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## The Outer-Sphere Formation of Complexes in the System of $\text{H}_2\text{PtCl}_6\text{-Ce}(\text{SO}_4)_2\text{-H}_2\text{SO}_4\text{-KI}$ in Conditions Of Electrochemical Determination of Platinum (IV).

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### ABSTRACT

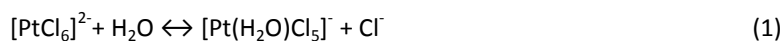
The examination of the system  $\text{H}_2\text{PtCl}_6\text{-Ce}(\text{SO}_4)_2\text{-H}_2\text{SO}_4$  by the method of NMR  $^{195}\text{Pt}$ -spectroscopy showed that under the input in  $\text{PtCl}_6^{2-}$  a sulfuric acid solution of cerium sulfate (IV) replacement of chloride ligands in the coordinating sphere  $\text{PtCl}_6^{2-}$  doesn't occur. It is found that under the potentiometric determination of platinum (IV) using KI outer-sphere complex  $\{[\text{PtCl}_6^{2-}(\text{Ce}(\text{SO}_4)_2)_3](\text{H}_2\text{SO}_4)_n(\text{HSO}_4^-)_m\}^{(m+2)-}$  facilitates the rapid exchange between the halide ions with forming the  $\text{PtI}_4\cdot\text{H}_2\text{SO}_4$ .

**Key words:** hexachloroplatinate, sulfuric acid, potassium iodide, cerium sulfate, the formation of complexes.

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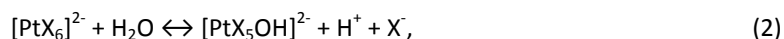
## INTRODUCTION

Platinum (IV) forms stable chloride complexes [1], which at the study of their aqueous solutions should take into account the possible aquatation:



Thus, the authors [2] suppose that at the 45-55°C to an appreciable extent hydrolysis proceeds in two stages ( $K_6=6 \cdot 10^{-3}$ ,  $K_5=2 \cdot 10^{-4}$ ,  $\mu=0.5$ ). Along with this, stepwise constants of stability for the reaction are presented in a number of studies (1):  $K_6=3,3 \cdot 10^{-2}$  ( $t=50^\circ\text{C}$ ,  $\mu=1$ ) [3],  $K_6=3,2 \cdot 10^{-2}$  ( $t=50^\circ\text{C}$ ,  $\mu=0.8$ ) [4],  $K_6 = 2,9 \cdot 10^{-2}$  ( $t = 60^\circ\text{C}$ ,  $\mu=3$ ) [5]. The calculation of these constants in solutes of 0.2M and 3M  $\text{H}_2\text{SO}_4$   $K_6 = 4,3 \cdot 10^{-3}$  and  $K_6 = 1.7 \cdot 10^{-3}$  ( $t = 25^\circ\text{C}$ ,  $\mu=0,6$ ), accordingly, indicates an increase in the stability of the complex  $\text{PtCl}_6^{2-}$  with the increasing concentration of sulfuric acid [6].

It is known [7] that under input the iodide ions into a solute of  $\text{PtCl}_6^{2-}$  to the ratios  $[\text{I}^-] / [\text{PtCl}_6^{2-}] \leq 6$  precipitate is forming  $\text{PtI}_4$ . Wherein the curve of solubility of the system  $\text{PtI}_4\text{-KI-H}_2\text{O}$  (at  $15^\circ\text{C}$ ) [7] consists of two branches: the first corresponds to dissolution  $\text{PtI}_4$  with formation of  $\text{PtI}_6^{2-}$ , the second corresponds to the decreasing in solubility of  $\text{PtI}_6^{2-}$  with increasing of concentration of KI. The hydrolysis of iodoplatinate in water at  $25^\circ\text{C}$  passes only the first stage [8]. These constants of balance for the hydrolysis on a reaction:



where  $\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-$ , for  $\text{K}_2\text{PtCl}_6$   $k_1=4 \cdot 10^{-8}$ , for  $\text{K}_2\text{PtBr}_6$   $k_1=6 \cdot 10^{-9}$ , for  $\text{K}_2\text{PtI}_6$   $k_1=2,5 \cdot 10^{-12}$  ( $t=25^\circ\text{C}$ , in the environment of 0,1M KCl, 0,1M KBr and 0,05M KI accordingly) [8] shows the increasing in the stability of the complexes of platinum (IV) in the rank  $\text{PtCl}_6^{2-} < \text{PtBr}_6^{2-} < \text{PtI}_6^{2-}$ . Calculated thermodynamic characteristics of balance shows the

formation of a more stable complex  $[\text{PtI}_6]^{2-}$  (3):  $\lg \beta_{6\text{Cl}^-} = 18,25$ ;  $\Delta H_{6\text{Cl}^-} = -(19 \pm 1) \text{ kcal / mol}$ ;

$\Delta S_{6\text{Cl}^-} = 10 \text{ en.un.}$  [9].



It is shown [10] that the presence of a small amount of iodide ions in the solution can catalyze the reaction of hydrolysis:



the presence of large quantities of the excess of yodid- or triiodide ions leads to the reaction:



In the study [10] there is a scheme of the balance which is taking place in the system of  $\text{PtI}_6^{2-}-\text{I}^--\text{H}_2\text{O}$  at  $\text{pH} \geq 6$ . The constants is calculated for the process of hydrolysis (4)  $k_1=3,98 \cdot 10^{-4}$  ( $t=25^\circ\text{C}$ ,  $\mu \leq 10^{-3}$ ).

According to conducted studies [11], in the presence of 10-fold excess of iodide the complex  $[\text{PtI}_6]^{2-}$  is forming (balance 3), as in the case of a large excess KI (500-1000 times) Pt(IV) restores to Pt(II) with the forming of the complex  $[\text{PtI}_4]^{2-}$  and free iodine is educted (balance 5).

It should be noted that in the presence of compounds of Ce(IV) the rate of reaction of platinum (IV), for example, with an 8-mercaptoquinoline at electrochemical determination significantly increases [12], and the point of equivalence corresponds to the total consumption of reagent in the dually occurring processes of the formation of complexes and redox. Nevertheless, this model [12] of the observed effect doesn't explain the need for the reaction of platinum (IV) in a medium 4M  $\text{H}_2\text{SO}_4$  with simultaneous presence of stoichiometric amounts of cerium (IV). We have found that the interaction of platinum (IV) with iodide уа potassium in the presence of Ce (IV) in the medium of sulfuric acid dramatically accelerates [13]. For generating ideas on the nature of the observed phenomenon it was acute to conduct the study both in the system  $\text{PtCl}_6^{2-}-\text{Ce}(\text{SO}_4)_n^{4-2n}-\text{H}_2\text{SO}_4$  (method NMR  $^{195}\text{Pt}$ - spectroscopy) and in the system  $\text{H}_2\text{PtCl}_6-\text{Ce}(\text{SO}_4)_2-\text{H}_2\text{SO}_4-\text{KI}$  (potentiometric

method), as well as the determination of the composition of the product of solid phase reaction of platinum (IV) with KI (IR-spectroscopy and X-ray diffraction).

### EXPERIMENTAL PART

Original solutions of  $\text{PtCl}_6^{2-}$  with a concentration of  $5 \cdot 10^{-2} - 3 \cdot 10^{-1} \text{M}$  were prepared by dissolving of the metal in a mixture of nitric and hydrochloric acids under heating and subsequent evaporating of the solute with regard to the necessity of removing oxides of nitrogen, as well as fixanal  $\text{H}_2\text{PtCl}_6$ . Solute of KI with a concentration of  $10^{-3} - 10^{-1} \text{M}$  were prepared by dissolving the corresponding salts (chemically pure) according to the technique [14]. The concentration of the solute of iodide of potassium was checked by titration with standard solute of silver nitrate (I). Acidified by sulfuric acid solute of cerium (IV) with a concentration of  $5 \cdot 10^{-2} \text{M}$  was prepared basing on sample  $\text{Ce}(\text{SO}_4)_2$  (chemically pure) according to the technique [14]. The concentration of sulfate cerium (IV) was carried out by potentiometric titration by solute of Mohr's salt which was standardized on dichromate. Solute were diluted for 2-20 times in the conditions of a real experiment. The required concentration of sulfuric acid was reached, taking into account the initial density of the commercial product of brand "chemically pure". All the preparations, which were used to carry out experimental studies, are consistent with the brand "chemically pure".

The spectra NMR  $^{195}\text{Pt}$  of reaction mixtures were recorded using spectrometer AVANCE 400 (Bruker, Germany) at a frequency of 86.015 MHz using a single-pulse sequence in the accumulation mode, the values of chemical shift  $\delta$  (ppm) are defined relatively to the position of signal of the standard solute  $\text{H}_2\text{PtCl}_6$ . Potentiometric measurements are carried out using a pH-meter pH 340 with a platinum counter electrode and saturated calomel reference electrode. Stirring of titrate solute is effected with a magnetic stirrer. Microburet with divisions of 0.02 ml is used in the process of titration. Infrared spectra of the compounds were recorded on the IR spectrophotometer "Specord": the samples were prepared as tablets with bromide of potassium. X-ray diffraction analysis, as well as other measurements, was performed on the device DRON-3 (Cu-K $\alpha$ -radiation), at room temperature.

### RESULTS AND DISCUSSION

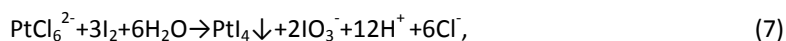
Input of iodide of potassium to solute  $\text{H}_2\text{PtCl}_6$  is accompanied with formation of a solid phase, moreover the simultaneous increasing of the current in the "biamperometric" control is not observed. After complete precipitation of the form of iodide of Pt(IV) at  $[\text{I}^-]:[\text{Pt}^{4+}] \leq 4$  further increasing of the content of iodide ions in the solute results to dissolution of the precipitate with forming  $\text{PtI}_6^{2-}$  [7]. In the presence of sulfate cerium(IV) the interaction  $\text{PtCl}_6^{2-}$  with KI, according to potentiometric titration (Figure 1), is associated both with the formation of the tetraiodide of platinum (IV), and redox transformation:



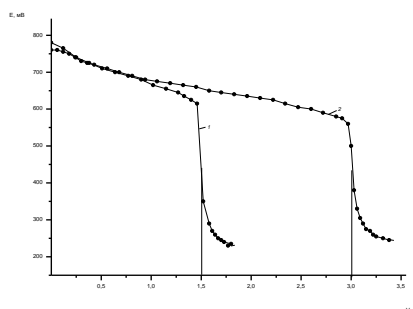
Values of standard redox potentials ( $E^0_{\text{Ce}(\text{SO}_4)_2 / \text{Ce}^{3+} + 3\text{SO}_4^{2-}} = 1,44\text{V}$ ;

$E^0_{\text{PtCl}_6^{2-} / \text{PtCl}_4^{2-} + 2\text{Cl}^-} = 0,72\text{V}$ ;  $E^0_{\text{I}_2 / 2\text{I}^-} = 0,54\text{V}$  [15] indicate that a cerium (IV) is a strong oxidizing agent in the system, which reacts with ions of iodide according to equation (6). In the absence of an excess of iodide ions in a solute of 6M sulfuric acid side interactions (reactions 3-5) take no place in the system.

By varying the composition of the medium of reaction it was found that quantitative determination of platinum(IV) in a concentration range of  $\text{PtCl}_6^{2-} 10^{-2}\text{M} - 10^{-4}\text{M}$  as  $\text{PtI}_4$  must be carried out using a solute of 6M  $\text{H}_2\text{SO}_4$  as the background electrolyte, as at  $C_{\text{H}_2\text{SO}_4} < 6\text{M}$  the results of the analysis of the output  $\text{PtI}_4$  have lower values. Thus, at the determination of 0,468 mg Pt(IV) with a solute of  $2,5 \cdot 10^{-2}\text{M}$  KI in the medium of 6M  $\text{H}_2\text{SO}_4$  it was found  $0,455 \pm 0,017$  mg, relative standard deviation  $S_r = 0,015$ ; in the medium of 1M  $\text{H}_2\text{SO}_4$  –  $0,430 \pm 0,047$  mg,  $S_r = 0,04$  ( $n=3$ ,  $P=0,95$ ). This difference can be explained by the fact that molecular iodine, formed by reaction (6), in conditions of  $C_{\text{H}_2\text{SO}_4} < 6\text{M}$  may be consumed in reaction [13]:



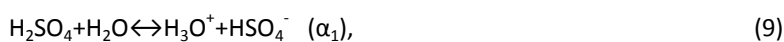
which in acidic media (6M  $\text{H}_2\text{SO}_4$ ) is inhibited that allows to provide reproducible quantitative results at the analysis of platinum-comprising objects.



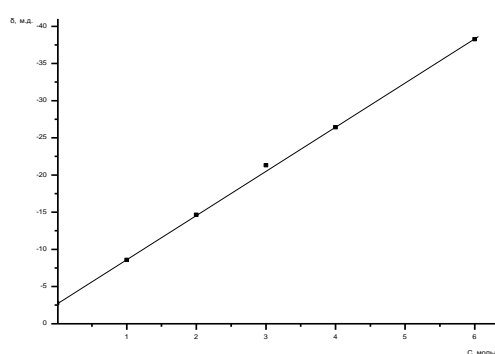
**Fig.1.** Curves of potentiometric titration  $2,5 \cdot 10^{-2}$  M by solute of KI: 1 - 5.5 ml  $7 \cdot 10^{-3}$  M  $\text{Ce}(\text{SO}_4)_2$ ; 2 - 2 ml of  $4,8 \cdot 10^{-3}$  M  $\text{PtCl}_6^{2-}$  + 5,5 ml  $7 \cdot 10^{-3}$  M  $\text{Ce}(\text{SO}_4)_2$

By the method of NMR  $^{195}\text{Pt}$  spectroscopy in solutes of the system  $\text{PtCl}_6^{2-} - [\text{Ce}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$  with increasing concentration of sulfuric acid it was found that in the range of 1÷6M  $\text{H}_2\text{SO}_4$  there was a continuous change in the structure of the solute, i.e. the composition of outer-sphere solvation medium changes at the alteration of concentration of sulfuric acid.

According to [16], the form of existence of sulfuric acid in solutes are linked by the balance:



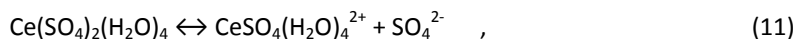
the final status of which is summarized in the chart [17], indicating the dominance in solutes of 1÷6M sulfuric acid ions  $\text{HSO}_4^-$ .



**Fig.2.** Dependence of the position of the signal spectra NMR  $^{195}\text{Pt}$  on the concentration of  $\text{H}_2\text{SO}_4$  at a ratio  $[\text{Ce}^{4+}]/[\text{Pt}^{4+}] \geq 3$ ;  $(8,1 \cdot 10^{-1}$  M  $\text{Ce}(\text{SO}_4)_2$  and  $1,9 \cdot 10^{-1}$  M  $\text{PtCl}_6^{2-}$ )

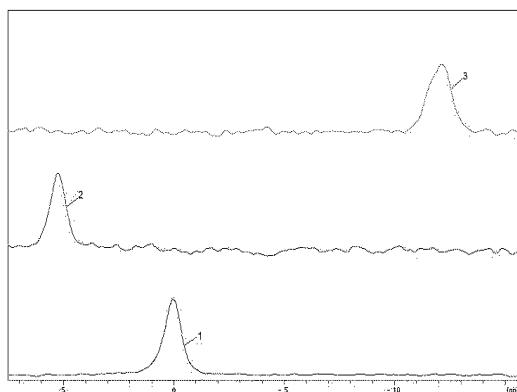
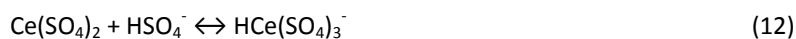
There is a linear relationship  $\delta - C_{\text{H}_2\text{SO}_4}$  (Figure 2) for the series of solutes  $\text{PtCl}_6^{2-} - [\text{Ce}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$ . According to studies [18], the change in the coordination sphere  $\text{PtCl}_6^{2-}$ , accompanied with the formation of  $[\text{PtCl}_5\text{H}_2\text{O}]^-$ , can be determined by the amount of displacement  $\delta$  on the magnitude of 504 ppm. Range of the changes of experimentally observed values of  $\delta$  (10-40 ppm), as well as the studies [6], indicate the stability of the complex  $\text{PtCl}_6^{2-}$  in terms of increasing of the concentration of sulfuric acid up to 6M, i.e. the preservation of

the composition of the coordination sphere  $\text{PtCl}_6^{2-}$  and the lack of inner-sphere substitution of chloride ions in the  $\text{H}_2\text{O}$ , sulfate or bisulfate ions, and the observed changes are caused by only outer-sphere transformations. At adding to the original solute  $\text{H}_2\text{PtCl}_6$  sulfate of the cerium (IV) in the spectrum of NMR  $^{195}\text{Pt}$  it is observed the change in the value of the chemical shift ( $\Delta\delta=5$  ppm; Figure 3, kr.2), which indicates the formation of ion associate  $\{\text{PtCl}_6^{2-}\cdot\text{Ce}(\text{SO}_4)_2\}$  or subject to dominance (according to equation 11) in these conditions of concentration ( $C_{\text{H}_2\text{SO}_4} \leq 0,1\text{M}$ ) monosulfate cation  $[\text{Ce}(\text{SO}_4)_2](\text{H}_2\text{O})_4$  [17]:



corresponding solvate-separated ion pair. At the same time, as it would be expected, due to the anisotropy of the forming of outer-sphere medium  $\text{PtCl}_6^{2-}$  downfield shift of the signal NMR  $^{195}\text{Pt}$  takes place.

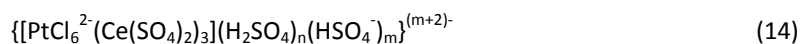
It is also important to note that in the solutions of the system Pt(IV)–Ce(IV) at a sulfuric acid concentration of 1÷2M in the spectra NMR  $^{195}\text{Pt}$  the lines with the values are detected  $\delta$  -11,75 и -12,18 ppm, which are indicating coexistence of outer-sphere complexes of variable composition (Figure 3, kr.3). It is known that cerium (IV) in a sulfuric acid medium (depending on the concentration of  $\text{H}_2\text{SO}_4$ ) exists in the form of complexes with two (Complex II), three (complex III) and four (complex IV) sulfate groups composed of the coordination sphere which are formed by the scheme [19,20]:



**Fig. 3.** The spectra NMR  $^{195}\text{Pt}$ : 1 –  $1,9 \cdot 10^{-1}\text{M}$   $\text{PtCl}_6^{2-}$ ; 2 –  $1,9 \cdot 10^{-1}\text{M}$   $\text{PtCl}_6^{2-} + 8,1 \cdot 10^{-1}\text{M}$   $\text{Ce}(\text{SO}_4)_2$ , 3 –  $[\text{Pt}^{4+}]:[\text{Ce}^{4+}]=1:3$  on the background of 1,3 M  $\text{H}_2\text{SO}_4$

With a significant increasing of the content of sulfuric acid in the solute the complex IV is dominant, for solutes of 6M  $\text{H}_2\text{SO}_4$ , according to calculations [19], the proportion of the complexes in the distribution of the forms of cerium (IV) is: II–15%, III–35%, IV–50%, and in case of 1M sulfuric acid the complex II (75%) predominates. In view of electrostatic representations, the outer- sphere interactions are more preferable between  $\text{PtCl}_6^{2-}$  and  $\text{Ce}(\text{SO}_4)_2^0$ , compared to interanion interactions ( $\text{PtCl}_6^{2-}$  and  $\text{Ce}(\text{SO}_4)_3^{2-}$  or  $\text{Ce}(\text{SO}_4)_4^{4-}$ ). It can be affirmed that among all forms of existence of cerium (IV), which were detected in experimental conditions (6M  $\text{H}_2\text{SO}_4$ ), a molecular complex II has the most competitive ability in the interaction with  $\text{PtCl}_6^{2-}$ , which participates in the outer-sphere formation of complexes.

The pattern of dependence  $\delta-[\text{Ce}(\text{IV})]/[\text{Pt}(\text{IV})]$  gives a reason to believe that the number of outer-sphere coordinating sulfate complexes Ce(IV) reaches three (Fig.4), i.e., the limiting dominant form has a composition:



Subsequently, the input of a complex (14) of iodide ions, which are nucleophilic reagents, into the system with a predominant existence is followed by conversion of the complex of hexachloroplatinate into

$PtI_4 \cdot H_2SO_4$ . The identification of the product of such a reaction was carried out by IR-spectroscopy and X-ray analysis. In the IR-spectrum absorption bands were revealed at 1060 and 1124  $cm^{-1}$ , the frequency characteristics of which correspond to the fluctuations of the molecules of sulfuric acid in the compound of the selected connection (Fig.5), where the symmetry of group  $SO_4^{2-}$  decreases at the coordination of  $PtI_4$ , and  $\nu_3$  splits into two bands [21].

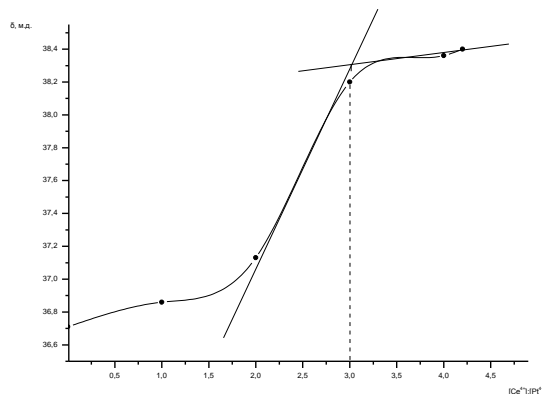


Fig. 4. The dependence of the value  $\delta^{195}Pt$  on the ratio  $[Ce^{4+}]/[Pt^{4+}]$  at  $C_{H_2SO_4} = 6M$ ,  $(8,1 \cdot 10^{-1} M Ce(SO_4)_2$  and  $1,9 \cdot 10^{-1} M PtCl_6^{2-})$

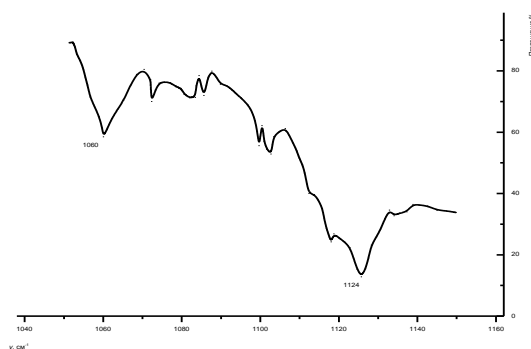
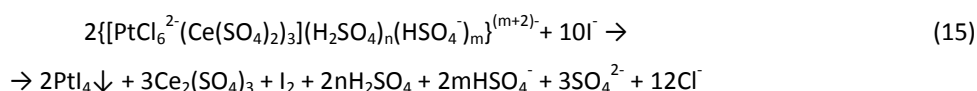


Fig.5 Infrared spectrum of absorption of the sample  $PtI_4$  (in tablets with KBr)

X-ray diffraction pattern (Cu-K $\alpha$  radiation) of the sample  $PtI_4$ , which was formed after processing  $PtI_4 \cdot H_2SO_4$  with water at 55°C and therefore it has no sulfate groups in the composition, shows (Fig.6) that its basis is constituted of crystal-amorphous phase, but fixed interplanar spacings (5,7 и 3,18) correspond to the values  $\alpha$  and  $\beta$  of orthorhombic form of lattice  $PtI_4$ .

The gradual flow of the iodide-ions to the zone of the reaction and simultaneously flowing release of cerium (IV) from the composition of the structure (14) provide its subsequent accessibility and participation in the act of redox interaction with iodide ions according to reaction (6).

Summarizing given observations, multi-step process can be totally represented by the following scheme:



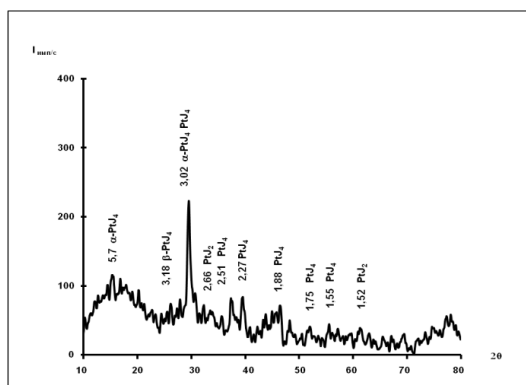


Fig 6. X-ray diffraction pattern of the sample  $PtI_4$  (Cu-  $K_{\alpha}$  radiation)

### CONCLUSIONS

Thus, during the electrochemical determination of platinum (IV) by the iodide of potassium there is excretion of Pt (IV) from the sphere of reaction as a precipitate  $PtI_4 \cdot H_2SO_4$ , wherein in conditions of conducting experiments (6M  $H_2SO_4$ , excess  $Ce(SO_4)_2$  with respect to  $PtCl_6^{2-}$ ) side interactions (hydrolysis reaction  $PtCl_6^{2-}$  with extracting (6)  $I_2$  during the reaction) don't occur.

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