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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

On Preparation of Platinum(IV) Nitrate Solutions from Hexahydroxoplatinates(IV)

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Abstract—The parameters of the processes underlying the current technology of preparation of a $Pt(NO_3)_4$ solution were studied and optimized. The basic problems of the process scheme were determined, including limited storage time of solid hexahydroxoplatinum (IV) acid. Approaches were suggested for increasing the yield and the storage time of intermediate products and for simplifying the conditioning scheme of platinum (IV) nitrate with a significant reduction of time and energy costs.

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To date, platinum (IV) nitrate (PN) may be considered as the most promising precursor for the preparation of supported platinum catalysts, used for post-combustion of exhaust gases, in particular. This is primarily due to the fact that a conditioned nitric acid solution of PN is virtually free from catalyst poisons, especially alkali metal and Cl^- ions, and is therefore superior to precursors with another ligand environment of platinum (IV). In addition, PN has a low thermal stability.

Studies of the acid solutions of NP by the ^{195}Pt NMR method showed that the solution composition substantially changes with time. The same conclusion was made in [1]. The chemistry of these processes remains unknown. Practically no data are available in the literature on the forms of platinum in solutions with a high concentration of metal (c_{Pt} ~ 2 M) and nitric acid (up to ~ 10 M), including existence, nuclearity, and time transformations of forms, and features of the transformation processes. Only two studies [1, 2] are published that have a catalytic orientation and are devoted to commercial PN solutions at deep alkalization ([OH-]: [Pt] ~ 10). Despite a number of discrepancies, the above studies confirmed polynuclearity of the Pt (IV) forms and presence of bridging hydroxo-and (or) oxo groups between mononuclear fragments. Though the above studies have used the most up-to-date methods (EXAFS, TEM, NMR), their conclusions are too general and contain no experimental data on the specific platinum forms in the solutions.

Available in Russia technology of the preparation of PN solutions is to a certain extent similar to that proposed in a patent [3], but is much simpler and improved. The essence of both methods is expressed by the scheme:

$$H_2PtCl_6 \xrightarrow{\text{MOH}} M_2Pt(OH)_6 \xrightarrow{HNO_3} H_2Pt(OH)_6$$

$$\xrightarrow{HNO_{3(\text{conc})}} \text{PN solution,}$$

where M is K^+ [3] or Na^+ (in a current process), with the Na^+ and Cl^- concentrations in the final product must be strictly controlled in the latter process.

The principal problem in terms of technology is small storage time of solid $H_2Pt(OH)_6$ prior to preparing PN solutions: 2 or no more than 3 months at best. After expiring these periods, the properties of the reagent change. As a result, the resulting final product, a nitric acid solution of PN, does not pass control tests.

The study is aimed at increasing the yield of targed products or simplifying the operations in the existing scheme of the preparation of platinum(IV) nitrate solutions.

EXPERIMENTAL

Chloroplatinic acid produced at a Krastsvetmet Open Joint-Stock Company plant with a platinum content of 39.1% was starting reagent in all experiments. We used in the experiments solid $H_2Pt(OH)_6$ (65.0% Pt) and a PN solution (16.6% Pt, $d = 1.68$ g·cm^{-3}, $c_{Pt} = 1.43$ M, [HNO_3] ≈ 13 M), prepared at the above plant. All other reagents used were no lower than chemical purity grade.

The X-ray phase analysis (XRA) of polycrystalline samples was carried out on a DRON-RM4 diffractometer ($Cu_{K\alpha}$ radiation, graphite monochromator in the reflected beam, scintillation detector with amplitude discrimination). The samples were prepared by applying a suspension in hexane on the polished side of the cell made of fused quartz. As an external standard was used a sample of polycrystalline silicon (a = 5.4309 Å), prepared similarly. The thermal analysis (DTA) was performed on a TG 209 F1 Iris Thermo Microbalance instrument (NETZSCH) in Al_2O_3 crucibles in a helium or hydrogen atmosphere at a heating rate of 10° min^{-1}. Experimental data were processed with a standard Proteus Analysis software package. In addition, a modified derivatograph Q-1000 was used for thermal analysis in different gaseous environments. IR spectra of samples (KBr pellets) were recorded on a Scimitar FTS 2000 spectrophotometer in the region 400–4000 cm^{-1}. The content of Cl$^-$ ions in solid samples was determined by capillary electrophoresis (Capel-103R instrument). Prior to the analysis, complexes were reduced to metallic platinum with hydrazine hydrate. The content of Na$^+$ was determined by the atomic absorption spectroscopy (AAS) on a Z 8000 spectrophotometer (Hitachi) equipped with Zeeman background correction. The pH values were measured with an Anion-4100 pH meter (Infraspak-Analit). The electron absorption spectra (EAS) were recorded on a MPC-310 spectrophotometer (Shimadzu) and ^{195}Pt NMR spectra, on an Avance III 500 Bruker spectrometer (frequency 107.5 MHz). Chemical shifts, positive in a weak field, were counted from the position of the 21.04-MHz line.

Sodium hexahydroxoplatinate(IV). A complex $Na_2Pt(OH)_6$ (**I**) is the starting product in a processing chain used for the preparation of PN solutions from $H_2PtCl_6 \cdot nH_2O$. According to current regulations, deposition of a compound **I** includes several operations with a total time of at least 48 hours, ensuring a product yield of about 72%. Therefore, first, we studied the possibility of shortening the process time and reducing the number of operations at the given stage. Moreover, we aimed at separating a compound **I** with a content of the residual Cl$^-$ ions not exceeding 0.5%, which corresponds to the existing requirements for platinum(IV) nitrate solution and makes preparation of the solution simpler.

The technique of the experiments was as follows. A sample of solid $H_2PtCl_6 \cdot nH_2O$ (2.44–2.58 g) was transferred into a narrow and high quartz vessel (capacity about 25 ml), to which necessary amount of a carbonate-free solution of NaOH (d = 1.42 g cm^{-3}) was introduced by weighing (to within ± 0.01 g) to the OH$^-$: Pt molar ratio about 12. Then, deionized water was added to the mixture to a total volume of 10–12 ml, the vessel was covered with a watch glass and heated to a boiling point without emissions and pushes of the fluid. The boiling point of the mixtures was 102 ± 1 °C. Boiling began after 12–15 min of switching on heating. After about 30 min elapsed, crystals of different sizes began to form in the systems and solutions changed color from a red-orange to yellow. The time of the reaction was fixed in each experiment. In some experiments, the reaction mixture was irradiated by the UV light (a DRSh mercury lamp).

After completing the reaction, solutions with the precipitates were cooled with an ice-water mixture, transferred onto a finely porous glass filter, and dried to constant weight. All the precipitate was quantitatively transferred from the reaction vessel onto the filter. For this purpose, we used only mother liquor, which was also cooled to about 0 °C in most experiments. The separated precipitates were washed with a minimal volume of ice-cold water and then with methanol to negative reaction for Cl$^-$ ions (the $AgNO_3$ tests). The maximum volume of methanol in the experiments was about 30 ml. The use of acetone instead of CH_3OH for washing precipitate **I** did not virtually allow removal of NaCl, whose presence was clearly seen on diffraction patterns. Evidently, this is because the solubility of the salt in methanol sharply increases compared to acetone (1.41 wt% in the first case [4]). The results of this series of experiments are shown in Fig. 1.

Analyzing the data in Fig. 1, we note the following. First, a simple cooling of the reaction mixtures to $T \approx 0$ C before separating precipitates **I** can significantly increase the product yield. At the reaction time $\tau = 180$ min the yield was 83.3–90.1%. The experiment at cooling to room temperature, with reaction time the same (lower point in Fig. 1), gives a 67% yield. Second, the reaction time can be reduced to at least 180 minutes, which will significantly reduce energy consumption. At first glance, it might seem that the results of some experiments have poor reproducibility. However, the spread does no exceed 10 rel% and is most likely explained by the fact that on cooling mother liquors used for transferring precipitates **I** from the reaction vessel the temperature was not controlled. A very large scatter of data at $\tau = 30$ min is hard to explain, and we can only conclude that this time of the reaction is unacceptable.

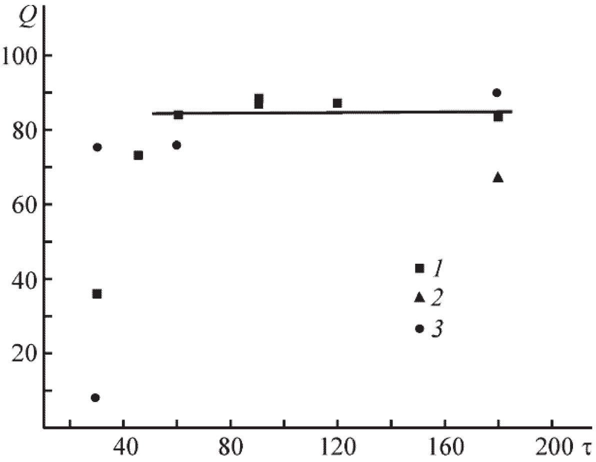

Fig. 1. Yield of $Na_2Pt(OH)_6$ Q (%) vs. the reaction time τ (min). Sample preparation: (*1*) cooling to $T \sim 0°C$, without UV irradiation, (*2*) cooling and UV irradiation, and (*3*) cooling, without UV irradiation.

The experiments with UV irradiation are based on the well-known phenomenon, photoactivation of $[PtCl_6]^{2-}$ complexes, which could facilitate formation of a compound **I**. At the same time, the effect of light is ambiguous (Fig. 1).

The obtained samples **I** were studied by XPA. All samples, except for those washed with acetone, were single-phase and their diffraction patterns clearly matched the available X-ray diffraction database for $Na_2Pt(OH)_6$ [5]. The above analysis cannot be applied for the determination of microcomponents, NaCl inclusions, in particular. The content of Cl^- ions was determined by the method of capillary electrophoresis. To eliminate influence of dominating $Pt(OH)_6^{2-}$ complexes, the starting sodium salt was reduced by hydrazine hydrate to platinum black, which was then filtered, and the filtrate was analyzed. In five samples of compound **I** from different experiments the content of chloride ions obtained in the three parallel determinations at $R_{conf} = 0.95$ was 0.21–0.44% at $S_r \leq 0.1$. Thus, the product of the first chain of the synthesis of a PN solution was quite conditioning in terms of the content of impurity chloride ion.

The attained easiness and simplicity of such purification of a compound **I** is associated with the use of methanol at the stage of washing of the separated precipitates. It is clear that this technique is solely for the laboratory use.

In addition to XPA, the obtained sodium hexahydroxoplatinates (IV) were studied by other methods. Determination of Na in a compound **I** gives a value of 13.1%, which within the error of the AAS (±0.4 abs %) coincides with the calculated value (13.40%). The EAS of aqueous solution of a compound **I** is an increasing exponent at $\lambda \leq 500$ nm not containing clearly resolved lines. IR spectra of a compound **I** completely coincide with the published data for $M_2Pt(OH)_6$ (M^+ is Li, Na, or K) [6–8]. The broad intense band in the region 3400–3500 cm^{-1} belongs to the stretching vibrations of OH groups. In the literature, assignment of two bands, at 1040 and 1110 cm^{-1}, is ambiguous. Most likely, these bands correspond to deformation vibrations of a PtOH fragment. The bands at 517 and 656 cm^{-1} may be due to the stretching vibrations of Pt–O bond and Pt–OH deformation vibrations [7].

A 0.117 M solution of compound **I** (pH 11.17) was titrated with a 0.100 N sulfuric acid. It was found that $H_2Pt(OH)_6$ is precipitated with a nearly quantitative yield at pH ≈ 2. Upon precipitation in acidic medium, the acid dissociation constants of the compound cannot be evaluated.

The thermolysis of a compound **I** in inert atmosphere (He) has no separated stages. Only products formed by thermal decomposition at $T = 800–850°C$, a mixture of metallic Pt with α-and β-Na_2PtO_3 were identified by XPA. The mass ratio of Pt^0 to the oxide phases is approximately 1 : 1. Most likely, the thermolysis process under the given conditions can be described by the equation

$$2Na_2Pt(OH)_6 \rightarrow Pt + \alpha\text{-}, \beta\text{-}Na_2PtO_3 + O_2 + Na_2O + 6H_2O. \quad (1)$$

Interestingly, the thermolysis of lithium salt up to $T \approx 1000°C$ in nitrogen proceeds by the total equation

$$Li_2Pt(OH)_6 > Li_2PtO_3 + 3H_2O \quad (2)$$

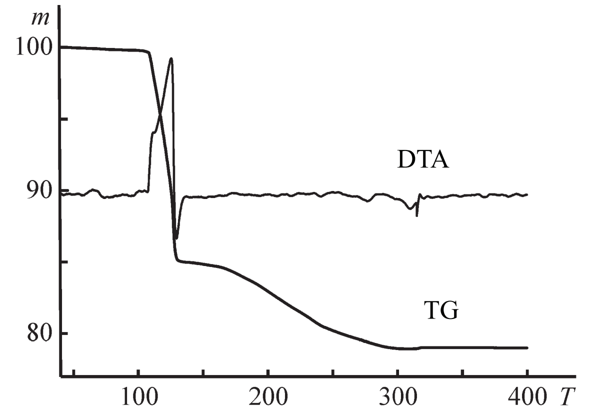

Fig. 2. Thermogram for salt (I) in hydrogen. (*m*) Sample mass (% of initial) and (*T*) temperature (°C); the same for Fig. 3

and is not accompanied by the formation of Pt^0 [6]. In [6], products of reaction (2) were identified solely by the mass loss, and no XPA was carried out.

Figure 2 shows the DTA curves of the salt **I** in hydrogen atmosphere. Replacement of the inert atmosphere for the reducing one substantially changes thermolysis process. In the comparable gaseous environments, the temperature of the end of the decomposition in H_2 is reduced by about 400°C, with the reaction proceeding by the equation

$$Na_2Pt(OH)_6 > Pt + 2NaOH + 4 H_2O. \quad (3)$$

The validity of equation (3) is confirmed by the XPA (only reflections of metallic platinum are present and reflections of Na_2PtO_3 are absent in the final products) and by the coincidence of the experimental mass loss (21.0%) with its calculated value (20.98%).

The ^{195}Pt NMR spectrum of an aqueous solution **I** has a single line with a chemical shift of 7830 ppm, which agrees well with a value of 7823 ppm from [9]. The spectrum does not change for at least 2 months of storage of the solution.

On storage, the color of the solid samples of $Na_2Pt(OH)_6$ varied from yellowish to gray and then to black. Only reflections of the original salt, regardless of the degree of blackening, were recorded on the diffraction patterns of these products. This phenomenon is explained only by the fact that "black" components, which may in principle be Pt^0 and (or) platinum oxide, are in the amorphous or very fine state. The observed phenomenon is spontaneous and random. Blackening of the solid samples **I** was observed during storage from several days to several months under normal conditions. The color of some samples remained unchanged after one year of receiving them.

Similar phenomenon was also observed in mother liquors after separating precipitates **I**: colloidal particles of black color were formed during storage of light yellow liquids in polypropylene terephthalate containers. According to XPA, they are a metallic platinum. Interestingly, mother liquors stored in a glass or plastic vessel with the addition of finely divided glass retain the initial state during the year, with metallic platinum not separated in these cases.

Probably, the above facts may indicate that the compound **I** is thermodynamically unstable. The thermal decomposition in an inert atmosphere is incomplete, proceeds in a very wide temperature range, and the reaction products themselves can not be characterized by reliable values of thermodynamic functions. However, the compound $H_2[Pt(OH)_6]$ related to the compound **I** is thermodynamically stable [10]. The standard Gibbs energy of formation of this compound is –989 kJ mol^{-1}. Therefore, the described changes in the state of the compound **I** on storage are most likely associated with another reasons than thermodynamic stability.

In conclusion, we note that the transformations of a compound **I** on storage (yellowish color changes to black color) at $T = -(12–14)$°C do not proceed.

Hexahydroxoplatrinum (IV) acid, $H_2[Pt(OH)_6]$. The crystal structure of $H_2[Pt(OH)_6]$ (compound **II)** and its salts with alkali metals is known [11, 12]. Solid preparations of **II** were characterized by means of DTA, XPA, and IR spectroscopy. Figure 3 shows the DTA curves for the acid (II).

A part of the TG curve within 440 ± 20 °C showing a mass loss of about 24% is due to the formation of PtO_2. The next step above 550°C corresponds to the mass loss Δm = const = 35.0%. According to the XPA, the product is a metallic platinum. The theoretical Δm value is 34.79%. Consequently, the thermolysis of the studied sample in inert atmosphere is well described by the scheme:

$$H_2[Pt(OH)_6] > PtO_2 + 4H_2O > Pt^0. \quad (4)$$

Figure 4 demonstrates diffraction patterns of a compound **II** obtained from different batches in comparison with the data of [13]. As seen, the KZTsM sample contains a highly crystalline phase (II) and no amorphous phase. At the same time, peaks corresponding to the insignificant

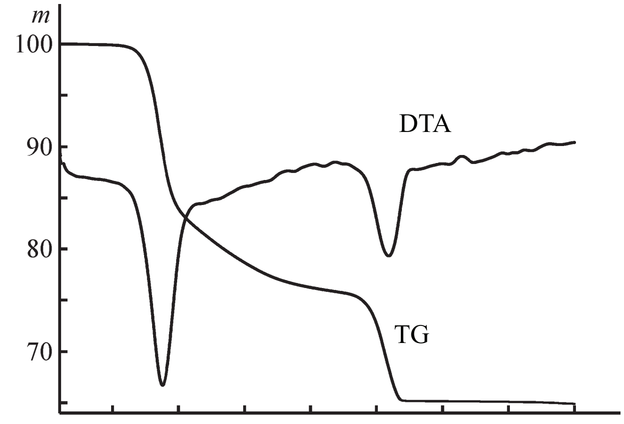

Fig. 3. Thermogram for $H_2[Pt(OH)_6]$ in helium.

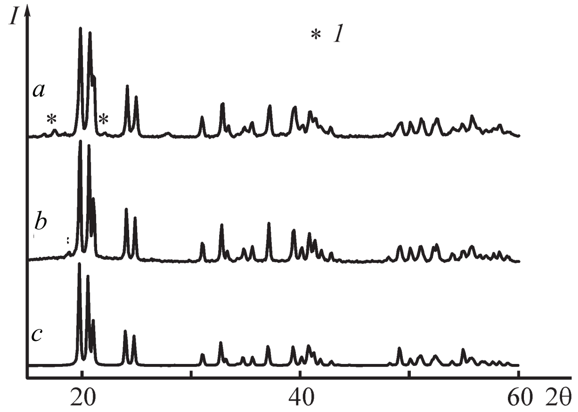

Fig. 4. Diffraction patterns of $H_2[Pt(OH)_6]$. Sample: (*a*) produced at a Krastsvetmed Open Joint-Stock Company, (*b*) synthesized in the study, and (*c*) data of [14]. (*I*) Intensity (rel. units), (2θ) scan angle (deg), and (*1*) reflections of impurity crystalline phases.

amount (less than 5 wt %) of crystalline phase of unknown composition are also present. The freshly synthesized sample of the acid is highly crystalline (Fig. 4b), with minority of the impurity crystalline phase, apparently a polymeric compound, also present. A certain basis for this assumption is the IR spectrum of the product (II). In contrast to the spectrum of the sodium salt, it is poorly resolved, contains a broad intense band centered at 3140 cm^{-1} and the low-intensity bands at 1620 and 530 cm^{-1}. The first two bands belong, respectively, to stretching and deformation vibrations of water molecules, which are present owing to polycondensation reactions proceeding with the formation of dimers or oligomers containing bridging OH groups [14].

In further experiments, we set two main goals: (1) simplification of the acid treatment to remove Na^+ and (2) determination of the conditions, at which the storage time of the acid (II) is the maximum admissible value. The first problem was solved by the procedure including preparation of a salt $Na_2[Pt(OH)_6]$ by the above method and washing it to a Cl^- content of 0.34 ± 0.03%. Sample (1.380 g) of the freshly prepared salt **I** was dissolved in 30 ml of deionized water (s : l = 1 : 22) for 25 min and the insoluble residue was separated by filtration in the form of a fine black powder (weight 0.138 g). The residue, while processed with HCl at low temperature, undergoes fast and qualitative passage into yellow solution, which, while heated on a water bath for a short time, very quickly turns to a clearly heterogeneous mixture of black-brown color. Consequently, it is another form than Pt^0. Then, $H_2[Pt(OH)_6]$ was precipitated from the resulting transparent colorless filtrate (initial pH 12.04) with $HNO_{3(conc.)}$ to pH 3.22. We carried out the following series of successive steps: (a) the separated deposit was stirred in a 0.001 M HNO_3 (volume 30 ml) for 0.5–1 h with a magnetic stirrer, (b) the pulp was settled for the same time in a water-ice mixture, (c) 3–5 ml of the transparent colorless solution were taken for the determination of Na^+ ions and then the solution was separated by decantation at $T \approx 0°C$ to minimum volume, with no solid phase entering into the decantate.

The above cycle was repeated ten times. The experimental results are presented in Table. 1. The total time of all the described procedures was about 12 h. As seen from Table 1, the proposed method can yield a product of necessary quality (containing no more than 0.5% Na^+) after the sixth cycle, which is lower by an order of magnitude than the time spent in the current plant regulation. Moreover, with use of ice nitric acid solution (0.001 M HNO_3) as a washing fluid the appearance of a white suspension after the sixth cycle may be a distinct sign of the completion of the process, and no additional control is necessary. At the end of the series, the remaining product (see diffraction pattern in Fig. 4b) was separated, dried, and weighed. Its mass was 1.064 g. With respect to a weighed portion (I), the yield of the acid (I) was 88.4%, with account taken for the weight of insoluble residue (98.2% by platinum). These values are significantly higher than those available in technology (up to 60% recovery for platinum).

As mentioned above, $H_2[Pt(OH)_6]$ is thermodynamically stable [12]. Therefore, we can assume that the sodium salt is stable. In this case, the reasons for the limited storage

Table 1. Results of experiments on $H_2[Pt(OH)_6]$ treatment by the proposed method to remove sodium ions

Cycle no.	c_{Na}, μg·ml^{-1}	m_{Na} in sample, mg	Na content in $H_2[Pt(OH)_6]$, %
1	4700	141	11.4
2	2030	60.9	4.90
3	1010	30.3	2.44
4	365	10.95	0.88
5	302	9.06	0.73
6	92.0	2.76	0.22
7	43.0	1.29	0.1
8	22.0	0.66	0.053
9	21.5	0.645	0.052
10	7.0	0.21	0.017

time of a compound **II** should be sought in another direction. Note, on diffraction patterns of $H_2[Pt(OH)_6]$ an unknown phase (or phases) is (are) clearly resolved (Fig. 4). The increase in the storage time of a compound **II** is achieved by maintaining the solid samples **II** in a freezing chamber [$T = -(13 \pm 1)$°C]. It turned out that in this case, the PN solutions obtained from the salt **II** sustain control plant tests, even after 10 months of preparation.

Solutions of Pt(IV) nitrate. An one-year monitoring of the platinum(IV) nitrate solutions prepared from frozen samples of $H_2[Pt(OH)_6]$ showed that the control properties of these solutions remain unchanged regardless of the storage temperature. The X-ray analysis of the PN solution at about –180 °C showed that under these conditions the substance is in a glassy, rather than in crystalline phase (no clear reflections are present on diffraction pattern).

The ^{195}Pt NMR spectra of the PN solutions prepared in accordance with the above recommendations were recorded. To do this, samples (0.70–0.73 g) of a freshly prepared acid (II) were inserted into a 3.0 ml of $HNO_{3(conc)}$. Preliminarily, aliquots of HNO_3 were heated to different temperatures in the range 0–65°C. The results of the NMR analysis are given in Table 2. Experiments nos. 1a, 1b, and 1c correspond to a solution of freshly precipitated product **II**, which was dissolved in $HNO_{3(conc)}$ for 30 s, with NMR signals successfully accumulated for 10 minutes. For experiments nos. 2–4, the PN solutions were kept for about 5 h prior to the measurements.

As seen from Table. 2, the ^{195}Pt NMR spectra of the PN solutions kept for about 5 h have a plenty of signals, which can hardly be attributed to the coexistence of mononuclear platinum forms in aqueous PN solutions with high HNO_3 concentrations. There are two reasons for this conclusion. First, the system $Pt(OH)_6^{2-}$–(H)NO_3–H_2O looks like a very dynamic system, which is very unusual for such extremely inert central atom as platinum (IV). Second, the difference in chemical shifts of some nearby signals is on the order $n \times 10^1$ ppm, which is extremely small value for the ligand substitution in platinum (IV) complexes [9]. Unfortunately, the nitric acid ate solutions of PN have no reliably identified reference compounds, which are formed in the course of the transformations in the system. Therefore, any interpretation of the data from Table 2 is ambiguous. Apparently, only one conclusion can be made: the signals in a weak field and their diversity in the ^{195}Pt NMR spectra are due to oligomeric compounds with minor changes in the coordination spheres. For the sulfate complexes of Rh (III) this result was established in [15]. Therefore, for Pt (IV) compounds, the similar interpretation seems reasonable. It may be assumed that the above oligomeric compounds are also formed in PN solutions, with some signals from monomeric compounds and their relative intensities in the strong field retained.

At the same time, spectra of the PN solutions kept during the year, irrespective of storage conditions, have no signals in the whole range of the currently available ^{195}Pt (IV, II) NMR signals, from –500 to 12200 ppm. In [1], similar result was explained by nucleation of initial monomeric Pt (IV) hydroxoforms to form oligomers with bridging OH groups. This can lead to splitting, shift (in weak field), and broadening of the signals until their complete disappearance in the spectrum.

CONCLUSIONS

(1) All stages of the preparation of platinum(IV) solutions from hexachloroplatinic acid were studied. The main features of the process chain were determined, which enabled a considerable reduction of time and energy expenditure along with simplification of the process and improvement of its performance.

(2) Simple and efficient method was suggested for prolonged storage of a target product, $H_2Pt(OH)_6$, and its treatment to remove sodium ions.

(3) It was found that "aging" of platinum(IV) solutions

Table 2. Chemical shifts in ^{195}Pt NMR spectra of Pt(IV) nitrate solutions

Line	Chemical shift, ppm, in experiment no.					
	1a (room)[b]	1b (room)	1c (room)	2 (0°C)	3 (65°C)	4[a] (room)
1	7863	7860	7858	–	–	–
2	7953	7953	7950	–	–	–
3	8056	8056	8056	–	–	–
4	8119	–	–	–	–	–
5	8166	8167	8167	8170	8170	8169
6	8174	8174	8174	8178	8178	8177
7	–	–	8271	8272	8273	8272
8	8286	8286	8286	8290	8290	8289
9	8389	8390	8390	8393	8394	8393
10	–	–	–	8398	8398	8398
11	–	–	8430	8431	8431	8431
12	–	–	8432	8434	8434	8434
13	–	–	–	–	8450	8450
14	–	–	–	8465	8465	8465
15	–	–	–	8473	8473	8473
16	–	–	–	8526	8526	8527
17	–	–	–	8546	8545	8546
18	–	–	–	8579	8579	8579
19	–	–	–	8607	8607	8607
20	–	–	–	8734	8734	8734
21	–	–	–	8740	8740	8740
22	–	–	–	8748	8748	8748
23	–	–	–	8762	8761	8762
24	–	–	–	8767	8767	8767
25	–	–	–	8856	8856	8856
26	–	–	–	–	9120	9120

[a] $H_2[Pt(OH)_6]$ sample was stored for 6 months at room temperature prior to dissolution in HNO_3.

[b] Temperature, at which a compound (II) was dissolved in nitric acid, is given in the brackets.

is result of oligomerization or polymerization of initially monomeric products.

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