

# Reactions of $\alpha$ - and $\beta$ -phenylalanines with transient Pt(III) complexes

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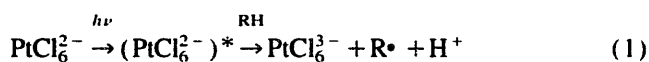
## Abstract

Laser pulse photolysis was used to show that the intermediate three-valent platinum complexes,  $\text{PtCl}_6^{3-}$  and  $\text{PtCl}_5^{2-}$ , appearing from photoreduction of the  $\text{PtCl}_6^{2-}$  complex, coordinate  $\alpha$ - and  $\beta$ -phenylalanines ( $\alpha\text{H}$  and  $\beta\text{H}$ ) with high rate constants. Spectroscopic and kinetic parameters of transient species are determined. At the first stage of irradiation of the three-valent platinum complex,  $\text{Pt}(\text{LH})_2\text{Cl}_4^-$  is formed, which at long-time photolysis converts to the diaminoacid Pt(II) complexes, in which aminoacid (LH) is bound to platinum through the  $\text{COO}^-$  group. The conclusion is drawn from laser flash photolysis data and the comparison of electronic and proton magnetic resonance (PMR) spectra of photolysis products with the spectra of free  $\alpha\text{H}$  and  $\beta\text{H}$ , and the known Pt(II) complexes involving these aminoacids, obtained by a thermal method. © 1997 Elsevier Science S.A.

**Keywords:** Phenylalanine; Platinum complexes; Photoreduction; Laser flash photolysis

## 1. Introduction

The primary photoreduction mechanism of the  $\text{PtCl}_6^{2-}$  complex in methanol and other alcohols is electron transfer from solvent molecules to excited complex [1–3]



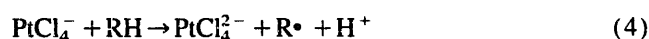
The primary three-valent platinum ( $\text{PtCl}_6^{3-}$ ) complex disappears in the fast reaction



The secondary intermediate  $\text{PtCl}_5^{2-}$  complex also dissociates

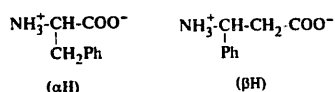


The  $\text{PtCl}_4^-$  complex disappears in the slow reaction with a solvent



The lifetimes of the successively alternating Pt(III) complexes,  $\text{PtCl}_6^{3-}$ ,  $\text{PtCl}_5^{2-}$  and  $\text{PtCl}_4^-$ , are equal to 1, 200 and 3000  $\mu\text{s}$  [1], respectively, which allows a new ligand molecule to coordinate with the Pt(III) ion at one of the conver-

sion steps. We have investigated the reactions of the intermediate Pt(III) complexes with such molecules as creatinine [4], pyrimidines [5,6], and aminoacids (proline and tryptophan) [7]. This paper continues these researches and reports the data on photochemical reactions in solutions, containing the  $\text{PtCl}_6^{2-}$  complexes and such aminoacids as  $\alpha\text{H}$  and  $\beta\text{H}$ . The structures of these aminoacids in solution are of the form



The thermally obtained Pt(II) complexes with  $\alpha\text{H}$  and  $\beta\text{H}$  have been described in refs. [8–11]. Among them note *cis*- and *trans*-dichlorides,  $[\text{Pt}(\text{LH})_2\text{Cl}_2]$ , in which aminoacids are bound to a platinum atom via the  $\text{NH}_2$  groups, *cis*- and *trans*-bischelates,  $[\text{PtL}_2]$ , with the Pt– $\text{NH}_2$  and Pt– $\text{OCO}$  bonds, as well as the Pt(II) *ortho*-platinated complexes with  $\alpha\text{H}$ , where the Pt– $\text{NH}_2$  and Pt– $\text{OCO}$  bonds exist along with that of Pt to the phenyl ring *ortho*-carbon bond.

## 2. Experimental details

The laser flash photolysis apparatus with an XeCl excimer laser (308 nm, 15 ns, 50 mJ), was described in [4]. Solu-

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tions were placed in optical cuvettes 1–10 mm thick. To remove oxygen, the solutions were bubbled with argon for 30 min. Optical spectra were detected on a Specord UV-visible spectrophotometer (Carl Zeiss). Solutions were prepared using spectrally pure solvents. The proton magnetic resonance spectra were detected on a MSL-400 Bruker spectrometer in  $\text{CD}_3\text{OD}$ .

### 3. Results and discussion

#### 3.1. The $\text{PtCl}_6^{2-}$ photolysis in methanol in the presence of $\beta\text{H}$

The photolysis of  $\text{PtCl}_6^{2-}$  solutions in alcohols give rise to a two-valent platinum,  $\text{PtCl}_4^{2-}$ , complex, as a final product [12]. The optical absorption spectra of  $\text{PtCl}_6^{2-}$  and  $\text{PtCl}_4^{2-}$  complexes are presented in refs. [13,14], respectively. Under radiation the addition of  $\beta\text{H}$  to the solution results in the appearance of a new optical spectrum (Fig. 1) which does not coincide with the  $\text{PtCl}_4^{2-}$  one. During photolysis the isosbestic point at  $39\,840\text{ cm}^{-1}$  is saved. The new spectrum fails to display an expressed maximum. However, the processing of a long-wave region permits one to allocate a band with the maximum at  $44\,000\text{ cm}^{-1}$  (spectrum 5 in Fig. 1), that is overlapped by other band, lying in a more short-wave range. For simplicity the new spectrum is named the absorption at  $44\,000\text{ cm}^{-1}$ . In the region of the d-d bands of  $\text{PtCl}_6^{2-}$  absorption, the isosbestic points are also observed at  $23\,400$  and  $22\,000\text{ cm}^{-1}$ .

The existence of isosbestic points allows one to evaluate the extinction coefficient of the new absorption at

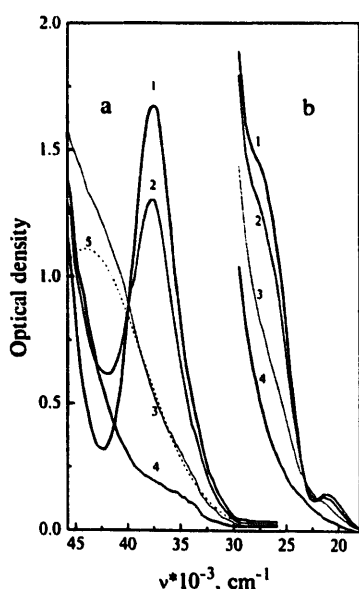


Fig. 1. Stationary  $\text{PtCl}_6^{2-}$  ( $6 \times 10^{-3}\text{ M}$ ) photolysis in methanol in the presence of  $\beta\text{H}$  ( $1.2 \times 10^{-2}\text{ M}$ ): (a) 0.01 cm cuvette thickness; (b) 0.5 cm cuvette. Spectra 1–4, irradiation by mercury lamp light with  $\lambda_{\text{irr}} > 310\text{ nm}$ , 0, 6, 180 and 500 s, respectively. Spectrum 5, processing of the spectrum 3 tail with Gauss functions ( $\nu_{\text{max}} = 44\,000\text{ cm}^{-1}$ ).

$44\,000\text{ cm}^{-1}$  ( $\epsilon \approx 19\,000\text{ M}^{-1}\text{ cm}^{-1}$ ). A longer irradiation results in the disappearance of the  $44\,000\text{ cm}^{-1}$  absorption, the destruction of isosbestic points, and the decrease in absorption intensity (spectrum 4 in Fig. 1). This testifies to that the photoproduct to which the absorption at  $44\,000\text{ cm}^{-1}$  belongs, is subjected to further photochemical transformations. If irradiation is stopped at the stage when isosbestic points still exist, in dark conditions, the partial regeneration of the initial  $\text{PtCl}_6^{2-}$  complex band with the maximum at  $37\,700\text{ cm}^{-1}$  begins.

The yield of absorption at  $44\,000\text{ cm}^{-1}$  grows with increasing relative contents of aminoacid in the range of  $[\beta\text{H}]/[\text{PtCl}_6^{2-}]$  ratio from 0 to 2. With large  $\beta\text{H}$  concentrations the change both in the spectrum and the position of isosbestic points are independent out of this ratio in the range from 2 to 10. Thus, the primary product of photochemical reaction (appearing before the destruction of isosbestic points) is a new platinum complex with two aminoacid molecules.

In addition, the photolysis of the  $\text{PtCl}_6^{2-} + \beta\text{H}$  systems with alkali-neutralized aminoacid was investigated. In the presence of alkali the  $\beta\text{H} = \text{NH}_3^+\text{RCOO}^-$  zwitterion was transformed to the  $\beta^- = \text{NH}_2\text{RCOO}^-$  form. However, the character of spectrum changes on irradiation in these systems (with and without alkali) was the same. The absence of the influence of NaOH additives can testify to the coordination of aminoacid via the  $\text{COO}^-$  group.

Fig. 2 depicts the optical spectra of  $\beta\text{H}$  and various two-valent thermally synthesized platinum complexes with two molecules of this aminoacid [8–11]. In the  $50\,000$ –

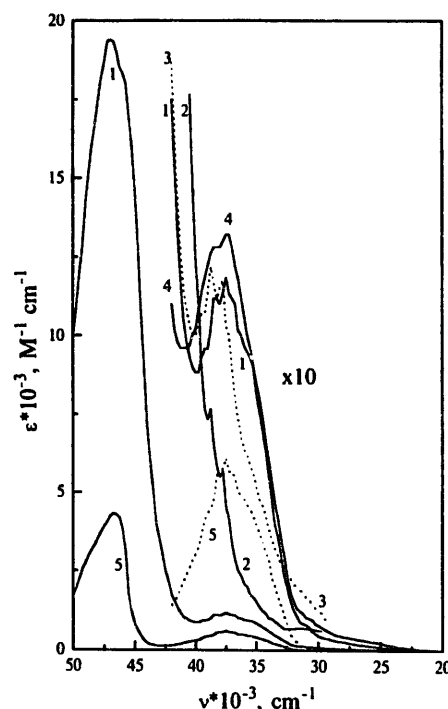


Fig. 2. Optical spectra of  $\beta\text{H}$  and its Pt(II) complexes in methanol. Spectra 1–4,  $\text{trans-}[\text{Pt}(\beta\text{H})_2\text{Cl}_2]$ ,  $\text{trans-Pt}(\beta)_2$ ,  $\text{cis-}[\text{Pt}(\beta\text{H})_2\text{Cl}_2]$ ,  $\text{cis-Pt}(\beta)_2$  complexes, respectively; Spectrum 5,  $\beta\text{H}$ .

35 000  $\text{cm}^{-1}$  region the spectrum of the complexes is basically defined by the absorption of coordinated  $\beta\text{H}$  molecules. Note that none of the complexes, the spectra of which are shown in Fig. 2, can give an isosbestic point at 39 840  $\text{cm}^{-1}$ , because the extinction coefficient for all species at this frequency does not exceed 1200  $\text{M}^{-1} \text{cm}^{-1}$ . The primary photochemical product at the isosbestic point at 39 840  $\text{cm}^{-1}$  has the extinction coefficient of about 14 000  $\text{M}^{-1} \text{cm}^{-1}$  which more than an order of magnitude higher than the absorption intensity of the Pt(II) complexes with  $\beta\text{H}$ . Only, under a long-time irradiation after the destruction of isosbestic points and the disappearance of the 44 000  $\text{cm}^{-1}$  absorption does a new weak absorption appear which can belong to the Pt(II) complexes with  $\beta\text{H}$ .

### 3.2. Laser flash photolysis of $\text{PtCl}_6^{2-}$ in the presence of $\beta\text{H}$

The action of a laser pulse on  $\text{PtCl}_6^{2-}$  solutions in methanol is followed by the formation (during 4  $\mu\text{s}$ ) of the three-valent platinum complex,  $\text{PtCl}_5^{2-}$ , absorption in the form of two bands with the maxima at 535 and 410 nm (the extinction coefficients of the 535 nm band is 3200  $\text{M}^{-1} \text{cm}^{-1}$  [1]).

The addition of bioligands (L) to the solution usually results in the acceleration of  $\text{PtCl}_5^{2-}$  optical absorption disappearance. However, the initial concentration of this species a 4  $\mu\text{s}$  after laser pulse is practically independent of the bioligand presence, as owing to short lifetime the primary three-valent platinum  $\text{PtCl}_6^{2-}$  complex it does not react with these ligands and is completely transformed to  $\text{PtCl}_5^{2-}$ . The increase in the disappearance rate of the secondary intermediate  $\text{PtCl}_5^{2-}$  complex is connected with the formation of the  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex



for which the existence of the wide bands of optical absorption in the 400–600 nm range [4–7] is quite typical.

A different situation has been observed for solutions containing  $\beta\text{H}$ . As follows from Fig. 3 (spectrum 1) in the solution with  $\beta\text{H}$  the optical absorption of the  $\text{PtCl}_5^{2-}$  intermediate complex can also be observed, although its yield at 4  $\mu\text{s}$  after a laser pulse is significantly less than in the case of zero aminoacid concentration (spectrum 3). At 50  $\mu\text{s}$  after a laser pulse a wide absorption band with the maximum at 485 nm appears. Similarly to the solutions with the additives of other bioligands [4–7], it can be assumed that a new band appears because of the  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex formation.

Fig. 4 gives the dependence of the  $\text{PtCl}_5^{2-}$  and  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  optical absorption yields on  $\beta\text{H}$  concentration in methanol. A decrease in the  $\text{PtCl}_5^{2-}$  yield can be assigned to two processes. The first one is the quenching of the excited state of the initial complex by  $\beta\text{H}$  molecule. However, in [1] from the nonlinear dependence of the  $\text{PtCl}_6^{2-}$  and  $\text{PtCl}_5^{2-}$  intermediate complexes yields on laser pulse intensity the lifetime of excited ( $\text{PtCl}_6^{2-}$ )\* complex was estimated to be about 100 ps. At these times with  $\beta\text{H}$  concentration being about  $3 \times 10^{-2} \text{ M}$  even for quenching at the diffusion rate

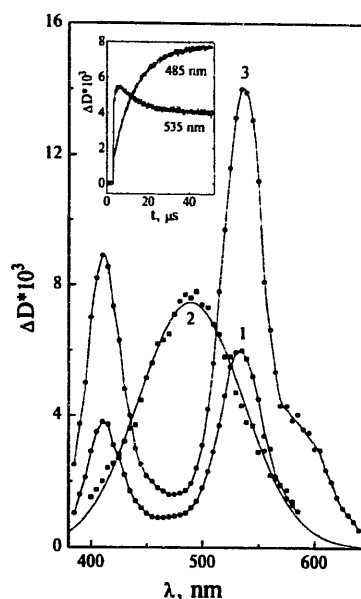


Fig. 3. Laser flash photolysis of  $\text{PtCl}_6^{2-}$  ( $3 \times 10^{-3} \text{ M}$ ) methanol solution. Spectra 1, 2, the spectra in the presence of  $\beta\text{H}$  ( $2 \times 10^{-2} \text{ M}$ ) at 4 and 50  $\mu\text{s}$  after laser pulse, respectively; spectrum 3, spectrum without  $\beta\text{H}$  at 4  $\mu\text{s}$  after laser pulse. Inset: the typical kinetic curves.

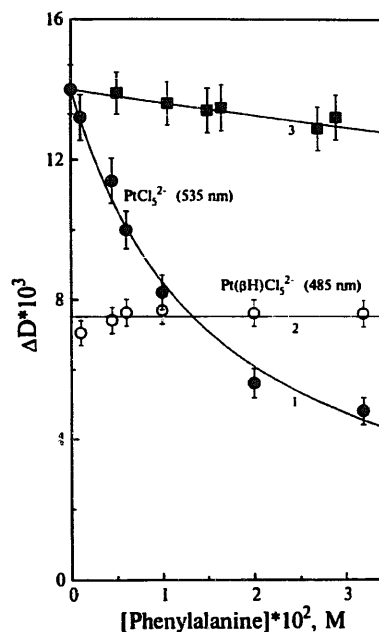


Fig. 4. Dependence of optical density of the  $\text{PtCl}_5^{2-}$  (535 nm) (curves 1, 3) and  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  (485 nm) (curve 2) complexes appearing in laser flash photolysis of  $\text{PtCl}_6^{2-}$  in methanol on the  $\beta\text{H}$  (curve 1) and  $\alpha\text{H}$  (curve 3) concentrations.

constant the decrease in the quantum yield will not exceed 4%, whereas the  $\text{PtCl}_5^{2-}$  yield decreases more than twice at the same concentration.

The second process which can reduce the  $\text{PtCl}_5^{2-}$  yield may be related to the interaction of the precursor (primary  $\text{PtCl}_6^{2-}$  complex) with aminoacid. This reaction can result in both the redox process and the formation of  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex. In the first case, the quantum yield of  $\text{PtCl}_6^{2-}$  disappearance and the product yield with the absorption at

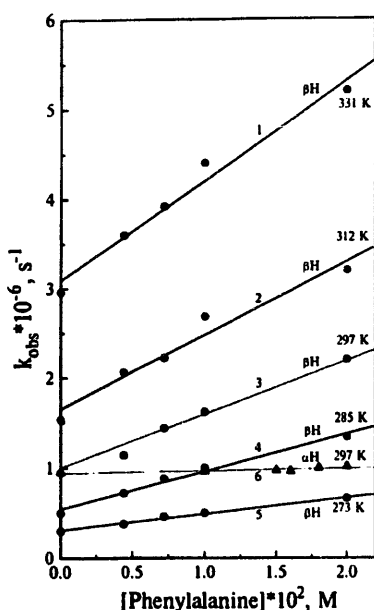
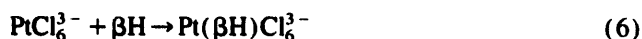


Fig. 5. The  $k_{\text{obs}}$  dependence of  $\text{PtCl}_5^{2-}$  absorption formation (535 nm) on the  $\beta\text{H}$  (curves 1–5) and  $\alpha\text{H}$  (curve 6) concentrations at different temperatures.

$44\,000\text{ cm}^{-1}$  should decrease considerably with increasing  $\beta\text{H}$  concentration. However, the measurements show that the quantum yield and the amplitude of  $44\,000\text{ cm}^{-1}$  absorption are independent of  $\beta\text{H}$  concentration with  $[\beta\text{H}]/[\text{PtCl}_6^{3-}] > 2$ . Thus, it is likely the formation of  $\text{Pt}(\beta\text{H})\text{Cl}_6^{3-}$  complex

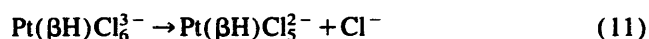
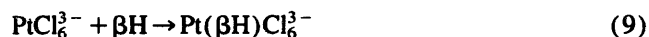


In this case, the solution of the kinetic equations for competitive reactions (2) and (6) shows that the observed rate constant of  $\text{PtCl}_5^{2-}$  appearance must obey equation

$$k_{\text{obs}} = k_2 + k_6[\beta\text{H}] \quad (7)$$

Indeed, in the presence of  $\beta\text{H}$  a decrease of the yield is accompanied by the acceleration of  $\text{PtCl}_5^{2-}$  absorption formation. Fig. 5 shows the linear  $k_{\text{obs}}$  dependence of  $\text{PtCl}_5^{2-}$  appearance on aminoacid concentration at various temperatures. For these lines the intercepts on the ordinate are equal to  $k_2$ , and the slope is determined by the  $k_6$  value. The activation energy of reaction (6) is  $27.8 \pm 1.5\text{ kJ mol}^{-1}$ . At room temperature (297 K)  $k_2 = (1.0 \pm 0.04) \times 10^6\text{ s}^{-1}$  and  $k_6 = (6.0 \pm 0.4) \times 10^7\text{ M}^{-1}\text{ s}^{-1}$ .

At  $50\text{ }\mu\text{s}$  after laser pulse a new absorption band with the maximum at  $485\text{ nm}$  forms, which belongs to the  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex. This complex results from two parallel reactions. The first reaction is the process of aminoacid coordination with the  $\text{PtCl}_5^{2-}$  complex, and the second is the transformation of the  $\text{Pt}(\beta\text{H})\text{Cl}_6^{3-}$  species to the  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex. Thus, the scheme of  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  formation consists of the following reactions



Two first reactions (8) and (9) end fast enough (for  $1\text{--}4\text{ }\mu\text{s}$ ) and the yield of the secondary intermediate  $\text{PtCl}_5^{2-}$  complex at this time is

$$[\text{PtCl}_5^{2-}]_{\infty} = \Delta[\text{PtCl}_6^{3-}] \frac{k_8}{k_8 + k_9[\beta\text{H}]} \quad (12)$$

where  $\Delta[\text{PtCl}_6^{3-}]$  is the quantity of decomposed initial  $\text{PtCl}_6^{3-}$  complex. Within the framework of this scheme the time dependence of the kinetics of the slower  $\text{PtCl}_5^{2-}$  disappearance and  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  appearance reactions is determined by the expressions (with  $[\beta\text{H}] \gg \Delta[\text{PtCl}_6^{3-}]$ )

$$[\text{PtCl}_5^{2-}](t) = \Delta[\text{PtCl}_6^{3-}] \frac{k_8}{k_8 + k_9[\beta\text{H}]} e^{-k_{10}[\beta\text{H}]t} \quad (13)$$

$$\begin{aligned} &[\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}](t) \\ &= \Delta[\text{PtCl}_6^{3-}] \left( \frac{k_8}{k_8 + k_9[\beta\text{H}]} (1 - e^{-k_{10}[\beta\text{H}]t}) \right. \\ &\quad \left. + \frac{k_9[\beta\text{H}]}{k_8 + k_9[\beta\text{H}]} (1 - e^{-k_{11}t}) \right) \quad (14) \end{aligned}$$

The  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  yield after the end of reactions (10) and (11) is

$$[\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}]_{\infty} = \Delta[\text{PtCl}_6^{3-}] \quad (15)$$

and does not depend on  $\beta\text{H}$  concentration. As the  $k_8$  and  $k_9$  rate constants are actually equal to the  $k_2$  and  $k_6$  constants determined above by direct kinetic measurements, the  $\text{PtCl}_5^{2-}$  yield can be calculated from formula (12). In Fig. 4 solid line 1 shows good agreement of the calculation of  $\text{PtCl}_5^{2-}$  absorption (535 nm) yield as the function of  $\beta\text{H}$  concentration with experimental data. According to formula (15) the final value of  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  absorption (485 nm) is independent of aminoacid concentration, confirming the existence of reaction (11). The complete conversion of the  $\text{Pt}(\beta\text{H})\text{Cl}_6^{3-}$  and  $\text{PtCl}_5^{2-}$  complexes to the  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex allows us to determine the extinction coefficient of its absorption band. The comparison of  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  and  $\text{PtCl}_5^{2-}$  absorption bands (spectra 2 and 3 in Fig. 3) shows that the extinction coefficient of absorption band with maximum on  $485\text{ nm}$  is equal to  $1750\text{ M}^{-1}\text{ cm}^{-1}$ .

If the experimental curves at  $485$  and  $535\text{ nm}$  (the maxima of  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  and  $\text{PtCl}_5^{2-}$  absorption bands) are processed at the initial site in the one-exponential approximation, then transforming Eqs. (13) and (14), the expressions can be obtained for observed rate constants

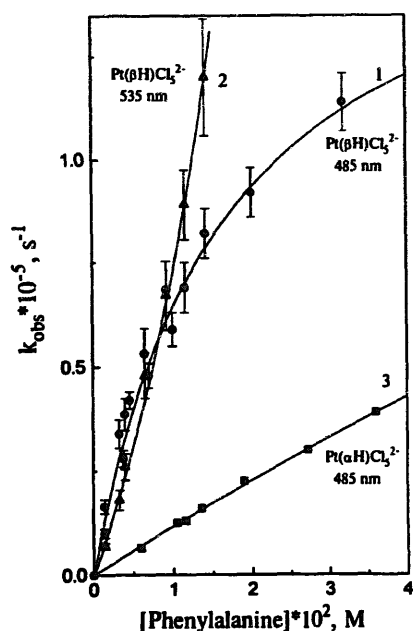


Fig. 6. The  $k_{\text{obs}}$  dependence of  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  (curves 1, 2) and  $\text{Pt}(\alpha\text{H})\text{Cl}_5^{2-}$  (curve 3) absorption formation on  $\beta\text{H}$  and  $\alpha\text{H}$  concentrations. The measurements at 485 nm (curves 1, 3) and 535 nm (curve 2).

$$k_{\text{obs}}^{485 \text{ nm}} = \frac{A}{1+B[\beta\text{H}]}[\beta\text{H}] \quad k_{\text{obs}}^{535 \text{ nm}} = \frac{C}{1-D[\beta\text{H}]}[\beta\text{H}] \quad (16)$$

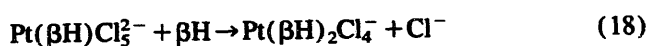
where

$$A = k_{10} + Bk_{11} \quad B = \frac{k_8}{k_9} = \frac{k_2}{k_6} = 60 \pm 6.4 \text{ M}^{-1}$$

$$C = k_{10} - Dk_{11} \quad D = \frac{\alpha}{(1-\alpha)}B \quad (17)$$

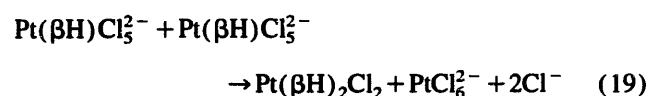
and  $\alpha = \varepsilon(\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}) / \varepsilon(\text{PtCl}_5^{2-})$  is the ratio of extinction coefficients at 535 nm. Fig. 3, where  $\text{PtCl}_5^{2-}$  and  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  optical spectra are submitted, allows to determine that  $\alpha \approx 0.3$ . Fig. 6 shows the dependence of the observed rate constants as a function of  $\beta\text{H}$  concentration. The solid lines denote the fitting of experimental data with formulas (16) by the least squares method. The values  $k_{10} = (6.7 \pm 1.6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{11} = (0.6 \pm 0.1) \times 10^5 \text{ s}^{-1}$  have been estimated from these data.

The  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex disappears in the millisecond time range. The dependence of observed rate constant at different aminoacid concentrations is given in Fig. 7 as a function of the initial optical density at 485 nm ( $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  concentration). The  $k_{\text{obs}}$  linear increase and the existence of an intercept on the ordinate testify that the decay of this complex happens in both the second- and first-order reactions. As the magnitude of intercept grows linearly with increasing  $\beta\text{H}$  concentration, the last process is certain to be the pseudo-first-order reaction, i.e. it is likely to be related to the coordination of the second aminoacid molecule



This reaction dominates at low light intensities. The bimolecular rate constant of reaction (18) is  $k_{18} = (3.4 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . As the characteristic time of this reaction can reach about 0.1 s and more (at low  $\beta\text{H}$  concentration), it is assumed then that the resulting product of photochemical conversions at stationary irradiation before the destruction of isosbestic points and the disappearance of the  $44\,000 \text{ cm}^{-1}$  absorption is likely to be the Pt(III) complex with two aminoacid molecules.

It is difficult to establish the nature of the second-order reaction proceeding at high laser pulse intensity. We consider that this reaction is that of disproportionation connected with simultaneous electron and aminoacid transfer between  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complexes.



In this case the Pt(II) complex with two aminoacid molecules is formed and the  $\text{Pt}(\beta\text{H})_2\text{Cl}_4^-$  complex yield decreases. The detection of optical spectra changes under laser pulses with the same intensity, when the contribution of the second-order reaction is certain, shows a decrease of absorption at  $44\,000 \text{ cm}^{-1}$  and a shift in the isosbestic point originally found at  $39\,840 \text{ cm}^{-1}$  (Fig. 8). The extinction coefficient of the absorption band of the  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex permits us to determine from a slope of linear dependence (Fig. 7) the rate constant of reaction (19) ( $k_{19} = (6.6 \pm 1.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ).

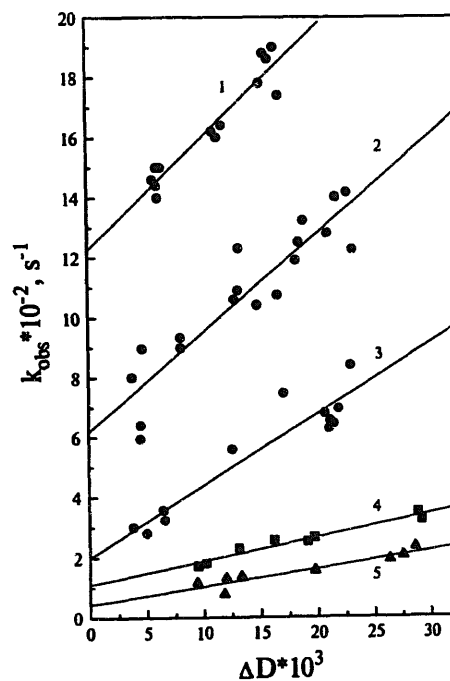


Fig. 7. The  $k_{\text{obs}}$  dependence of  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  (curves 1–3) and  $\text{Pt}(\alpha\text{H})\text{Cl}_5^{2-}$  (curves 4, 5) disappearance on the optical density of these complexes absorption (485 nm). Curves 1–3, 0.036, 0.018 and 0.006 M  $\beta\text{H}$  concentrations; curves 4, 5, 0.0186 and 0.0078 M  $\alpha\text{H}$  concentrations.

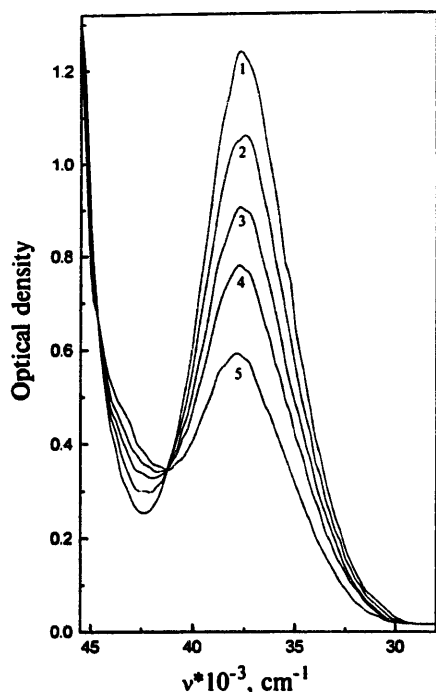


Fig. 8. Stationary  $\text{PtCl}_5^{2-}$  ( $6 \times 10^{-3}$  M) photolysis in methanol in the presence of  $\beta\text{H}$  ( $1.2 \times 10^{-2}$  M) in cuvette of 0.01 cm thickness. Irradiation by eximer XeCl pulse laser light (308 nm). Curves 1–5, 0, 20, 40, 60 and 100 pulses, respectively.

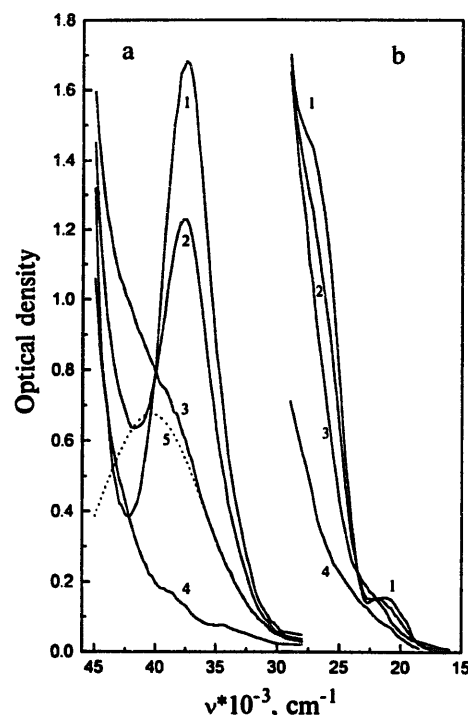


Fig. 9. Stationary  $\text{PtCl}_5^{2-}$  ( $6 \times 10^{-3}$  M) photolysis in methanol in the presence of  $\alpha\text{H}$  ( $1.2 \times 10^{-2}$  M): (a) 0.01 cm cuvette thickness; (b) 0.5 cm cuvette. Curves 1–4, irradiation by mercury lamp light with  $\lambda_{\text{irr}} > 310$  nm, 0, 20, 60, and 500 s, respectively. Curve 5, processing of the spectrum 3 tail with Gauss functions ( $\nu_{\text{max}} = 40\,400$   $\text{cm}^{-1}$ ).

### 3.3. Stationary and laser flash photolysis of $\text{PtCl}_5^{2-}$ in methanol in the presence of $\alpha\text{H}$

The photolysis of the  $\text{PtCl}_5^{2-}$  and  $\alpha\text{H}$  system in methanol gives a new spectrum displaying the absorption at  $40\,400$   $\text{cm}^{-1}$  (Fig. 9, spectrum 5). During irradiation the isosbestic points are presented at  $40\,030$ ,  $23\,530$  and  $21\,920$   $\text{cm}^{-1}$ . As for  $\beta\text{H}$ , the yield of new absorption grows with increasing relative aminoacid content in the range of the  $[\alpha\text{H}]/[\text{PtCl}_5^{2-}]$  ratio from 0 to 2. At large  $\alpha\text{H}$  concentrations the change in the spectrum and positions of isosbestic points is independent of this ratio. Studying phototransformation in solutions with alkali-neutralized aminoacid shows that the character of the spectral changes does not depend on the presence of alkali. Fig. 10 shows the optical spectra of  $\alpha\text{H}$  and the various complexes of two-valent platinum with two molecules of this aminoacid, synthesized by a thermal method. None of these complexes can give the isosbestic point at  $40\,030$   $\text{cm}^{-1}$ .

Fig. 4 (curve 3) shows that the yield of  $\text{PtCl}_5^{2-}$  absorption at  $4$   $\mu\text{s}$  after laser pulse decreases less rapidly with increasing  $\alpha\text{H}$  concentration than in the case of  $\beta\text{H}$ . Thus, the dissociation of primary  $\text{PtCl}_5^{2-}$  complex (reaction (2)) successfully competes in this case with its disappearance in the reaction with  $\alpha\text{H}$ . The processing of the dependence of the  $\text{PtCl}_5^{2-}$  yield on  $\alpha\text{H}$  concentration in terms of formula (12) gives the value  $k \leq 10^6$   $\text{M}^{-1} \text{s}^{-1}$  for the rate constant of the reaction between  $\text{PtCl}_5^{2-}$  and  $\alpha\text{H}$  which is an order of magnitude less than that for the  $\text{PtCl}_5^{2-}$  and  $\beta\text{H}$  pair. A similar estimation

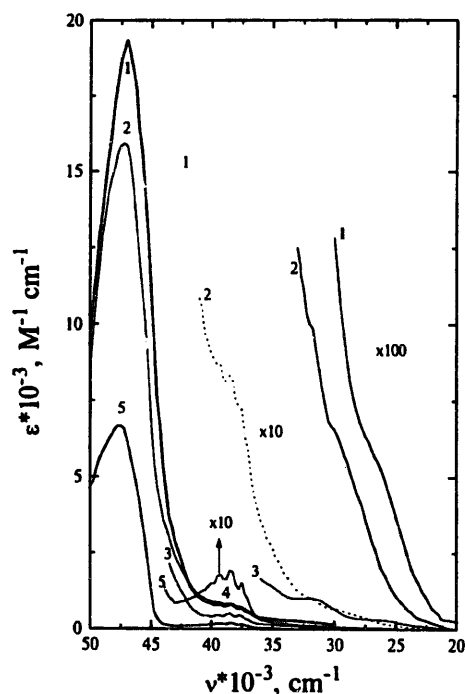


Fig. 10. Optical spectra of  $\alpha\text{H}$  and its Pt(II) complexes in methanol. Curves 1–4,  $\text{trans-}[\text{Pt}(\alpha\text{H})_2\text{Cl}_2]$ ,  $\text{trans-Pt}(\alpha)_2$ ,  $\text{cis-}[\text{Pt}(\alpha\text{H})_2\text{Cl}_2]$ ;  $\text{cis-Pt}(\alpha)_2$  complexes, respectively; curve 5,  $\alpha\text{H}$ .

can also be deduced from a weak dependence of the observed rate constant of  $\text{PtCl}_5^{2-}$  appearance on  $\alpha\text{H}$  concentration (formula (7) and Fig. 5).

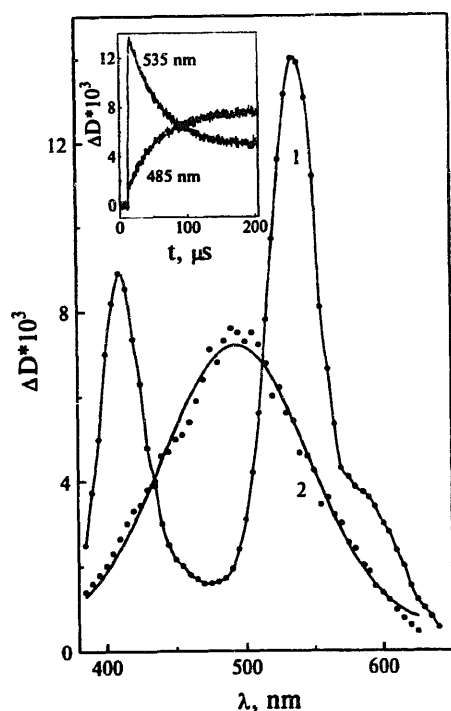
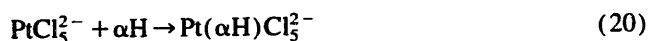


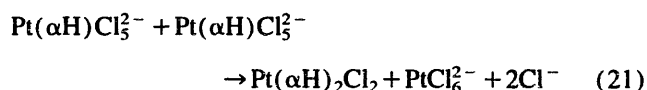
Fig. 11. Laser flash photolysis of  $\text{PtCl}_5^{2-}$  ( $3 \times 10^{-3}$  M) methanol solution in the presence of  $\alpha\text{H}$  ( $2 \times 10^{-2}$  M). Curves 1, 2, the spectra at 4 and 200  $\mu\text{s}$  after laser pulse, respectively. Inset: the typical kinetic curves.

At 200  $\mu\text{s}$  after the laser pulse a new absorption appears in the form of a wide band with maximum at 490 nm (Fig. 11), due to the formation of the  $\text{Pt}(\alpha\text{H})\text{Cl}_5^{2-}$  complex

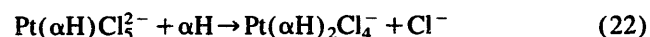


This band is almost identical to that of the  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex (Fig. 3). The optical density of  $\text{Pt}(\alpha\text{H})\text{Cl}_5^{2-}$  absorption is independent of aminoacid concentration, as in case of  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  formation. The dependence of the observed rate constant of  $\text{Pt}(\alpha\text{H})\text{Cl}_5^{2-}$  appearance is shown in Fig. 6 as a function of  $\alpha\text{H}$  concentration. The slope of linear dependence determines a bimolecular rate constant of this reaction. At room temperature  $k_{20} = (1.1 \pm 0.1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

The disappearance of the  $\text{Pt}(\alpha\text{H})\text{Cl}_5^{2-}$  complex follows two reactions. Fig. 7 shows the dependence of the observed rate constant of absorption decay at 490 nm as a function of optical density at this wavelength. The linear increase demonstrates the availability of channel determined by second-order reaction (similarly to the  $\beta\text{H}$  case)



From the slope the bimolecular rate constant was determined to be  $k_{21} = (1.4 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . The intercept on the ordinate in the dependence  $k_{\text{obs}} \sim \Delta D$  and its increase with  $\alpha\text{H}$  concentration show that at small intensities of exciting light, the main channel of  $\text{Pt}(\alpha\text{H})\text{Cl}_5^{2-}$  decay is the coordination of the second aminoacid molecule



with the rate constant  $k_{22} = (5.8 \pm 0.5) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

### 3.4. Analysis of the resulting products by proton magnetic resonance spectroscopy

The resulting product of long-time photolysis is the Pt(II) complex with two aminoacid molecules which can be represented by both the  $[\text{Pt}(\text{LH})_2\text{Cl}_2]$  and  $[\text{Pt}(\text{L})_2]$  complexes. Thermally synthesized complexes of such types contain the Pt–NH<sub>2</sub> bonds, and in the proton magnetic resonance (PMR) spectra (methanol, DMSO) the NH<sub>2</sub> group protons of the *cis*- and *trans*- $[\text{PtL}_2]$  complexes have signals in the range  $\delta = 5.6$ – $5.9$  ppm, and for the *cis*- and *trans*- $[\text{Pt}(\text{LH})_2\text{Cl}_2]$  complexes in the region  $\delta = 4.9$ – $5.5$  ppm.

The PMR spectra of the  $\text{PtCl}_5^{2-}$  long-time photolysis products in the presence of  $\alpha\text{H}$  and  $\beta\text{H}$  show no signal in the range  $5.9$ – $4.9$  ppm and contain only the signals (Table 1) which are close to free aminoacid signals. The absence of the NH<sub>2</sub> group proton signals allows one to assume that amino group is protonized and does not participate in coordination, i.e. the coordination is realized by the COO<sup>−</sup> group.

## 4. Conclusions

Stationary and laser flash photolysis allowed us to show that  $\beta\text{H}$  coordinates with the primary  $\text{PtCl}_6^{3-}$  complex at a high rate constant. The resulting  $\text{Pt}(\beta\text{H})\text{Cl}_6^{3-}$  complex decays during about 20  $\mu\text{s}$  to form  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$ . The latter results also from the coordination of aminoacid by the secondary transient  $\text{PtCl}_5^{2-}$  complex. The  $\text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$  complex disappears after the coordination of the second aminoacid molecule thus forming the next three-valent platinum complex,  $\text{Pt}(\beta\text{H})_2\text{Cl}_4^-$ . This complex is subjected to a slow photoreduction and the resulting product of photochemical transformations is the two-valent platinum  $\text{Pt}(\beta\text{H})_2\text{Cl}_2$  com-

Table 1

The data ( $\delta$ , ppm) of PMR spectra of long-time photolysis products and free  $\alpha\text{H}$  and  $\beta\text{H}$  aminoacids

Group	Free $\beta\text{H}$	Photolysis product of $\text{PtCl}_6^{3-} + \beta\text{H}$ system	Free $\alpha\text{H}$	Photolysis product of $\text{PtCl}_6^{3-} + \alpha\text{H}$ system
Ph	7.47	7.47	7.34	7.37
CH	4.55	4.75	3.80	4.30
CH <sub>2</sub>	2.79	3.07	3.37, 3.03	3.37, 3.20

Table 2  
The rate constants of the transient Pt(III) complexes reactions

Reaction	Rate constant	Reference
$\text{PtCl}_6^{3-} \rightarrow \text{PtCl}_5^{2-} + \text{Cl}^-$	$1.0 \times 10^6 \text{ s}^{-1}$	[1]
$\text{PtCl}_5^{2-} \rightarrow \text{PtCl}_4^- + \text{Cl}^-$	$5.0 \times 10^3 \text{ s}^{-1}$	[1]
$\text{PtCl}_4^- + \text{CH}_3\text{OH} \rightarrow \text{PtCl}_4^- + \text{CH}_2\text{OH} + \text{H}^+$	$3.0 \times 10^2 \text{ s}^{-1}$	[12]
$\text{PtCl}_6^{3-} + \beta\text{H} \rightarrow \text{Pt}(\beta\text{H})\text{Cl}_5^{2-}$	$(6.0 \pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{Pt}(\beta\text{H})\text{Cl}_5^{2-} \rightarrow \text{Pt}(\beta\text{H})\text{Cl}_4^- + \text{Cl}^-$	$(0.6 \pm 0.1) \times 10^5 \text{ s}^{-1}$	This work
$\text{PtCl}_5^{2-} + \beta\text{H} \rightarrow \text{Pt}(\beta\text{H})\text{Cl}_4^-$	$(6.7 \pm 1.6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{Pt}(\beta\text{H})\text{Cl}_4^- + \beta\text{H} \rightarrow \text{Pt}(\beta\text{H})_2\text{Cl}_4^- + \text{Cl}^-$	$(3.4 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{Pt}(\beta\text{H})\text{Cl}_5^{2-} + \text{Pt}(\beta\text{H})\text{Cl}_4^- \rightarrow \text{Pt}(\beta\text{H})_2\text{Cl}_4^- + \text{PtCl}_6^{3-} + \text{Cl}^-$	$(6.6 \pm 1.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{PtCl}_6^{3-} + \alpha\text{H} \rightarrow \text{Pt}(\alpha\text{H})\text{Cl}_5^{2-}$	$\leq 6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{PtCl}_5^{2-} + \alpha\text{H} \rightarrow \text{Pt}(\alpha\text{H})\text{Cl}_4^-$	$(1.1 \pm 0.1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{Pt}(\alpha\text{H})\text{Cl}_4^- + \alpha\text{H} \rightarrow \text{Pt}(\alpha\text{H})_2\text{Cl}_4^- + \text{Cl}^-$	$(5.8 \pm 0.5) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{Pt}(\alpha\text{H})\text{Cl}_5^{2-} + \text{Pt}(\alpha\text{H})\text{Cl}_4^- \rightarrow \text{Pt}(\alpha\text{H})_2\text{Cl}_4^- + \text{PtCl}_6^{3-} + \text{Cl}^-$	$(1.4 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	This work

plex with aminoacids, coordinated through  $\text{COO}^-$  group. The reactions for  $\alpha\text{H}$  proceed similarly, but at lower rate constants. The rate constants of all above mentioned reactions are shown in Table 2.

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