



Physicochemical investigation of platinum dichloride polymorphism

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ABSTRACT

The physicochemical characteristics of phase transitions of PtCl_2 were investigated for the first time. The irreversible character of the transition from β -modification to α -form of PtCl_2 and the temperature range of process were established (570–870 K). α - PtCl_2 has one reversible transition at a temperature of 660 ± 5 K; the thermal effect of this process is $+167 \pm 17$ J/mol.

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1. Introduction

One of the most important systems in chemistry and technology of precious metals is Pt–Cl. Investigation of the polymorphism of platinum chlorides is especially interesting in view of the possibility to use them in the modern technologies of platinum refining and secondary raw material processing. As far as the polymorphism of platinum tetra- and trichloride is concerned, no data were reported in literature. The data on platinum dichloride polymorphism are scarce and partially contradictory. There are some indications for the existence of several modifications but only two polymorphous forms have been characterized by present; according to the classification proposed in ref. [1], we will call β - PtCl_2 ($\text{Pt}_6\text{Cl}_{12}$) (low-temperature) and α - PtCl_2 (high-temperature).

The single crystals of β - PtCl_2 were obtained by the authors of ref. [2] by transferring β - PtCl_2 (the latter was synthesized by the thermal decomposition of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in chlorine flow at 750 K) [3] at 820 K in a flow system (with Cl_2 as a carrier gas) for several days. Those authors carried out a detailed investigation of the crystal structure of β - PtCl_2 and found that the substance belongs to the rhombohedral system with unit cell parameters $a = 13.11 \pm 0.02$ Å and $c = 8.59 \pm 0.03$ Å (trigonal arrangement). In addition, they established that platinum dichloride is composed as a cluster based on $\text{Pt}_6\text{Cl}_{12}$ groups. Along with paper [2], publication [4] appeared. The interplanar spacings reported therein for PtCl_2 are in good agree-

ment with the data of ref. [2]. Differences are observed only for the first two lines in the region of small angles and for some weak lines. The indicated line intensities are in good agreement with the values calculated on the basis of structural data [2]. These facts indicate that the authors of refs. [2,4] studied the same crystal form of platinum dichloride, namely β - PtCl_2 ($\text{Pt}_6\text{Cl}_{12}$). It should be noted that the authors of ref. [4] did not describe synthesis method and the results of chemical analysis of PtCl_2 under investigation.

Platinum dichloride in the α -form [1] formed either during the direct interaction between the elements in a sealed ampoule at 820 K or during annealing β - PtCl_2 ($\text{Pt}_6\text{Cl}_{12}$) for 2 days at 770 K (evacuated ampoule). The authors of ref. [5] determined the structure of this compound and established that it belongs to the monoclinic system, with the space group $C2/m$; unit cell parameters are: $a = 13.258$ Å, $b = 3.194$ Å, $c = 6.802$ Å, $\beta = 107.75^\circ$, $Z = 4$.

The IR spectroscopic data for β - PtCl_2 are reported in refs. [6–8]; no data on the IR spectra for α -form were found in literature.

So, the goal of our work was to establish the regions of existence of α - PtCl_2 and β - PtCl_2 and to determine the quantitative characteristics of the transition β - $\text{PtCl}_2 \rightarrow \alpha$ - PtCl_2 .

2. Experimental

2.1. Synthesis

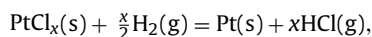
α - PtCl_2 was obtained by sublimation of platinum β -dichloride in a sealed ampoule under the temperature gradient along the ampoule 870 \rightarrow 820 K (the substance transfer from the hot zone to the cold one occurred) [1].

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β -PtCl₂ was synthesized by means of the thermal decomposition of H₂PtCl₆·6H₂O in the flow of chlorine ($P(\text{Cl}_2) = 1$ atm) at 750 K [3].

2.2. Identification

The chemical analysis of synthesis products was carried out using the method of platinum and chlorine determination in platinum chlorides from one weighed portion; the method is based on the separation of metal platinum from chlorine by means of reduction:



with the simultaneous absorption of hydrogen chloride in water.

The optimal conditions for the reduction were determined with the derivatograph "Paulik–Paulik–Erdey" [9]. The results showed that in the case of platinum dichloride the reduction proceeds with a noticeable rate even at 340 K; the maximal rate is observed at a temperature of 400 K. Reduction was carried out as follows. A weighed portion of the substance (0.08–0.15 g) was loaded into a quartz cup reduced to a fixed weight; it was placed into a flow quartz reactor. The system was blown with hydrogen for 10 min and the reactor temperature was increased gradually (at a rate of about 50 °C/h) to 473 K. The reduction was carried out for 40 min. Then the reactor was cooled in hydrogen flow to the room temperature, the cup with reduced platinum was taken out of the reactor and annealed to remove adsorbed hydrogen at 1000 K for 20–30 min. Platinum was determined in the form of metal platinum using the gravimetric method. Aqueous solutions from absorption vessels, as well as rinsing water from the reactor with adsorbed hydrogen chloride, were transferred into a volumetric flask with a volume of 100–200 ml. Chloride ions were determined by means of the potentiometric titration with 0.05N AgNO₃ solution under standard conditions.

Relative error of platinum determination was 0.2–0.5% (depending on the weighed portion), chlorine $\pm 0.5\%$.

X-ray investigation was carried out with DRON-2 diffractometer with the filtered copper radiation (Cu K α , Ni-filter) at a rate of 1 °C/min.

The IR spectra of samples were recorded with «PerkinElmer 325» instrument within the range 200–400 cm⁻¹ using the windows made of CsI, protected with a polyethylene film; the samples (10–15 mg) were ground in a mortar with anhydrous vaseline oil.

A comparison of the X-ray data for PtCl₂, presented in Tables 1 and 2, gives us reasons to state that the synthesized products are identical to β - and α -forms of platinum dichloride, respectively. The results of identification of the β - and α -forms (the chemical analysis and the IR spectra) are shown in Table 3.

Our results on the IR spectra of β -PtCl₂ are in satisfactory agreement with those reported in refs. [6–8]. The IR spectra of β - and α -forms of PtCl₂ have insignificant differences from each other. Mainly the difference is in the ratios of intensities of the main maxima of the β - and α -forms.

2.3. Investigation methods

2.3.1. Thermal annealing followed by quenching

The sample (~0.1 g) was loaded into quartz ampoules with the volume about 1 ml, the ampoules were evacuated at room temperature and sealed. The ampoules were placed in an electric resistance furnace in small metal containers (to achieve temperature leveling) and kept at a fixed temperature for two weeks. After the experiment, the containers were rapidly cooled by immersing into cold water, the ampoules were opened, the resulting prod-

Table 1

Data of X-ray phase analysis for PtCl₂ on the basis of literature data.

β -PtCl ₂			α -PtCl ₂		
[2]	[4]		[1,5]		
d_α (Å)	hkil	Intensity	d_α (Å)	Intensity	d_α (Å)
6.852	1011	Middle	8.16	100	6.482
6.520	1120	Strong	6.69	100	6.309
4.735	0221			50	5.428
4.019	0112	Middle	4.03	10	3.322
3.776	3030	Middle	3.78	10	3.255
3.424	2022	Very weak	3.47	30	3.242
3.274	2240	Middle	3.25	80	3.156
3.034	1232			30	3.104
2.953	1341	Strong	2.932	30	2.885
2.863	0003			10	2.713
2.692	4041	Middle	2.675	30	2.581
2.552	1123			50	2.544
2.540	3142	Very strong	2.536	30	2.236
2.475	3251	Very weak	2.462	30	2.224
		Very weak	2.374	10	2.106
2.282	3033	Weak	2.286	50	1.909
2.226	2352			30	1.845
2.193	3360	Weak	2.190	10	1.781
2.110	1014	Weak	2.107	10	1.700
2.005	5052	Strong	2.008	50	1.674
1.889	6060	Middle	1.871	30	1.656
1.821	4371	Very weak	1.810	50	1.622
1.784	5270	Strong	1.772		1.601
1.736	3363	Very weak	1.713		
1.637	4480	Middle	1.637		

ucts were investigated by means of X-ray phase analysis and IR spectroscopy.

2.3.2. Differential thermal analysis of the samples in sealed ampoules

Differential thermal analysis of the samples in sealed ampoules was carried out using a set-up described in ref. [10]. A sample (~1 g) and the reference (annealed aluminum oxide) were placed in thermographic ampoules made of quartz glass; they were placed in an

Table 2

Experimental data of X-ray phase analysis for β - and α -forms of PtCl₂.

β -form*		α -form**	
Intensity	d_α (Å)	Intensity	d_α (Å)
100	6.87	100	6.56
60	6.56	80	6.39
6	4.745	10	5.471
20	4.040	5	3.969
15	3.786	20	3.262
15	3.267	10	3.175
5	3.038	5	3.106
20	2.955	5	2.719
8	2.885	20	2.582
8	2.690	20	2.556
8	2.637	10	2.238
60	2.543	10	2.215
8	2.475	5	2.108
8	2.368	15	1.985
8	2.292	15	1.845
8	2.186	10	1.821
4	2.122	10	1.781
10	2.006	5	1.701
8	1.877	10	1.656
4	1.821	10	1.623
15	1.781	5	1.578
8	1.636	5	1.539

* $d_{r0}(\beta\text{-PtCl}_2) = 6.22 \text{ g cm}^{-3}$.

** $d_{r0}(\alpha\text{-PtCl}_2) = 6.44 \text{ g cm}^{-3}$.

Table 3
Identification of platinum dichloride.

Chemical analysis (mass%)		Color	IR spectrum, ν (cm^{-1})
β -PtCl ₂		Olive green	Experimental data: 280 (shoulder), 302 (middle), 323 (middle), 327 (strong), 352 (strong), 368 (shoulder). Literature data: 329 (strong), 345 (strong), 357 (weak) [6], 200 (weak), 318 (very strong) [7], 317 (strong) [8].
Found			
Pt 73.42	Cl 26.47		
Calculated			
Pt 73.34	Cl 26.66		
α -PtCl ₂		Dark violet	Experimental data: 267 (weak), 304 (middle), 330 (strong), 350 (strong), 367 (shoulder). Literature data: –
Found			
Pt 73.26	Cl 26.67		
Calculated			
Pt 73.34	Cl 26.66		

aluminum unit. The unit was situated in the resistance furnace. Linear heating was carried out with the help of the linear voltage device and a precision [11] isodromic thermoregulator PIT-3. Temperature of the effects was recorded with the help of Pt–PtRh thermocouples. A direct thermocouple was calibrated over melting and solidification temperatures of Sn, Pb and K₂Cr₂O₇. Total error of temperature measurement was estimated to be $\pm 1^\circ\text{C}$. Heating rates were varied within the range 5–10 °C/min. Experiments were carried out in sealed ampoules with a capillary to seal off chlorine. Thermographic ampoules were filled with the substance in a dry box in nitrogen; then the ampoules were evacuated and sealed.

2.3.3. Differential scanning calorimetry

Using instrument of “Setaram” company was investigated curves of heating and cooling of α -PtCl₂ in evacuated ampoule. Instrument of «Setaram» company [12].

3. Discussion of results

Thermal annealing of β -PtCl₂ followed by quenching demonstrated changes in the character of diffraction patterns depending on annealing temperature (Fig. 1). The samples may be conventionally divided into three groups.

The first group includes the samples of the initial and annealed at 510 K β -PtCl₂ (curves 1 and 2, respectively). These products are similar in the appearance, color and have similar diffraction patterns. The latter is an evidence of the fact that annealing at a temperature up to 510 K causes no structural changes in β -form.

The second group includes the samples annealed at 590, 660, 760 K. The observed shifts of some most intensive maxima, disappearance of a number of reflections and the appearance of two new lines at $2\theta = 12.4^\circ$ and 24.95° with the intensity increasing with an increase in annealing temperature provide evidence of a rearrangement occurring in the structure of β -PtCl₂. In addition, a number of reflections belonging to the samples of the third group appear on curve 5 (Fig. 1, annealing at 760 K). Their intensity increases as the annealing temperature increases. The color of samples annealed at 590 and 660 K is almost the same as that of the β -form, while the product obtained after annealing at 760 K becomes dark brown (Table 3).

The third group includes the samples kept at 830 and 890 K.

The diffraction patterns of the samples (curves 6 and 7, Fig. 1) kept at these temperatures almost coincide with those for the α -form (curve 8). Some difference is observed for the sample annealed at 830 K: its diffraction patterns contain a maximum at $2\theta = 24.95^\circ$, belonging to the substances of the second group, while the maximum at $2\theta = 22.45^\circ$ characteristic of the α -form. The samples of the third group are dark violet.

The IR spectra of the samples from three groups exhibit almost no differences from each other. With an increase in annealing temperature, only some changes are observed in the bands and in the ratio of the intensities of the main maxima at 327 and 352 cm^{-1} (see Fig. 2 and Table 3).

So, it may be stated on the basis of the results of thermal annealing that the $\beta \rightarrow \alpha$ transition occurs within temperature range 570–870 K and is accompanied by amorphization of the initial structure. As temperature increases, the nucleation and accumu-

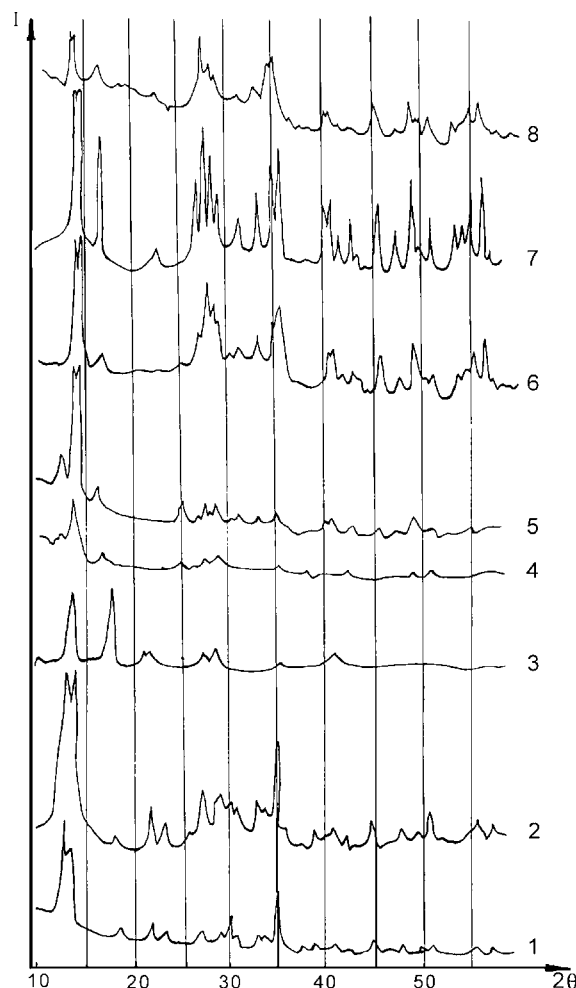


Fig. 1. Diffraction patterns of the products of thermal annealing at a temperature of: 510 K (2), 590 K (3), 660 K (4), 760 K (5), 830 K (6), 890 K (7). (1 and 8) Diffraction patterns of β -PtCl₂ and α -PtCl₂ at room temperature, respectively.

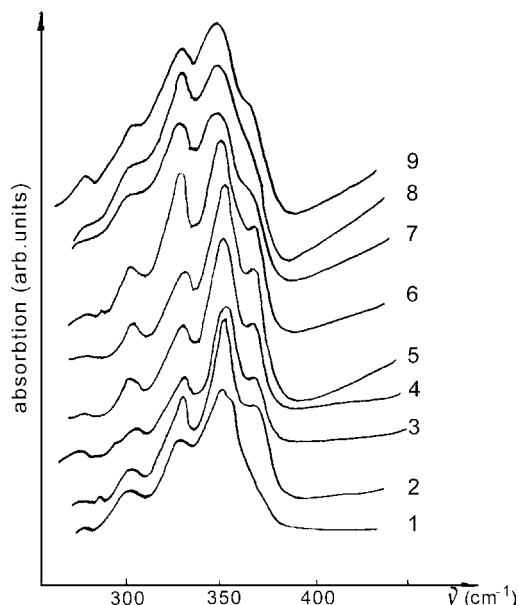


Fig. 2. IR spectra of the products of thermal annealing at a temperature of 510 K (2), 590 K (3), 660 K (4), 760 K (5), 830 K (6), 860 K (7), 890 K (8). (1 and 9) IR spectra of β -PtCl₂ and α -PtCl₂ at room temperature, respectively.

lation of the α -phase occurs. Some structural units of the β -phase may be conserved.

The data on the temperature and time of $\beta \rightarrow \alpha$ transition was obtained also by means of differential thermal analysis of the samples in sealed ampoules within temperature range 500–900 K. The appearance of the samples after experiment pointed to the presence of the α -form, which was then confirmed by the results of X-ray phase analysis and IR spectroscopy. However, within the instrument sensitivity limits, no thermal effects were observed on β -PtCl₂ thermograms.

With the help of the differential scanning calorimeter of «Setaram» [12] company within temperature range 570–900 K, a reversible phase transition was discovered for α -PtCl₂ at a temperature of 660 ± 5 K and thermal effect $+167 \pm 17$ J/mol (Fig. 3).

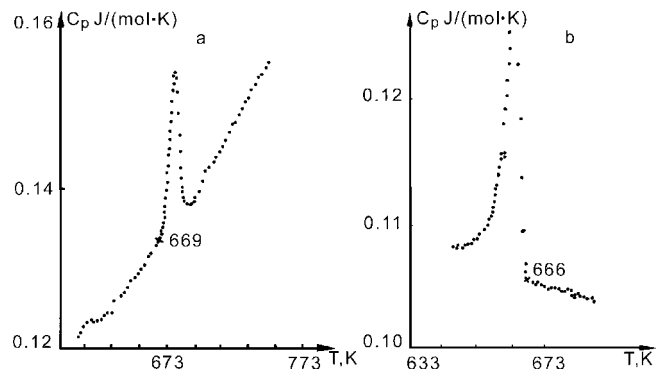


Fig. 3. Heating and cooling curves for α -PtCl₂ (differential scanning calorimetry): (a) heating; (b) cooling.

Thermal annealing followed by quenching of α -PtCl₂ showed that this phase does not exhibit any changes of the crystal structure during annealing at a temperature up to 900 K: the IR spectra and diffraction patterns of the samples before and after annealing were identical. This circumstance is likely to point to the monotropic character of the transition β -PtCl₂ \rightarrow α -PtCl₂.

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