ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 11, pp. 824–829. © Pleiades Publishing, Ltd., 2009.
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# $^{103}$Rh and $^{17}$O NMR Study of Oligomer Rhodium(III) Sulfates in Aqueous Solutions

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Received February 26, 2009

**Abstract**—By virtue of $^{103}$Rh-, $^{17}$O-NMR, electrophoresis in agarose gel, and pH-metry, we report on the formation of rhodium(III) sulfate complexes in aqueous solutions. At higher concentrations of sulfuric acid (above 3 M), more than 90% of metal was found to stay in the state of symmetric polynuclear complexes containing magnetically equivalent rhodium atoms. We also labeled the $^{103}$Rh-NMR chemical shifts for the complexes with 3, 4 and 6 metal atoms in the spectra.

**DOI:** 10.1134/S1070328409110062

The NMR technique for heavy nuclei provides us with a deeper understanding of solution chemistry. The investigation of complex formation in the system Rh(III)–$H_2SO_4$–$H_2O$ by $^{103}$Rh-NMR showed [1–3] that the number of reliably detectable lines in rhodium spectra could not be approximated exclusively by the formation of mononuclear complexes. The detected lines lie both in strong and weak fields relative to the line of a aquaion whose position had been clearly established [2, 4]. While the lines in the stronger field were attributed with sufficient confidence to mononuclear sulfate complexes, in the weaker field, there were only lines belonging to dimer complexes $[(H_2O)_4Rh(\mu\text{-}SO_4)_2Rh(H_2O)_4]^{2+}$ and $[(H_2O)_4Rh(\mu\text{-}SO_4)(\mu\text{-}OH)Rh(H_2O)_4]^{3+}$. The content of rhodium corresponding to the lines in the weaker field in comparison to the lines of dimers was measured at 30% of overall rhodium in the system; the lines were assumed to represent oligomers with a nuclearity above 2. Nevertheless, all attempts at chemical synthesis failed and resulted in the formation of X-ray amorphous phases of alternating composition predominantly containing basic rhodium sulfates [5–7].

The actual work was devoted to the study of concentration conditions favoring the maximum formation of oligomer complexes in solution, attribution of top lines in $^{103}$Rh-NMR spectra to individual forms, and establishment of their structure and composition.

## EXPERIMENTAL

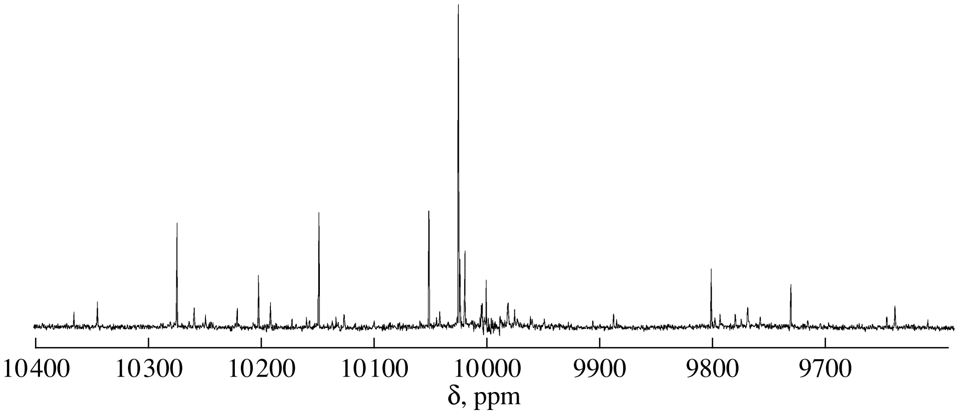
For the investigation, two types of the rhodium solution were prepared. In the first case, the precise weight of basic rhodium sulfate with a known content of Rh and $SO_4^{2-}$ was dissolved in a measured volume of water or sulfuric acid solution. In the second case, the calculated weight of freshly precipitated "active" rhodium hydroxide containing a predetermined quantity of the metal, was dissolved in the required volume of sulfuric acid to ensure the desirable Rh : $SO_4^{2-}$ ratio.

The samples of active rhodium (III) hydroxide being prepared by neutralization of sulfurous or nitrous solutions of rhodium, ordinary slightly contaminated with $Cl^-$, by solid NaOH until pH 9 at room temperature. The precipitate was rinsed with water until the negative test on chloride ion and then immediately dissolved in a calculated amount of sulfuric acid. The solution was then transferred to a 5 ml volumetric flask. If necessary, the concentration of rhodium was determined by atomic absorbance spectroscopy and that of sulfate ions, by gravimetry.

To avoid local supersaturation, the neutralization of stable acidic solutions of rhodium was achieved by gaseous ammonia as follows: the glass with the rhodium solution and a magnetic stirrer bar were placed in a vessel which contained the calculated quantity of concentrated aqueous ammonia on the bottom. The vessel was sealed and the solution was stirred at ambient temperature until the neutralization reaction completed. When the vessel was opened, the pH value was measured; the solution was left to store for two days at room temperature and was investigated by NMR.

From here on, the term "stable solution" means the solution which with an unchanged NMR spectrum for a period of 2–3 months after completion of the process at the specified concentration and temperature and storage at ambient temperature for 2 days.

Acidity during neutralization was controlled using an Anion-410 ionometer; the glass electrodes were calibrated using standard buffer solutions.



$^{103}$Rh-NMR spectrum of basic rhodium sulfate in 0.45 M $H_2SO_4$ stored for 7 days at room temperature, $c_{Rh} = 1.0$, $c_{SO_4} = 1.45$ M.

Electrophoresis experiments were performed in a water-cooled glass column with an inner of diameter 3 mm furnished with a hole for the injection of samples. As a medium we used 0.8% agarose gel dispersed in a $5 \times 10^{-3}$ M aqueous solution of sodium sulfate; the sample volume was 30 μl, the time of experiment was 60–120 min, the current intensity was 0.8–1.0 nA, and the potential gradient was 6 V/cm.

The NMR spectra were recorded on a Bruker AVANCE-400 spectrometer with working frequencies of 54.24 ($^{17}$O) and 12.77 ($^{103}$Rh) MHz. The oxygen spectra were recorded at 323–343 K for better line resolution. The chemical shift values were determined referring to water as an outer standard and to $\Xi$= 3.16 MHz adjusted to the spectrometer's own field in the case of $^{17}$O and $^{103}$Rh nuclei, respectively. All spectra were recorded with the natural content of the isotopes.

The partial content of rhodium forms was calculated on the basis of the intensity of the respective $^{103}$Rh-NMR lines referring to the sum integration. The concentration of free sulfate and hydrogen ions was derived from the complex signal of sulfate in $^{17}$O-NMR spectra in the field of 172–159 ppm after decomposition into individual components by WINNMR software.

## RESULTS AND DISCUSSION

Figure 1 shows the typical view of the $^{103}$Rh NMR spectrum of basic rhodium sulfate of the composition $[Rh(SO_4)(OH)(H_2O)_3]$ in 0.45 M $H_2SO_4$ stored for 7 days at room temperature. There were up to 43 lines of various intensities located in three intervals: 9820–9620 (**I**), 10080–10020 (**II**), and 10380–10140 ppm (**III**). In the area of chemical shifts characteristic for $(\mu\text{-OH})_2$ oligomers, we identified the lines of $[Rh_2(\mu\text{-OH})_2(H_2O)_8]^{4+}$ with $\delta$ = 9996 ppm (4%) [4], and ionic pair $\{[Rh(H_2O)_6]^{3+}SO_4^{2-}\}^+$, $\delta$ = 9901 ppm (~1%).

The most intensive lines of interval **I** refer to mononuclear sulfate rhodium complexes, whose partial content was approximately 10%, on the basis of the following speculation. It had been reported that the formation of mononuclear complexes of rhodium (III) shifts the line in the $^{103}$Rh-NMR spectrum into the stronger field in comparison to the line of the rhodium aqua ion [8–10]. As well, the partial intensity of the complex form in this case depends on the equilibrium concentration of the ligand, which we observed in our case. The stronger acidity resulted in the reduction of $[SO_4^{2-}]$ according to the equation $SO_4^{2-} + H^+ = HSO_4^-$, ; thus, the intensity of the lines relating to interval **I** decreased and disappeared at acidity values above 0.3 M.

In range **II**, we identified the lines of the $[(H_2O)_4Rh(\mu\text{-SO}_4)_2Rh(H_2O)_4]^{2+}$ ($\delta$ = 10068 ± 2 ppm) and $[(H_2O)_4Rh(\mu\text{-SO}_4)(\mu\text{-OH})Rh(H_2O)_4]^{3+}$ ($\delta$ = 10040 ± 2 ppm) complexes, which together amounted to ~36%, while the entire interval amounted to 54%. The lines of the interval had been attributed earlier [2, 7, 11] based on data on the dynamics of changes in the $^{103}$Rh-NMR spectra due to shifts in equilibrium. Also, the results of chromatographic separation of the solutions and determination of the composition for individual fractions was taken into account. Interval **III** represented lines in the weaker field relative to the line of the rhodium aqua complex; therefore, the lines were assumed to correspond to the oligomer complex as well. A similar behavior had been observed for hydroxo complexes before [12]. In this range, the most intensive lines were ~20% on the total content within an interval of 30%. The lines were located in the areas of 10380–10350, 10300–10270, 10240–10230 and 10180–10140 ppm.

The most intensive line of each interval was accompanied by a pair of reliably detected lines five to ten times less intensive than was most clearly observed in the case of interval **II**. As well, the major line relating to $[(H_2O)_4Rh(\mu\text{-SO}_4)(\mu\text{-OH})Rh(H_2O)_4]^{3+}$ complex ($\delta$ =

**Table 1.** Neutralization of sulfurous solution of rhodium by gaseous ammonia, $C_{Rh} = 0.19$ mol/l, $c_{SO_4^{2-}} = 1.75$ mol/l, $[H^+]_0 =$ 1.25 mol/l, Rh : $SO_4^{2-}$ = 1 : 9

| pH | δ, ppm | Complex | Partial content, % | $I_{10068}/I_{9901}$ |
|---|---|---|---|---|
| 0.5 | 10069 | $[(H_2O)_4Rh(\mu\text{-}SO_4)_2Rh(H_2O)_4]^{2+}$ | 67 | 2.0 |
| | 9901 | $\{[Rh(H_2O)_6]^{3+}SO_4^{2-}\}^+$ | 33 | |
| 1.6 | 10067 | $[(H_2O)_4Rh(\mu\text{-}SO_4)_2Rh(H_2O)_4]^{2+}$ | 54 | 1.7 |
| | 10042 | $[(H_2O)_4Rh(\mu\text{-}SO_4)(\mu\text{-}OH)Rh(H_2O)_4]^{3+}$ | 7 | |
| | 9893 | $\{[Rh(H_2O)_6]^{3+}SO_4^{2-}\}^+$ | 33 | |
| | 10263 | ? | 6 | |
| 3.5 | 10068 | $[(H_2O)_4Rh(\mu\text{-}SO_4)_2Rh(H_2O)_4]^{2+}$ | 40 | 1.6 |
| | 10042 | $[(H_2O)_4Rh(\mu\text{-}SO_4)(\mu\text{-}OH)Rh(H_2O)_4]^{3+}$ | 23 | |
| | 9887 | $[Rh(H_2O)_5SO_4]^+$ | 24 | |
| | 10261 | ? | 3 | |
| | 10288 | ? | 10 | |

10040 ± 2 ppm, 26%) was detected along with two minor ones with δ = 10037 ± 2 (5%) and 10034 ± 2 (6%) ppm. Due to the high resolving ability of the spectrometer, individual detection of the lines was achieved despite the rather low spread between the lines. The ratio of line intensities did not stay constant and depended on the way the solution had been prepared, which indicated the occurrence of different similar but not identical complexes. For example, the ratio of intensities $I_{10040}/I_{10037}$ was 2.1 at pH 3 upon storage for 2 days, or 0.2 in 0.94 M $HClO_4$ solution in 55 days. In contrast, in 3.85 M aqueous sulfuric acid in 5 days, no lines were detected at all; lines with δ = 10034 ± 2 (13%), 10160 (14%), 10070 (42%), and 9480 (32%) ppm were detected instead. A year-long storage of the solution at room temperature led to the disappearance of all lines except lines of the dimer with a double sulfate bridge δ = 10070 ppm (85%) and ionic pair δ = 9893 ppm (15%). In our opinion, the observed changes corresponded to the following processes:

$$[Rh_2(\mu\text{-}SO_4)(\mu\text{-}OH)(H_2O)_8]^{3+} + H_3O^+ = [Rh_2(\mu\text{-}SO_4)(H_2O)_{10}]^{4+},$$

$$[Rh_2(\mu\text{-}SO_4)(H_2O)_{10}]^{4+} \longrightarrow [Rh_2(\mu\text{-}{*}SO_4)(H_2O)_{10}]^{4+},$$

where $\mu\text{-}{*}SO_4$ is a monodentate coordinated sulfate bridge; alternatively – bridge $HSO_4^-$. The complexes that formed appeared metastable and converted into more stable species slowly.

To determine the influence of pH on the formation of oligomer rhodium complexes, the neutralization of stable sulfate solution by gaseous ammonia was performed. The procedure described in the Experimental made it possible to maintain unchanged all concentration parameters except acidity. The results are presented in Table 1.

To isolate the possible coordination of ammonia to rhodium, all neutralized solutions were examined by $^{14}$N-NMR. The test indicated the presence of ammonium ion exclusively, or the versatile equilibrium of the ammonium ion–free ammonia molecule exchange.

In stable acidic solutions at pH 0.5 and below, two forms dominated: the dimer with the double sulfate bridge and ionic pair. The partial content of the dimer with the double $(\mu\text{-}SO_4)(\mu\text{-}OH)$ bridge did not exceed 6%; moreover, the form proved metastable and disappeared completely upon extra storage at ambient temperature for 3 months. The ratio of the molar concentration dimer : ionic pair in such a solution was measured at 1 : 1, which gave a solid basis for the statement of equilibrium station of the system. It was reported in [13] that in the $^{103}$Rh-NMR spectrum of sulfurous solution after storage for more than 20 years, two lines were detected only at 10092 and 9925 ppm with a ratio of ~2. Since the conditions of recording and concentration parameters of the solution were not given, we supposed that the entire spectrum was shifted by 22 ppm into the weaker field; therefore, the lines under discussion corresponded to $[Rh_2(\mu\text{-}SO_4)_2(H_2O)_8]^{2+}$ and $\{[Rh(H_2O)_6]^{3+}SO_4^{2-}\}^+$. From all of the above it follows that the local equilibrium dimer–ionic pair with an equilibrium constant around 1 was achieved at room temperature in acidic sulfurous rhodium (III) solutions containing ~0.2 mol/l of metal at a fixed content of sulfate.

The pH variation in the range 0.5–3.5 at 300 K and sulfate concentration of 1.75 mol/l showed no change in the chemical shift at δ = 10068 ± 2 ppm relating to $[(H_2O)_4Rh(\mu\text{-}SO_4)_2Rh(H_2O)_4]^{2+}$, which indicated less acidic properties of terminal aqueous molecules in contrast to, for instance, the $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ complex, for which the p$K_a$ value was reported at 1.59

**Table 2.** Parameters of rhodium (III) sulfurous solutions, Rh : $SO_4^{2-}$ = 1 : 9 storage time 3 months

| $c_{Rh}$ | $[SO_4^{2-}]$ | $[H^+]$ | δ $^{103}$Rh-NMR, ppm (partial content, %) | Sum of oligomers, % |
|---|---|---|---|---|
| mol/l | | | | |
| 0.19 | 0.14 | 1.25 | 10263(<1), 10163 (<1), 10069(63), 9902 (31) | 70 |
| 0.19 | 0.16 | 1.47 | 10168 (6), 10071 (73), 9906 (20) | 80 |
| 0.19 | 0.14 | 1.53 | 10360 (<1) , 10168 (<1),10070 (78), 9903 (17) | 80 |
| 0.62 | 0.27 | 4.38 | 10335 (9), 10268 (8), 10143 (9), 10072(58), 9892 (17) | 84 |
| 0.67 | 0.26 | 4.85 | 10335 (9), 10269 (7), 10143 (10),10072(62), 9892 (13) | 88 |
| 0.72 | 0.27 | 5.09 | 10332 (10), 10268 (7), 10145 (6), 10072 (57), 9892 (20) | 80 |

at 298 K [14]. The effect was likely caused by the reduction in total positive charge of the complex molecule. Nevertheless, the decrease in acidity to 1.6–3.5 led to occurrence of the line at 10043 ppm, which was known to correspond to the ion $[Rh_2(\mu\text{-}SO_4)(\mu\text{-}OH)(H_2O)_8]^{3+}$ [2], accompanied by a drop in intensity for the line at 10068 ppm. Hence, the $[Rh_2(\mu\text{-}SO_4)_2(H_2O)_8]^{2+}$ underwent substitution of one sulfate bridge, while the terminal water molecules remained untouched.

With increasing pH, the position of exchangeable line $\{[Rh(H_2O)_6]^{3+}SO_4^{2-}\}^+$ moved from 9901 to 9886 ppm, which was is probably explained by the elevated equilibrium concentration of $SO_4^{2-}$ and respective input of the ionic pair into the signal. The content of the form dropped as new lines in the weaker field appeared, which apparently indicated the formation of new complexes derived from the mother species. It could not be ruled out that at pH values above 3, the ionic pair converted into a mononuclear complex containing monodentate coordinated sulfate. Further transition to the area with pH > 4 made the solution heterogeneous, and the fast precipitation of a lemon-yellow solid was observed. The subsequent dissolution of the solid in nitric acid and return to the initial acidity value did not lead to the known $^{103}$Rh-NMR spectrum.

Thus, the oligomer rhodium complexes with sulfate bridges appeared quite stable in the area with pH < 1.6; the range 1.6–4.0 was characterized by an equilibrium transfer to the species with $(\mu\text{-}SO_4)(\mu\text{-}OH)$-bridges. At higher pH values, we detected quick substitution of sulfate bridges to hydroxyls and deprotonation of terminal water molecules [15] that resulted in sequential condensation, increased nuclearity, and precipitation.

To chart the area of existence for the oligomer complexes, we recorded and analyzed the $^{103}$Rh-NMR spectra of solutions obtained by dissolving active rhodium hydroxide in sulfuric acid with various Rh : $SO_4^{2-}$ ratios in the range from 1 : 24 to 1 : 2. The analysis of spectrum for the solution with Rh : $SO_4^{2-}$ ratio 1 : 9 is shown in Table 2.

The performance of the process in a strong acidic medium resulted in drastic simplification of the entire spectrum: all lines moved into the weaker field relative to the line of the ionic pair, their number dropped to four with the obvious domination of that corresponding to the complex $[Rh_2(\mu\text{-}SO_4)_2(H_2O)_8]^{2+}$ (δ = 10070 ± 2. In the recalculation with respect to the content of rhodium in the form of ionic pair, the average coordination number of sulfate was found to be 1. Since the form of the ionic pair contained no ligated sulfate and the major form had a stoichometric ratio of Rh : $SO_4^{2-}$ = 1 : 1, retention of the coordination number likely meant that the other complexes had identical stoichometry.

In the $^{17}$O-NMR spectra the complex signal of coordinated water consisted of two components: –138 (57%) and –142 (43%) ppm, which related to $\mu\text{-}SO_4\text{–}Rh\text{–}H_2O$ and $H_2O\text{–}Rh\text{–}H_2O$ containing species, respectively [2]. The absence of a signal at –123 ppm clearly indicated that a bond like $\mu\text{-}OH\text{–}Rh\text{–}H_2O$ did not form.

In our opinion, the lines of 10335, 10268 and 10143 ppm in the $^{103}$Rh-NMR spectra represented three different complexes containing more than two metal atoms which were also magnetically equivalent. The chosen technique of solution preparation included simultaneous a linear change of $c_{Rh}$ and $[H^+]$, therefore, the character and degree of the influence could not be stated unambiguously. The data of $^{103}$Rh-NMR analysis of solutions, obtained at various Rh : $SO_4^{2-}$ ratios, are presented in Table 3.

The partial content of the oligomers with nuclearity >2 varied from 6 to 26% dependending on the intial concentration parameters. In the acidity interval 0.1–0.25 M, the chemical species with δ > 10168 ppm were not detected at any metal concentration. At a stronger acidity of 3–5 M and lower metal concentration, no line was detected in the area either; however, the increase in metal concentration by more than three times lead to the appearance of the line with δ = 10143 ppm.

**Table 3.** Parameters of rhodium(III) sulfurous solutions, storage time 3 months

| Rh : $SO_4^{2-}$ | $c_{Rh}$ | $[H^+]$ | δ $^{103}$Rh-NMR, ppm, of major forms in weaker field (partial content, %) | Partial content of oligomers with nuclearity >2, % |
|---|---|---|---|---|
| | mol/l | | | |
| 1 : 24 | 0.22 | 5.12 | 10321 (7), 10267 (9) | 16 |
| 1 : 20 | 0.22 | 4.13 | 10322 (6), 10268 (7) | 13 |
| 1 : 16 | 0.20 | 3.13 | 10271 (9) | 15 |
| 1 : 9 | 0.19 | 1.25 | 10168 (6) | 6 |
| 1 : 9 | 0.72 | 5.10 | 10335 (9), 10269 (7),10143 (10) | 26 |
| 1 : 3 | 0.93 | 1.10 | 10158 (8) | 12 |
| 1 : 2 | 0.26 | 0.10 | 10168 (8) | 16 |

To refine the information on multiplicity of rather weak lines (below ~10%) in interval **III**, an additional analysis of experimental data was performed. The line at 10268 ppm kept its position, measured with a precision of ±2 ppm through the line of independent $^{103}$Rh-NMR spectra of different samples ($n = 13$). The content of rhodium in this form was found at a level of 7–9% in strong acidic and 1–3% in weak acidic media. The line at 10165 ± 3 ppm with an observed intensity of up to 10% was detected in solutions 0.1–1.25 M acidic, and those of basic, rhodium sulfate ($n = 9$). Finally, the line with δ = 10143 ± 2 ppm was discovered exclusively in the strong acidic solution with a rather high content of rhodium ($n = 7$).

Due to the dissolution of basic rhodium sulfate in 0.45 M $H_2SO_4$, we also reliably detected the lines of δ = 10385, 10364, 10293, 10278, **10267**, 10239, 10220, 10209, 10177, 10174, **10165**, 10153, 10150, and **10143** ppm, each containing a considerable quantity of metal which in total amounted to 30%. Bold lines marked corresponded to the complexes most abundant in the solutions of active rhodium hydroxide in sulfuric acid.

The observed alteration of ionic composition could be rationalized by the difference in starting materials:

$$(H_2O)_3Rh(OH)_3 + 3H_2SO_4$$

$$\longrightarrow [Rh(H_2O)_6]^{3+} + 3HSO_4^- \longrightarrow \text{oligomers},$$

$$[Rh(SO_4)(OH)(H_2O)_3] + H_2SO_4 \longrightarrow \text{oligomers}.$$

The processes are far from equilibrium; therefore, only the lines of quickly forming and most stable chemical forms coincide in both spectra.

All observed chemical shifts of oligomer complexes are grouped into four specified areas of interval **III**; as well, the most intensive lines of each group were shifted relative to the others into a weaker field by 80–90 ppm. The line of dimer $[Rh_2(\mu\text{-}SO_4)_2(H_2O)_8]^{2+}$ was taken as a control point. The substantial difference in chemical shifts and unstable behavior of the ratio of line intensities probably points to the fact that we are dealing with at least the formation of four complexes of different stoichometry and structure.

Presumably, the lines δ = 10165 and 10143 ppm correspond to trimers; 10295 and 10 268 ppm to tetramers; and 10380 and 10322 ppm, to hexamers—all species with magnetically equivalent atoms of rhodium. The lines of 10239, 10220 and 10 209 ppm, which had relative intensities of 1 : 2 : 1, were not observed in strong acidic media. In our opinion, the signals could be related to a metastable tetramer formed by fragmentation from bigger complexes of basic rhodium sulfate.

The formation of oligomer complex was also proved by electrophoresis experiments. For sulfurous solutions of rhodium, the frontier of samples shifted to the cathode by 2 cm in 120 min. No move toward the anode was detected. Nevertheless, no separation of samples to individual zones was observed either. In addition, some test experiments with aqueous $[Co(NH_3)_5Cl]Cl_2$ and $K_3[RhCl_6]$ were performed. The first complex showed motion toward cathode area by 8–10 cm in 60 min, while for the freshly prepared solution of the second complex, the zone shifted toward the anode area by ~10 cm in the same amount of time. Apparently, the lower mobility of sulfate complexes in comparison to mononuclear particles showed a substantial difference between their hydrodynamic radii at identical charge.

In acidic solutions, the motion of complexes only to the cathode area is allowed in the presence of a somewhat positive charge of particles. The contribution of the electroosmosis effect to the resulting distance of motion was determined based on the specific mobility of $[RhCl_3(H_2O)_3]$ and made the value 1 cm in 120 min. Therefore, the occurrence of positive charge on the particles of oligomer complexes led to the assumption of general complex stoichometry $(Rh : SO_4^{2-})_n$. The ratio of metal : sulfate stayed constant 1:1 at various oligomer degree $n$.

The growth in concentration for complexes with a nuclearity >2 resulted in broadening of the lines of 170 and 159 ppm of sulfate in $^{17}$O-NMR spectra. In 0.19 and 0.67 mol/l rhodium solutions with a ratio of Rh : $SO_4^{2-}$ = 1 : 9, the linewidths were 120 and 70 Hz for the first concentration, whereas it was 370 and 150 Hz for the other. For the solution with the ratio Rh : $SO_4^{2-}$ = 1:16 at $c_{Rh}$ = 0.20 mol/l, the detected values of the parameters were 170 and 80 Hz, and at $c_{Rh}$ = 0.74, the only exchangeable line was detected at δ = 155 ppm, with a width of 400 Hz. The observed alteration might have been derived from elevated viscosity of solutions with increased concentration of the oligomer complex.

Upon rapid heating of the latter solution to 80°C, two lines were detected in its $^{103}$Rh-NMR spectrum only, at 10388 (47%) and 10153 (53%) ppm. Due to the subsequent storage at room temperature, the system appeared metastable and drifted slowly to increase the number of complexes present. After one year in the spectrum, we detected the lines of δ = 10381 (3%), 10367 (31%), 10165 (8%), 10154–10152 (8) and 10141 (42%) ppm; the line of dimer $[Rh_2(\mu\text{-}SO_4)_2(H_2O)_8]^{2+}$ (δ = 10070 ± 2 ppm) was absent in both spectra. According to the preliminary notion, the complex (δ = 10388 ppm) probably converted into the form with δ = 10367 ppm, while the complex (δ = 10153 ppm) might have fragmented into two particles with δ = 10165 and 10141 ppm. The tiny difference between the chemical shifts of the initial and resulting forms (~10 ppm) indicate that the chemical bonds in the coordination environment of rhodium remained nearly unchanged, and only some minor rearrangement with the retention of the nuclearity value of the complexes took place.

The experimental data point to the presence of several rhodium complexes of various nuclearity in their sulfurous solutions in the concentration range 0.2–2.0 mol/l; more than 90% of metal was contained within. The growth in nuclearity was favored by elevated concentrations of rhodium and sulfuric acid; higher temperatures had the same effect. The elemental fragment of polynuclear complexes contained the bond sequences $\mu$-$SO_4$–Rh–$H_2O$ and $H_2O$–Rh–$H_2O$ in approximately equal amounts and had a charge of +1. The majority of oligomer complexes appeared to be symmetrical structures with magnetically equivalent rhodium atoms.

Since there was no opportunity to isolate the polynuclear rhodium species in an individual crystalline state, which would have permitted their further study by X-ray, for the time being, the discussion of the structure of complexes in detail appears groundless.

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