

Formation of Mononuclear Rhodium(III) Sulfates: ^{103}Rh and ^{17}O NMR Study

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Abstract—It was shown that the monomeric rhodium sulfate complexes $[\text{Rh}(\text{H}_2\text{O})_4(\text{SO}_4)]^+$, *trans*- $[\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2]^-$, *cis*- $[\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2]^-$, and $[\text{Rh}(\text{SO}_4)_3]^{3-}$ were not predominant forms in aqueous solutions. The ^{103}Rh NMR chemical shifts of the complexes were assigned, and the conditions for their formation in solutions, concentration parameters, and acidity at which the fraction of the monomers was maximal were determined. The constants of formation of the complexes and ion pair (IP) were estimated: $K_{\text{IP}} = 8 \pm 3.5$, $K_1 \approx 8$, $K_{2\text{trans}} \approx 1$, $K_{2\text{cis}} \approx 1$, and $K_3 \approx 2$.

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INTRODUCTION

No convincing information on the existence of mononuclear Rh(III) sulfate complexes in aqueous solutions and solid phases was available up to the recent time. An attempt to study the complex formation by the ^{103}Rh NMR method [1] did not answer this question, because the $[\text{Rh}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_8]^{4+}$ dimer was the initial form that reacted with sulfuric acid, and all detected chemical shifts lied in a weak field relatively to the line of the rhodium aqua ion, which contradicts the general regularity of the displacement of the chemical shift of the central atom upon mononuclear complex formation [3–5]. The study of rhodium migration under the action of the electric field in sulfuric acid media [6] showed that both cationic and anionic complexes existed in the solutions, but the nuclear character of the species observed was not discussed.

We showed [7] that two mutually related systems of mononuclear and polynuclear complexes existed in sulfuric acid solutions of rhodium at room temperature, and the former was not predominant. Red rhodium sulfate $\text{Rh}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ isolated to the solid phase [8] contains the coordinately bound sulfate ion, which is almost insoluble in water and amorphous to X-rays, being a polynuclear compound. Its anhydrous form is crystalline [9] and also polynuclear. Soluble yellow rhodium sulfate $\text{Rh}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ [8, 10] and binary rhodium and cesium sulfate [11–13] are crystalline and contain no coordinately bound sulfate ion.

The purpose of this work is to search for conditions of the formation of mononuclear Rh(III) sulfate complexes, to determine the region of sulfuric acid con-

centrations providing a sufficient fraction of the $[\text{Rh}(\text{H}_2\text{O})_{6-2y}(\text{SO}_4)_y]^{3-2y}$ form, and to estimate their constants of formation.

EXPERIMENTAL

Two series of solutions were prepared for the study: for the first type, active rhodium hydroxide was dissolved in a calculated volume of 4.5 M H_2SO_4 , and the solution was quantitatively transferred to a volumetric flask. For the second type, an exact weighed sample of basic rhodium sulfate with the known content of the metal and SO_4^{2-} was dissolved in a calculated volume of water or the corresponding solution of acid. If necessary, the Rh concentration was determined by atomic adsorption spectroscopy after it was transformed into the chloride complexes, and the concentration of the sulfate ion was determined gravimetrically in the form of BaSO_4 after rhodium was separated as hydroxide. The rhodium concentration in solutions was varied from 0.2 to 2.0 mol/l, and that of H_2SO_4 ranged from 1×10^{-3} to 5 mol/l. The ^{103}Rh and ^{17}O NMR spectra of the prepared solutions were recorded from time to time, monitoring the change in the ion composition in the time interval from several days to two years.

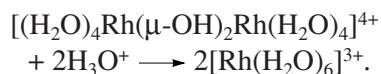
For the synthesis of the monomeric rhodium sulfate complexes, $[\text{Rh}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ (1.00 g) was dissolved in a saturated K_2SO_4 solution (6 ml). The resulting yellow solution was heated in a water bath at 90°C for 8 h, and the solution turned intensely red.

The NMR spectra were recorded on an AVANCE-400 spectrometer (Bruker) at 54.24 (^{17}O) and 12.77 (^{103}Rh) MHz with an accumulating rate of 33 and 0.1 Hz, respectively. The ^{17}O NMR spectra were measured at 323–343 K to increase the line resolution. The chemical shifts (δ) for ^{17}O were read from the external standard H_2O , and those for ^{103}Rh were read from $\Xi = 3.16$ MHz reduced to the field of the spectrometer. The NMR spectra were recorded at the natural content of isotopes.

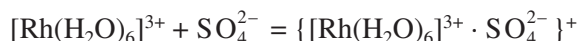
To isolate the fraction of the anionic complexes, ion-exchange chromatography was carried out on a column using the Dowex 50X8 cation-exchange resin in the H-form as described earlier [14].

RESULTS AND DISCUSSION

After active rhodium hydroxide was dissolved in HClO_4 , 95% metal were presented by the form with $\delta = 9918$ ppm at 302 K. The temperature coefficient of the line is ~ 2 ppm/deg, and the variation of the line position at a change in the acid concentration in the interval from 9.4 to 3.2 mol/l is at most 3 ppm. Since the temperatures and ion compositions of the solutions differ, it can be asserted that the line belongs to the rhodium aqua ion and its position agrees well with published data [1, 2, 15]. Less than 5% rhodium in these solutions are presented by the form $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{H}_2\text{O})_4]^{4+}$, which disappears after several weeks, transforming into the aqua ion by the equation



The line of the aqua ion is absent from the spectra of the sulfuric acid solution, and the predominant line belongs to the labile ion pair $\{[\text{Rh}(\text{H}_2\text{O})_6]^{3+} \cdot \text{SO}_4^{2-}\}^+$ [7] with $\delta = 9903$ ppm at 302 K. The concentration of the dihydroxo form $\mu\text{-OH}$ is approximately the same as in chloric solutions. The fast (in the NMR time scale) exchange in the process



is a reason for the detection of the exchange line for which $\delta = \alpha_1\delta_1 + \alpha_2\delta_2$, where α_1 and α_2 are the fractions and δ_1 and δ_2 are the chemical shifts of the corresponding forms. In this case, the exchange line position depends on the equilibrium concentration of SO_4^{2-} .

In the system under study, the ^{103}Rh NMR exchange signals are observed for the rhodium complexes involved in acid-base equilibria. For the inert rhodium complexes (slow exchange in the NMR time scale), the line position remains constant and its intensity is proportional to the number of atoms. In the ^{17}O NMR spectra the exchange line is assigned to the equilibrium $\text{HSO}_4^- + \text{H}_2\text{O} = \text{SO}_4^{2-} + \text{H}_3\text{O}^+$. We estimated $pK_2 = 0.7 \pm$

0.1 at room temperature from the functional dependence of the chemical shift of the pH of solutions $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$.

The ^{17}O NMR spectra of hydrochloric and sulfuric solutions exhibit the symmetric line of the rhodium-coordinated water molecules with $\delta = -142$ ppm, indicating that the nearest environment of the central atom in the ion pair remains unchanged. The ion composition of the sulfuric solution is stable at room temperature for several weeks. Two lines are detected in the region of chemical shifts of the oxygen atoms of the sulfate ion. The assignment of these lines was given [7], and the line at 163–159 ppm is a superposition of the lines of the donor oxygen atoms of the coordinated sulfate ion and the exchange line of $\text{SO}_4^{2-} - \text{HSO}_4^-$.

After the complicated signal was decomposed into individual components, the concentrations of the coordinated sulfate ion and equilibrated bisulfate and sulfate ions can be calculated as follows.

The balance equations based on protons and sulfates at the known initial concentrations of sulfuric acid and rhodium are written in the form

$$[\text{H}^+] + [\text{HSO}_4^-] = 2c_{\text{SO}_4^{2-}} - 3c_{\text{Rh}} = B,$$

$$[\text{SO}_4^{2-}] + [\text{HSO}_4^-] + {}^k\text{SO}_4^{2-} = c_{\text{SO}_4^{2-}}$$

or

$$[\text{SO}_4^{2-}] + [\text{HSO}_4^-] = c_{\text{SO}_4^{2-}} - {}^k\text{SO}_4^{2-} = A,$$

where ${}^k\text{SO}_4^{2-}$ was calculated from the integral intensity of the ^{17}O NMR line with $\delta = 171$ ppm

$$K_2 = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-],$$

where K_2 is the second constant of sulfuric acid dissociation determined by the NMR method and equal to 0.16 at room temperature.

The solution of the system of three equations gives the expression

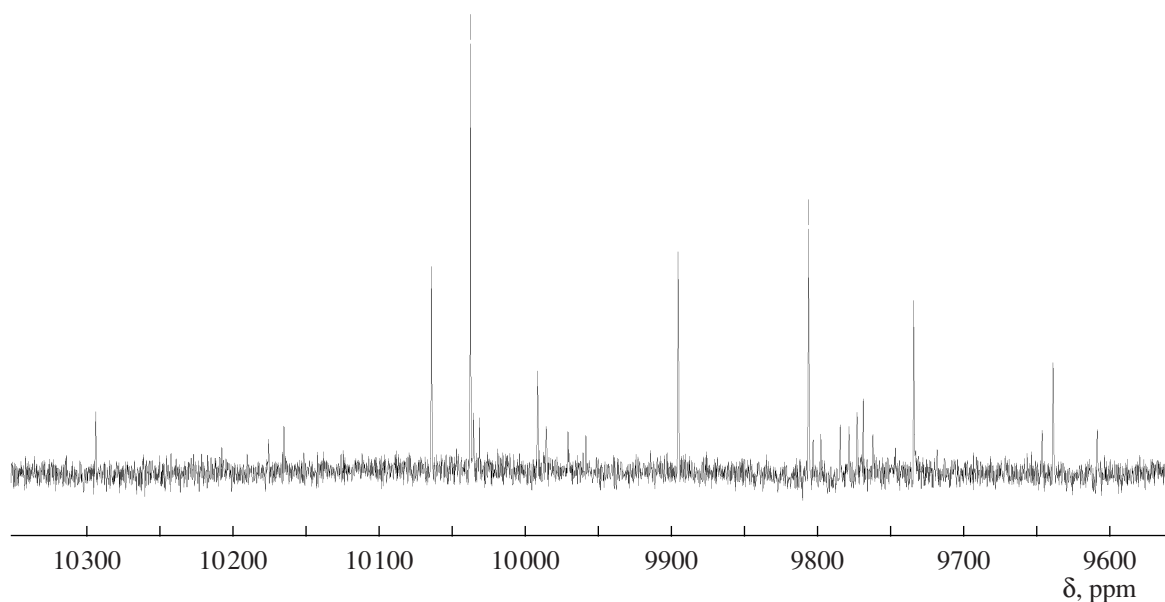
$$[\text{SO}_4^{2-}]^2 + (B - A + K_2)[\text{SO}_4^{2-}] - K_2A = 0,$$

from which

$$\begin{aligned} [\text{SO}_4^{2-}] &= -(B - A + K_2)/2 \\ &\pm \sqrt{\{(B - A - K_2)/2\}^2 + K_2A}, \quad [\text{HSO}_4^-] = \\ &= A - [\text{SO}_4^{2-}], \quad [\text{H}^+] = B - A + [\text{SO}_4^{2-}]. \end{aligned}$$

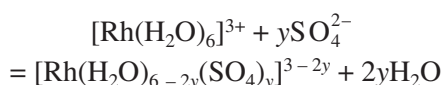
At $[\text{H}^+] \geq 2$ mol/l, $[\text{SO}_4^{2-}] \ll [\text{HSO}_4^-]$, and $[\text{HSO}_4^-] \approx A$, then $[\text{H}^+] = B - A$.

When rhodium hydroxide is dissolved in sulfuric acid, after the neutralization process achieved equilibrium, $c_{\text{H}^+} < c_{\text{SO}_4^{2-}}$, and their ratio depends on the initial



The ^{103}Rh NMR spectrum ($c_{\text{Rh}} = 0.792$, $c_{\text{SO}_4} = 0.792$ mol/l, pH 2, $T = 300$ K).

ratio $\text{Rh} : \text{SO}_4^{2-}$. This parameter was varied to prepare solutions with the ratio from 1:1 to 1:24. The equilibrium H^+ concentration changed from 1×10^{-3} to 10 mol/l, and that of SO_4^{2-} changed from 0.60 to 0.15 mol/l. It was revealed that the ^{103}Rh NMR spectra of solutions with the ratio $\text{Rh} : \text{SO}_4^{2-} = 1 : 16$ and higher contain only the exchange line of the ion pair, and other lines were observed in the high field relatively to the aqua ion line, regardless of the time of solution storage. This means that for the formation of the mononuclear rhodium sulfate complexes by the equation



the upper boundary of the equilibrium acidity lies at a level of 0.26 mol/l, and $[\text{SO}_4^{2-}] \approx 0.2$ mol/l in this case. Lines begin to appear in the high field below this acidity, and their intensity increases with a decrease in the acidity and an increase in the equilibrium concentration of the sulfate ion.

The typical ^{103}Rh NMR spectrum is shown in the figure. It should be noted that intending to increase the equilibrium sulfate ion concentration one should not decrease the acidity to $\text{pH} > 3$, because strong polynuclear hydroxo complexes begin to form rapidly in this region.

Solutions of the second type exhibit another pattern of the formation of the mononuclear sulfate complexes in the solution. The spectra of the freshly prepared solutions with the storage time to 2 days contain only lines of the polynuclear complexes in the low field, and the

main part of rhodium exists in large aggregates, which are not detected by the NMR method. The concentration of ionic sulfate in the system is at the level 1×10^{-4} mol/l.

The further fragmentation of large fragments of the solid phase occurs with an increase in the storage time of the solutions (7–15 days) and is accompanied by an increase in the ionic sulfate concentration to the level $(1-2) \times 10^{-1}$ mol/l and the appearance of lines of the mononuclear complexes in the high field. The high-field lines, whose positions coincide in two series, were assigned to the monomeric rhodium(III) sulfate complexes (at $T = 300$ K) and have the following values:

| Complex | δ , ppm |
|---|----------------|
| $\{[\text{Rh}(\text{H}_2\text{O})_6]^{3+}(\text{SO}_4)^{2-}\}^+$ | 9889 ± 2 |
| $[\text{Rh}(\text{H}_2\text{O})_5(\text{SO}_4)]^+$ | 9883 ± 2 |
| $[\text{Rh}(\text{H}_2\text{O})_4(\text{SO}_4)]^+$ | 9813 ± 2 |
| <i>trans</i> - $[\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2]^-$ | 9742 ± 2 |
| <i>cis</i> - $[\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2]^-$ | 9692 ± 2 |
| $[\text{Rh}(\text{SO}_4)_3]^{3-}$ | 9650 ± 5 |

The following can serve as additional arguments in favor of validity of the assignment. An additional amount of NaHSO_4 equal by the metal content in the solution was introduced into the solution in order to increase the equilibrium SO_4^{2-} concentration. After two days, the fraction of the mononuclear sulfate complexes increases by three times, indicating that the position of complex formation equilibrium shifts rather rapidly.

Table 1. Dynamics of generation of the $[\text{Rh}(\text{H}_2\text{O})_{6-2y}(\text{SO}_4)_y]^{3-2y}$ forms in aqueous solutions of basic rhodium sulfate (solutions of series 2)*

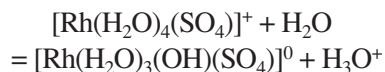
| Complex | Time (τ) | | | | | |
|---|-------------------------------------|----------------------|---------------------|---------------------|------------------------|------------------------|
| | 7 days ^a | 15 days ^b | 2 days ^c | 6 days ^d | 17 months ^d | 31 months ^d |
| | $[\text{SO}_4^{2-}]_{\tau}$, mol/l | | | | | |
| | 0.09 | 0.24 | 0.05 | 0.10 | 0.45 | 0.45 |
| | Content, % | | | | | |
| $\{[\text{Rh}(\text{H}_2\text{O})_6]^{3+} \text{SO}_4^{2-}\}^+$ | 2 | 3 | 0 | 8 | 10 | 13 |
| $[\text{Rh}(\text{H}_2\text{O})_4(\text{SO}_4)]^+$ | 9 | 3 | 0 | 9 | 13 | 10 |
| <i>trans</i> - $[\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2]^-$ | 7 | 7 | 6 | 3 | 7 | 7 |
| <i>cis</i> - $[\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2]^-$ | 0 | 3 | 4 | 0 | 5 | 6 |
| $[\text{Rh}(\text{SO}_4)_3]^{3-}$ | 3 | 3 | 3 | 0 | 6 | 4 |

* Initial concentrations: ^a $c_{\text{Rh}} = 1.00$, $c_{\text{SO}_4} = 0.80$, $c_{\text{HClO}_4} = 0.16$; ^b $c_{\text{Rh}} = 1.00$, $c_{\text{SO}_4} = 0.85$, $c_{\text{HClO}_4} = 0.16$; ^c $c_{\text{Rh}} = 1.00$, $c_{\text{SO}_4} = 0.85$;

^d $c_{\text{Rh}} = 0.86$, $c_{\text{SO}_4} = 0.73$.

The solutions stored for six and nine months were separated by chromatography. According to the data of atomic adsorption spectroscopy, the first fraction eluted with 1×10^{-3} mol/l HClO_4 contained 13 and 17% metal, which was in the samples, respectively. The content of the metal in these species was calculated from the intensity of the ^{103}Rh NMR lines with $\delta = 9813$, 9742, 9692, and 9650 pm. The metal content turned out to be 15 and 20%, respectively. It is clear that the cation-exchange resin in the H-form does not sorb the anionic complexes. In our opinion, the presence of $[\text{Rh}(\text{H}_2\text{O})_4(\text{SO}_4)]^+$ in this fraction is due to the fact that the solutions with the high rhodium concentration (0.84 and 1.95 mol/l) were separated, which resulted in a sharp increase in the acidity of the aqueous phase of the first fraction. The high acidity prevented the sorption of the cation with the positive charge equal to one.

An alternative explanation of the observed fact can be the shift of the acid-base equilibrium position



during the separation process. The existence of this equilibrium is confirmed by the detection of the exchange signal of the monosulfate form: at $[\text{H}^+] = 1 \times 10^{-3}$ mol/l $\delta = 9813$, whereas at $[\text{H}^+] = 0.65$ mol/l $\delta = 9824$ ppm.

The study of the dynamics of mononuclear complex formation in the both types of solutions shows that the rates of the processes and the fractions of the complexes differ strongly for each type of solutions at approximately equal initial concentrations of the metal and SO_4^{2-} , pH, and storage time of the solutions. The data on the dynamics of mononuclear form generation

in aqueous solutions of basic rhodium sulfate are presented in Table 1.

The fast formation of the mononuclear species in the solution at low storages and low concentrations of ionic sulfate can be explained by the fact that these forms are generated by the fragmentation of large aggregates of the dissolved solid phase rather than by the stepped complex formation of the rhodium aqua ion with SO_4^{2-} , as it occurs in the solutions of the first series. The terminal positions of the large symmetric high-nuclearity complexes with the double sulfate bridges contain the mononuclear fragments $\{\text{Rh}(\text{H}_2\text{O})_4(\text{SO}_4)\}^+$ and $\{\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2\}^-$ coordinated through the ordinary sulfate bridge. These fragments are cleaved by water in such a way that a water molecule adds to the core and the mononuclear fragment becomes an individual chemical form. This fragmentation mechanism makes it possible to consistently explain the formation of the mononuclear sulfate complexes at very low concentrations of ionic sulfate in the solution. No cleavage of the OH bridges occurs, because the pH in the systems remains almost unchanged (3.0–2.5) even upon a prolonged storage of the solutions.

The fragmentation rate increases sharply at a high acidity. The dynamics of the process in 0.94 M HClO_4 is presented in Table 2.

In strongly acidic solutions after two days, the fraction of the mononuclear complexes is by three times higher than that in weakly acidic solutions and then remains unchanged for a long time. This is due to the fact that both the ordinary sulfate bridges and ordinary hydroxide bridges are rapidly cleaved at the acidity 0.94 M HClO_4 . The double bridges in oligomeric low-nuclearity complexes are cleaved with a considerably

Table 2. Dynamics of fragmentation of the solid phase $[\text{Rh}(\text{SO}_4)_{0.85}(\text{OH})_{1.30}(\text{H}_2\text{O})_{3.03}]$ in 0.94 M HClO_4 , $c_{\text{Rh}} = 0.22$, $c_{\text{SO}_4} = 0.19$ mol/l

| Complex (δ , ppm) | Storage time of solution | | |
|--|---|-------------------------|---------------------------|
| | 2 days | 55 days | 11 months |
| | $[\text{HSO}_4^-] + [\text{SO}_4^{2-}]$, mol/l | | |
| | $\sim 4 \times 10^{-3}$ | $\sim 4 \times 10^{-2}$ | $\sim 3.4 \times 10^{-2}$ |
| | content, % | | |
| $[\text{Rh}_2(\mu\text{-SO}_4)_2(\text{H}_2\text{O})_8]^{2+}$ (10064) | 14 | 17 | 17 |
| $[\text{Rh}_2(\mu\text{-SO}_4)(\text{H}_2\text{O})_{10}]^{4+}$ (10038) | 45 | 44 | 48 |
| $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ (9917) | 0 | 9 | 5 |
| $[\text{Rh}(\text{H}_2\text{O})_4(\text{SO}_4)]^+$ (9824) | 14 | 11 | 10 |
| $[\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2]^-$ (9742) | 12 | 6 | 4 |
| $[\text{Rh}(\text{SO}_4)_3]^{3-}$ (9650) | 5 | 6 | 4 |

lower rate, which is indicated by the fact that the fraction of the $(\mu\text{-SO}_4)_2$ dimers and $\sim 10\%$ oligomers with the $(\mu\text{-OH})_2$ bridges retained constant at the moment of the experiment end.

At low concentrations of ionic sulfate in the system, the mononuclear sulfate complexes and dimers with the $\mu\text{-SO}_4$ bridges compete for the coordination of SO_4^{2-} . The acidity of the solution changes from 0.94 to 0.72 mol/l during the experiment. As a whole, the system did not reach the equilibrium state. No local equilibrium of the mononuclear sulfate complexes was achieved, which is indicated by a change in the fraction of the rhodium aqua ion and the absence of the *cis*- $[\text{Rh}(\text{H}_2\text{O})_2(\text{SO}_4)_2]^-$ form. As shown [16], isomerization is the slowest process in the system of rhodium complexes.

The stepped constants of formation of the mononuclear sulfate complexes were estimated. The equilibrium concentration of the sulfate ion was calculated from the ^{17}O NMR spectra, and the concentration of the complex forms was obtained from the ^{103}Rh NMR spectra. After the corresponding concentrations were substituted into the equations of the constants, we obtained the following values: $K_1 \approx 8$, $K_{2\text{trans}} \approx 1$, $K_{2\text{cis}} \approx 1$, and $K_3 \approx 2$. The K_{IP} value (IP is the radical pair) was obtained by independent experiments, being equal to 7 ± 3.5 .

As should be expected, the mononuclear rhodium sulfate complexes turned out to be weak with the close stepped constants equal to ~ 1 .

We performed an experiment to isolate the monomeric rhodium sulfate complexes into the solid phase.

For this purpose, a weighed sample of the rhodium aqua ion sulfate was dissolved in a saturated solution of K_2SO_4 , and the solution was heated at 90°C for 8 h. Although the color changed intensely, the subsequent cooling of the obtained solution and its concentrating gave no isolated solid phase. The analysis of the ^{103}Rh NMR spectra shows that the fraction of the formed monomeric complexes was at most 13% and the major part of the metal existed as dimers (45%) and oligomeric complex forms (20%). For a total rhodium concentration in the solution of 0.5 mol/l, the concentration of the monomeric sulfate complexes was ~ 0.06 mol/l, which is, most likely, lower than the saturation threshold of potassium salts of di- and trisulfatorhodiates. Thus, to date no monomeric rhodium sulfate complexes were isolated into the crystalline phase by traditional methods.

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