordinatively bonded water molecules during salt dehydration process. For rhodium complexes, such examples are provided by hexaaquarhodium(III) phosphates.

Attempted isolation of rhodium phosphate complexes into solid phase was reported in two works [1, 2]. In the first work, a twenty-fold excess of phosphoric acid reacted with a solution of sodium hexanitrorhodate at 150°C to give complex of composition $\text{Na}_3(\text{H}_2\text{O})\text{Rh}_2(\text{HPO}_4)_5 \cdot 5\text{H}_2\text{O}$, while $\text{Na}_{10}(\text{H}_2\text{O})_2\text{Rh}_2(\text{H}_2\text{P}_2\text{O}_7)_9 \cdot 4\text{H}_2\text{O}$ was obtained at 200°C. The second paper discloses the reaction of a solution of rhodium hydroxide in nitric acid with a calculated amount of phosphoric acid, the mixture was evaporated to dryness and then homogenized for a long time at 700°C. An increase in annealing temperature to 875°C leads to emergence of wide unidentified reflections in X-ray powder diffraction patterns. The annealing at 970°C for 24 h leads to formation of the

RhPO_4 phase, which is isomorphic to the high-temperature CrPO_4 phase (orthorhombic, $a = 10.391$ Å, $b = 13.091$ Å, $c = 6.391$ Å). At 1000°C, the phase degrades to give Rh_2O_3 ; rhodium metal forms at 1070°C. Anhydrous rhodium phosphate is a dark brown powder insoluble in concentrated mineral acids and aqua regia.

Using a modified procedure [2], followed by transport under a chlorine atmosphere at 1050 → 950°C, dark red single crystals of RhPO_4 were prepared, and their structure was determined [3].

The aim of this work is to prepare solid phases of hexaaquarhodium(III) phosphates, characterize them by different physicochemical methods, and study thermal dehydration process.

EXPERIMENTAL

Prepared compounds were used: $[\text{Rh}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ with rhodium content 25.8% (calculated 25.73%), KH_2PO_4 , Na_2HPO_4 of reagent grade, and NaOH of analytical grade.

IR spectra were recorded on a SCIMITAR FTS 2000 Fourier-transform spectrometer in KBr pellets in wave number range 400–4000 cm^{-1} .

X-ray diffraction study was carried out on a DRON-3M diffractometer ($R = 192$ mm, CuK_α radiation, Ni filter, scintillation detector with Soller slit amplitude discrimination at the primary and reflected beams 2.5°) within 2θ angle range 5°–60° with scan

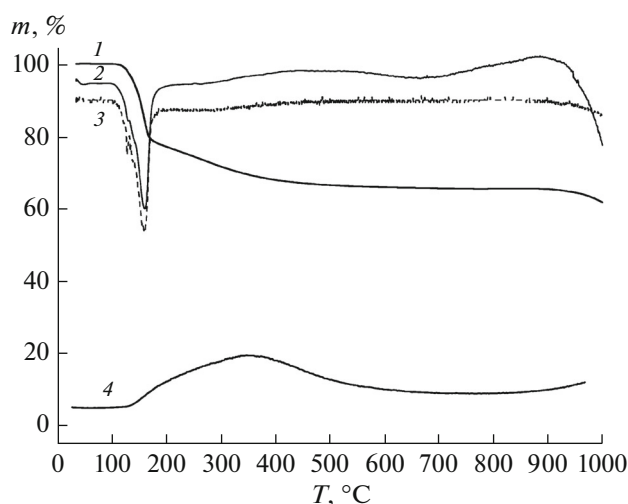


Fig. 1. Thermogram of compound I. (1) TG curve, (2) DSC curve, (3) DTG curve, (4) water evolution into gas phase curve.

angle step 0.02° . Samples were prepared by application of an alcoholic suspension on a polished side of a standard quartz cuvette. A sample of polycrystalline silicon ($a = 5.4309 \text{ \AA}$) obtained by similar manner was used as an external reference.

Thermogravimetric measurements with monitoring of gas phase composition were performed on a NETZSCH STA 409 PC Luxx[®] DSC/TG installation with QMS 100 mass spectrometer (sample weight 10–20 mg, $g\text{-Al}_2\text{O}_3$ crucible, helium flow rate 40 mL/min, heating rate 10 K/min in the range 20–1000°C).

Thermodynamic properties were studied on a NETZSCH DSC 204 F1Phoenix differential scanning calorimeter (DSC). DSC measurements were conducted by heat flux method at constant heating rate of 3 K/min in an open aluminum crucible in Ar flow (rate 25 mL/min). Base line signal obtained on heating of two empty crucibles was abstracted from experimental values. The values of temperature T_{onset} and enthalpy ΔH were averaged over three measurements.

NMR spectra were recorded on a Bruker Avance-III-500 NMR spectrometer (in external magnetic field $H_0 = 11.74 \text{ T}$). Solid-state magic angle spinning ^{31}P NMR spectra (spinning frequency 10 kHz) were recorded at 296 K. A 85% H_3PO_4 was used as an external reference.

RESULTS AND DISCUSSION

Synthesis and Characterization of Compounds

To obtain $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4$ (I), an equimolar solution of $\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$ with concentration toward phosphate 0.25 mol/L was added dropwise to a freshly prepared solution of $[\text{Rh}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3 \cdot$

$5\text{H}_2\text{O}$ (1 g in 150 mL of water) on vigorous stirring until pH 3.0–3.2. The resultant precipitate was kept under mother liquor for 3 h, separated by filtration, washed three times with water and twice with ethanol, and dried in air. The substance is a yellow crystalline powder insoluble in water and ethanol. Yield ~50%. For $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4$ (I) anal. calcd. (%): Rh, 33.64; P, 10.13. Found (%): Rh, 33.7; P, 9.9.

IR (ν , cm^{-1}): $\nu(\text{O-H})$ 3386–2818, $\delta(\text{O-H})$ 1582, $\nu(\text{P-O})$ 959, $\delta(\text{P-O})$ 591, 535, 502.

The crystal structure of compound I is described in [4].

To obtain $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4 \cdot \text{H}_2\text{O}$ (II), 1 g of $[\text{Rh}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 6.5 mL of water, quickly mixed with 20 mL of $\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$ buffer solution (concentration toward phosphate 0.25 mol/L), solution pH was adjusted to pH 6 with 2 M NaOH solution, the solution with the precipitate was kept for 3 h. The precipitate was separated by filtration, washed three times with water and twice with ethanol, and dried in air. The substance is a yellow crystalline powder insoluble in water and ethanol. Yield ~98%. For $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4 \cdot \text{H}_2\text{O}$ (II) anal. calcd. (%): Rh, 31.77; P, 9.57. Found (%): Rh, 31.7; P, 9.5.

IR (ν , cm^{-1}): $\nu(\text{O-H})$ 2940, $\delta(\text{O-H})$ 1629, $\nu(\text{P-O})$ 983, $\delta(\text{P-O})$ 733, 583, 536.

We failed to obtain single crystal suitable for X-ray diffraction analysis, therefore the structure was established by Professor S. D. Kirik by X-ray powder diffraction. Cubic syngony, space group $Pa\bar{3}$, $a = 9.3361(2) \text{ \AA}$, $V = 813.76(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.640 \text{ g/cm}^3$.

Thermal Properties

Figure 1 shows the thermogram of compound I. DTG curve (3) exhibits an endothermic effect at 150–170°C, which also appears on DSC curve (2). Weight loss curve of TG (1) shows two regions that differ in the rate of loss of volatile component in temperature ranges 120–200 and 200–650°C. Only water molecules were found in the gas phase (curve 4). The curves for compound II have the same shape except for the presence of supplementary small endothermic effect at 105°C because of the loss of hydration water molecule.

To reveal process stoichiometry, we conducted dehydration of the compounds at different temperatures under isothermal conditions. The results for compound I are presented in Fig. 2.

At temperature $<100^\circ\text{C}$, the constant value of weight loss is not reached over measurable time intervals of several tens of hours. The constant value of weight loss is achieved above 200°C for 1 h and remains constant for several hours. The compound loses all six molecules of coordinated water at 600°C and constant weight of compound $[\text{RhPO}_4]$ retains until 850–900°C. The sample changes color from light

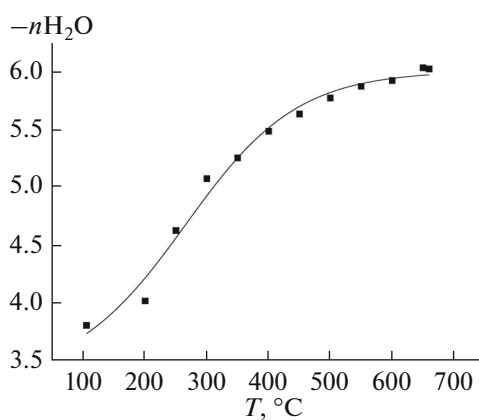


Fig. 2. Isothermal dehydration of $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4$ (I).

yellow through brown to black. The dehydration at temperature $>100^\circ\text{C}$ leads to violation of crystal structure of the samples and phases become X-ray amorphous. In contrast to the initial crystalline compounds readily soluble in 0.3 M H_2SO_4 , the X-ray amorphous phases are virtually insoluble under these conditions.

Thermodynamic Properties

The samples of complexes **I** and **II** (10–15 mg) were studied in temperature range $25\text{--}230^\circ\text{C}$. The irreversibility and completeness of dehydration processes were verified by repeated heating of the samples immediately after the first measurement.

For initial samples of complex **I**, the temperature dependence of DSC signal (Fig. 3a, curve 1) exhibits two thermal anomalies corresponding to the loss of adsorbed water at $T_{\text{onset}} = 105.8 \pm 0.2^\circ\text{C}$ and coordinatively bound water molecules at $t_{\text{onset}} = 116.7 \pm 0.3^\circ\text{C}$. To reveal heat effects, the samples of complex **I** were annealed in Ar flow 50 mL/min for 2 h followed by measurement in temperature range $25\text{--}230^\circ\text{C}$ (Fig. 3a, curve 2). The thermal effect due to loss of 4.04 ± 0.4 coordinated H_2O molecules per formula units was found to be 187 ± 4 kJ/mol.

The temperature dependence of DSC signal for the initial samples of complex **II** (Fig. 3b, curve 1) displays two thermal anomalies corresponding to the loss of hydration water molecules at $T_{\text{onset}} = 91.3 \pm 0.1^\circ\text{C}$ and coordinated water molecules at $T_{\text{onset}} = 106.2 \pm 0.1^\circ\text{C}$. To reveal thermal effects, the samples of the complex were annealed in Ar flow 50 mL/min for 2 h followed by measurement in temperature range $25\text{--}230^\circ\text{C}$ (Fig. 3b, curve 2). Weight loss for complex **II** in heating cycles corresponds to composition $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4 \cdot 0.82\text{H}_2\text{O}$. The thermal effects due to loss of 0.82 ± 0.01 hydration molecules and 4.06 ± 0.04 coordinated H_2O molecules per formula units were found to be 54 ± 1 and 172 ± 4 kJ/mol, respectively.

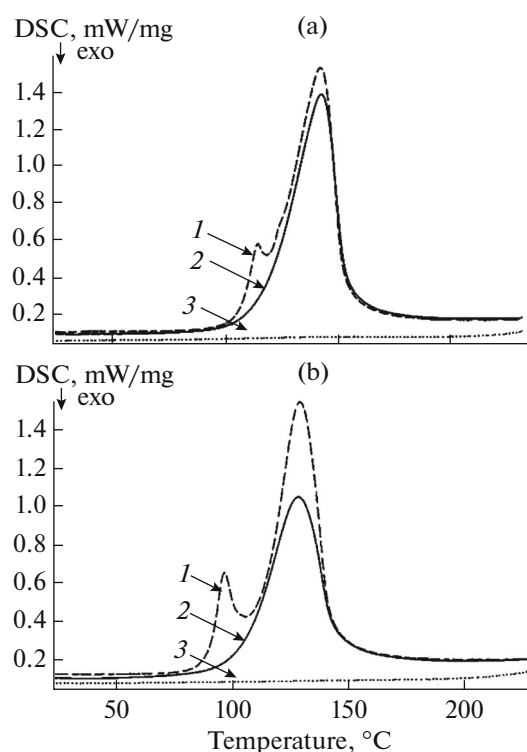


Fig. 3. Temperature dependences of heat flux for complexes $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4$ (a) and $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4 \cdot 0.8\text{H}_2\text{O}$ (b): (1) initial sample, (2) sample kept at 100°C , (3) repeated measurement for sample heated to 230°C .

In the studied temperature range, both initial compounds form stable X-ray amorphous phase of composition $[\text{Rh}(\text{H}_2\text{O})_2\text{PO}_4]$. Thermal effects for the elimination of one coordinated water molecule are 47 ± 1 and 43 ± 1 kJ/mol for compounds **I** and **II**, respectively. The main contribution to these characteristics is provided by the difference in bond energy in coordinates $\text{Rh}\text{--}\text{OH}_2$ and $\text{Rh}\text{--}\text{OPO}_3$. However, since complexes **I** and **II** have different structures (monoclinic $C2/c$ and cubic $Pa\bar{3}$) and therefore different hydrogen bond systems, a slight difference in thermal effects beyond measurement error is caused by difference in these components. The elimination of one molecule of hydration water from crystal structure requires larger energy expenses as compared with energy cost for elimination of one water molecule from the inner coordination sphere of rhodium aqua ion. This situation appears because the energy expense for elimination of water molecule from coordination sphere is partially compensated by the formation energy of the $\text{Rh}\text{--}\text{O}\text{--}\text{PO}_3$ bond. The shape of peaks in Figs. 3a and 3b indicates that there is no difference in the energy of sequential elimination of water molecules from inner coordination sphere.

According to diffractograms, the dehydration of compound **II** at 70°C with loss of one water molecule

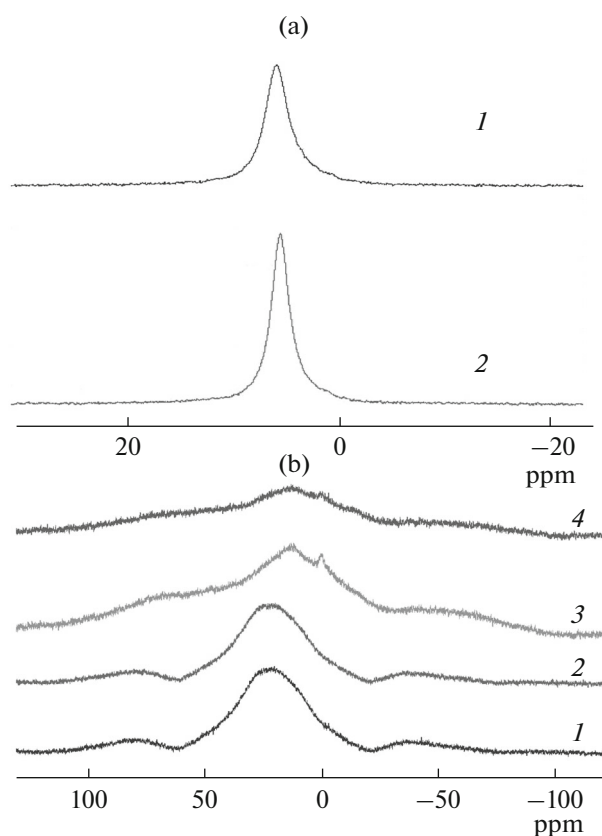


Fig. 4. (a) ^{31}P MAS NMR spectra of (1) $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4$ and (2) $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4 \cdot \text{H}_2\text{O}$. (b) ^{31}P MAS NMR spectra: (1), (2) spectra of the $[\text{Rh}(\text{H}_2\text{O})_2\text{PO}_4]$ phase; (3), (4) spectra of the $[\text{RhPO}_4]$ phase. Compounds I and II were used as initial complexes for odd and even spectra, respectively.

does not degrade the crystal structure of the initial compound but makes it slightly more defect that affects reflections at far angles.

NMR Spectroscopy

The initial samples of $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4$ I and $[\text{Rh}(\text{H}_2\text{O})_6]\text{PO}_4 \cdot \text{H}_2\text{O}$ II are characterized by singlet NMR signals with chemical shifts $\delta = 5.44$ ppm ($W = 2.7$ Hz) and $\delta = 5.10$ ppm ($W = 2.1$ Hz) (Fig. 4a) typical for $[\text{PO}_4]^{3-}$ ion in aqueous solutions [5]. The slight difference in δ values seems to be caused by the difference in the crystal structures of the complexes and related hydrogen bond systems. The latter is confirmed by IR spectra: $\nu(\text{P}-\text{O})$ is observed at 959 cm^{-1} for compound I and 983 cm^{-1} for compound II.

The dehydration of complexes I and II at 170°C leads to the formation of the $[\text{Rh}(\text{H}_2\text{O})_2\text{PO}_4]$ phase, and the signal is shifted downfield and strongly broadened: $\delta \sim 22$ ppm ($W \sim 33$ Hz). For a sample of phase $[\text{RhPO}_4]$, the position of ^{31}P NMR signal is shifted to

13 ppm and undergoes strong broadening (Fig. 4b) in spite of magic angle spinning. Broadening value exceeds 50 ppm, which corresponds to the scattering of local magnetic fields larger than 6 G and the observed broadening may be caused by the emergence of magnetic moments. We failed to record NMR spectra for the samples calcined at 970°C on account of large broadening.

The character of spectral changes is similar to that previously revealed in the study of solid-phase condensation of hexaaquarhodium(III) sulfates [6]: line broadening in NMR spectra and downfield shift on increase in dehydration degree indicates the formation of polymeric compounds.

The conducted study shows that the thermal dehydration of rhodium(III) aqua ion in phosphate phases proceeds in three stages. At the first stage, elimination of adsorption or hydration water occurs, it requires small energetic expense at process onset temperature of 105.8 and 91.3°C . The elimination of four molecules of coordinated water at the second stage leads to formation of kinetically stable X-ray amorphous phase of composition $[\text{Rh}(\text{H}_2\text{O})_2\text{PO}_4]$. Dehydration onset temperature for anhydrous rhodium phosphate is only $\sim 10^\circ\text{C}$ higher than adsorption water elimination temperature, whereas these values differ for monohydrate only by $\sim 15^\circ\text{C}$. Such a small difference allows us to assume that these stages at isothermal process are not separated and the reactions proceed simultaneously, which is observed for monohydrate dehydration at 70°C .

Energy expense for the cleavage of $\text{Rh}-\text{OH}_2$ bond is partially compensated by advantage in the formation of $\text{Rh}-\text{OPO}_3$ bond. In octahedral aqua ion, the elimination of any of six water molecules is equally probable and the process seems to be random. The subsequent monodentate coordination of phosphate ion at vacant site in rhodium coordination sphere leads to formation of X-ray amorphous phase. When this stage of dehydration is completed, all donor atoms of phosphate ion produce chemical bonds with rhodium providing bridging and the donor ability of the ligand becomes exhausted. Therefore the elimination of two remaining water molecules requires considerably higher energy cost and occurs in temperature range $250-650^\circ\text{C}$.

The resulting X-ray amorphous phase of composition $[\text{RhPO}_4]$ is relatively stable in temperature range $650-850^\circ\text{C}$. In our opinion, the phase of such a structure is metastable because rhodium(III) ion after removal of two last water molecules forms two unoccupied coordination sites. Its metastability is eliminated due to reconstruction that causes two of four donor atoms of phosphate ion to accomplish μ function, while two other atoms perform μ_2 function, which is confirmed by structure analysis presented in [3].

At temperature $>1000^\circ\text{C}$ in open system, the phase quantitatively decomposes according to equation

$2[\text{RhPO}_4] = 2\text{Rh} + \text{P}_2\text{O}_5 + 3/2\text{O}_2$. Weight loss is observed experimentally on the prolonged calcination of sample even at 970°C along with the emergence of reflections in diffractograms that confirm the formation of anhydrous crystalline rhodium phosphate. The proposed process sequence for the dehydration of hexaaquarhodium(III) phosphates does not contradict the observed experimental facts.

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