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Photochemistry of $\text{Pt}(\text{SCN})_6^{2-}$ complex in aqueous solutions

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The UV irradiation of the $\text{Pt}(\text{SCN})_6^{2-}$ complex in aqueous solutions results in its photoaquation by a heterolytic metal-to-ligand bond cleavage mechanism.

The photochemical activity of platinum complexes is well known.¹ The photochemistry of the halide complexes of platinum group metals is of considerable current interest in the context of photocatalysis and the photodynamic therapy (PDT) of cancer.

A fundamental problem in photocatalysis is to shift the absorption spectrum of titanium dioxide to the visible spectral region. The photochemical modification of a TiO_2 surface with platinum is used to solve this problem. In particular, PtCl_4 and PtCl_6^{2-} complexes were utilized for this modification.^{2–4} The use of Pt complexes in PDT^{5,6} is a prospective way to combine the cytotoxicity of platinum and the advantages of photodynamic therapy (selectivity and low toxicity).

For the successful application of Pt complexes, it is necessary to know the detailed mechanisms of photochemical reactions in solutions containing the simplest systems such as the halide and pseudohalide complexes of Pt^{IV} .

Here, we consider primary processes in the photochemistry of a pseudohalide Pt^{IV} hexathiocyanate complex, $\text{Pt}(\text{SCN})_6^{2-}$, in aqueous solutions under conditions of both stationary and nanosecond laser flash photolysis. In the published study⁷ on the photochemistry of $\text{Pt}(\text{SCN})_6^{2-}$ in acidic water and acetonitrile mixtures (pH 1) it was found that photosolvation was the only process with the participation of $\text{Pt}(\text{SCN})_6^{2-}$ in these solvents. However, the results of quantitative measurements⁷ (in particular, the conclusion that the quantum yield of photoaquation increases with the wavelength of excitation light) are doubtful.

It was interesting to compare the mechanisms of photochemical reactions for $\text{Pt}(\text{SCN})_6^{2-}$ and the hexahalide complexes of Pt^{IV} . In particular, the photoaquation of PtBr_6^{2-} occurs *via* the heterolytic cleavage of a metal–ligand bond.⁸ In this case, the platinum cation remains tetravalent in the course of the reaction, and the total reaction time is as small as several tens of picoseconds.^{8(d),(e)} However, in the case of the PtCl_6^{2-} complex, photoaquation redox processes are sufficient.⁹ Several Pt^{III} intermediates were detected in the course of PtCl_6^{2-} photolysis.^{9(e),(f)} The total reaction time exceeds one millisecond, and the chain process of photoaquation becomes possible under certain conditions.^{8(a),(c),(f)}

The complex salt $\text{K}_2[\text{Pt}(\text{SCN})_6]$ synthesized in accordance with a published procedure¹⁰ was used as a source of $\text{Pt}(\text{SCN})_6^{2-}$ complex anions. The electronic absorption spectrum of the complex is consistent with that reported previously.^{7,11} As a source of free SCN^- anions, chemically pure sodium thiocyanate was used

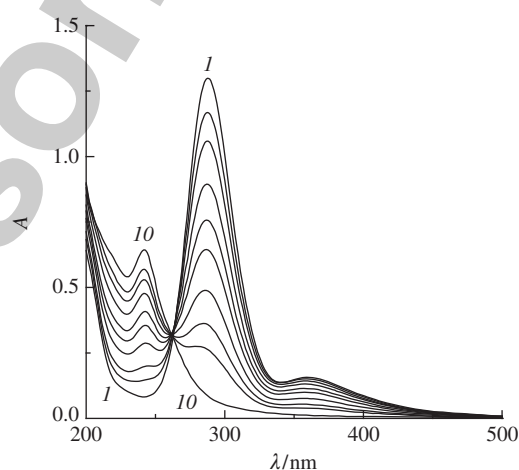


Figure 1 Changes in the UV spectra caused by the stationary photolysis (313 nm) of $\text{Pt}(\text{SCN})_6^{2-}$ in aqueous solution. 1 cm cell, initial concentration of $\text{K}_2[\text{Pt}(\text{SCN})_6]$, $2.6 \times 10^{-5} \text{ mol dm}^{-3}$. Curves 1–10 correspond to irradiation for 0, 20, 40, 60, 80, 100, 120, 140, 160 and 220 s, respectively.

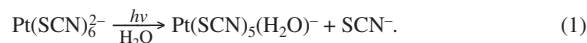
without additional purification. The test solutions were prepared using deionized water.

The absorption spectrum of $\text{Pt}(\text{SCN})_6^{2-}$ in aqueous solutions (curve 1 in Figure 1)[†] contains two absorption bands in the near UV region. The molar absorption coefficients measured at 288 and 360 nm were 50000 ± 1000 and $6300 \pm 200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. According to published data,¹¹ these maxima correspond to ligand-to-metal charge transfer bands (${}^1\text{A}_{1g} \rightarrow \text{a}^1\text{T}_{2u}$ and ${}^1\text{A}_{1g} \rightarrow \text{a}, \text{b}^1\text{T}_{2u}$).

The stationary photolysis of $\text{Pt}(\text{SCN})_6^{2-}$ was performed with excitation at 313 and 365 nm. A new absorption band at 243 nm appeared in the UV absorption spectrum after the photolysis (Figure 1), and an isosbestic point at 270 nm was conserved to

[†] The electronic absorption spectra were recorded using Agilent 8453 (Agilent Technologies) and CARY 50 (Varian) spectrophotometers. Stationary photolysis was performed by means of a high-pressure mercury lamp (DRSh-500) with a set of glass filters. For the calculation of quantum yields, light intensity was measured directly by means of a SOLO 2 power and energy meter (Gentec EO). Laser flash photolysis was performed as described in detail elsewhere.¹² The third harmonic of a YAG laser (355 nm) was used for excitation; the overall time resolution was about 50 ns.

the very deep stage of the photochemical process indicating that the consumption of the substrate was equal to the formation of the product. The initial complex was almost completely converted into the product, which was not involved in either thermal or photochemical reactions. Based on reported data⁷ and by analogy with the photochemistry of the hexahalide complexes of Pt^{IV},^{13,14} we can conclude that the observed one-step reaction is the photoaquation of the initial complex



The conservation of the isobestic point to the very deep stage of the process was used to determine the quantum yield of reaction (1). For curve 10 in Figure 1 the absorption at 288 nm [the absorption band maximum of $\text{Pt}(\text{SCN})_6^{2-}$] is less than 6% of the initial absorption (curve 1). It allows one to calculate the quantum yield (referred to both the consumption of the substrate and to the formation of the product) in assumption that the $\text{Pt}(\text{SCN})_5(\text{H}_2\text{O})^-$ complex does not absorb at 288 nm. The quantum yields for excitation at 313 and 365 nm are 0.28 ± 0.04 and 0.20 ± 0.04 , respectively.

In the experiments on the laser flash photolysis of aqueous $\text{Pt}(\text{SCN})_6^{2-}$ solutions only instant changes in the initial complex absorption bands were observed [Figure 2(a)]. The spectrum of these changes [Figure 2(b)] corresponds to the difference in the absorption spectra of the $\text{Pt}(\text{SCN})_5(\text{H}_2\text{O})^-$ and $\text{Pt}(\text{SCN})_6^{2-}$ complexes taken from the stationary experiment (Figure 1). Therefore, the characteristic time of photoaquation is less than the resolution of the experimental setup (50 ns). No intermediate absorption, which could be assigned to Pt^{III} species (like those observed in the case of PtCl_6^{2-} photolysis in aqueous solutions^{9(e),(f)}), was formed. Based on both stationary and laser flash photolysis data, we can conclude that the photoaquation of $\text{Pt}(\text{SCN})_6^{2-}$ occurs *via* the mechanism of the heterolytic cleavage of a metal–ligand bond, like in the case of PtBr_6^{2-} complex.⁸

On the laser flash photolysis of $\text{Pt}(\text{SCN})_6^{2-}$ in water with the addition of high concentrations of free SCN^- anions ($>0.5 \text{ mol dm}^{-3}$), the formation and decay of intermediate absorption were recorded.

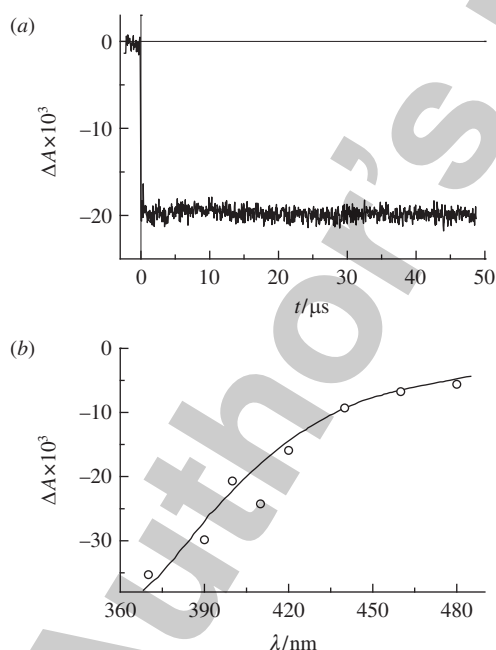


Figure 2 (a) Kinetic curve at 420 nm and (b) transient absorption spectrum recorded immediately after the laser excitation (355 nm) of $\text{K}_2[\text{Pt}(\text{SCN})_6]$ ($9.0 \times 10^{-5} \text{ mol dm}^{-3}$, 1 cm cell) in air-saturated H_2O (dots). Full line is the difference between $\text{Pt}(\text{SCN})_5(\text{H}_2\text{O})^-$ and $\text{Pt}(\text{SCN})_6^{2-}$ spectra (matched at 440 nm).

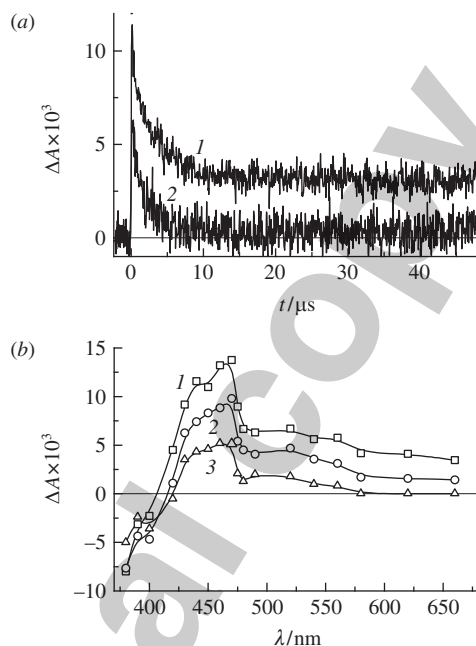


Figure 3 (a) Kinetic curves at (1) 475 and (2) 620 nm and (b) transient absorption spectra recorded (1) 0.4, (2) 2 and (3) 48 μs after the laser excitation (355 nm) of $\text{K}_2[\text{Pt}(\text{SCN})_6]$ ($9.1 \times 10^{-5} \text{ mol dm}^{-3}$, 1 cm cell) in air-saturated H_2O + 1 M NaSCN.

The occurrence of the $(\text{SCN})_2^-$ pseudodihalide radical anion was expected, similar to Br_2^- formation in the case of PtBr_6^{2-} photolysis in the presence of free Br^- anions.¹⁵ The typical kinetic curves and intermediate absorption spectra are shown in Figure 3. The intermediate absorption possesses the following properties. (1) The negative value of differential absorption at $\lambda < 410 \text{ nm}$ [Figure 3(b)] corresponds to a decrease in the concentration of the initial $\text{Pt}(\text{SCN})_6^{2-}$ complex after a laser pulse. (2) The maximum of the intermediate absorption spectrum [curve 1 in Figure 3(b)] lies at 470 nm, which corresponds to the maximum of $(\text{SCN})_2^-$ visible absorption band known from pulse radiolysis experiments.¹⁶ (3) After the termination of the processes in a microsecond time scale, the residual absorption remains at $\lambda < 580 \text{ nm}$ (Figure 3). Stationary photolysis of $\text{Pt}(\text{SCN})_6^{2-}$ in the presence of free SCN^- anions does not result in the formation of products absorbing in the visible region. Therefore, a slow reaction (with a characteristic

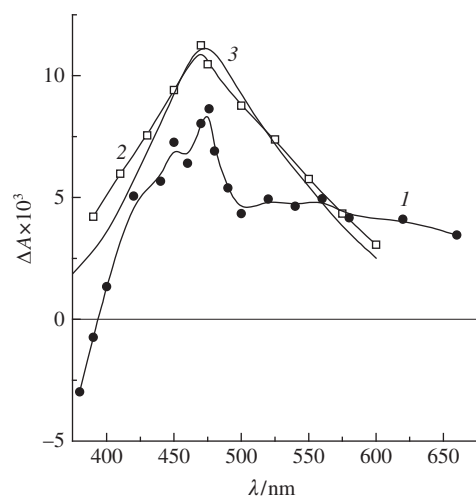
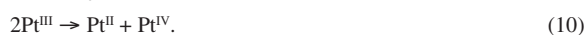
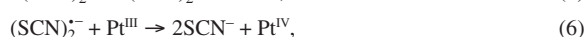
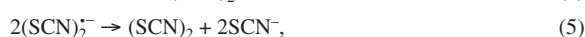


Figure 4 (1) Difference in the intermediate absorption spectra recorded 0.4 and 48 μs after the laser excitation (355 nm) of $\text{K}_2[\text{Pt}(\text{SCN})_6]$ ($9.1 \times 10^{-5} \text{ mol dm}^{-3}$, 1 cm cell) in air-saturated H_2O + 1 M NaSCN (treatment of the data from Figure 3); (2) intermediate absorption spectrum recorded 0.4 μs after the laser excitation (355 nm) of 4 M aqueous NaSCN solution; (3) normalized $(\text{SCN})_2^-$ spectrum taken from ref. 17.

time of a millisecond or more) should occur. (4) The intermediate absorption spectrum does not completely coincide with the spectrum of the $(\text{SCN})_2^{\cdot-}$ radical anion (Figure 4). Curve 1 in Figure 4 is a difference between intermediate absorption spectra (1) and (3) in Figure 3(b). Curve 2 is the intermediate absorption spectrum recorded in the experiment on the laser flash photolysis of a 4 M aqueous solution of NaSCN (note that the intermediate is formed in a two-quantum process), and curve 3 is the spectrum of $(\text{SCN})_2^{\cdot-}$.¹⁷ While the spectrum of the NaSCN photolysis product completely coincides with that of $(\text{SCN})_2^{\cdot-}$, the intermediate absorption spectrum obtained by $\text{Pt}(\text{SCN})_6^{2-}$ photolysis seems a combination of the spectra of $(\text{SCN})_2^{\cdot-}$ and one more species. It is likely that the intermediate responsible for the absorption in the region of 520–700 nm is a Pt^{III} complex. Its possible structure is $\text{Pt}(\text{SCN})_6^{3-}$, but a fewer number of coordinated SCN^- anions could not be ruled out.

The tentative mechanism of $(\text{SCN})_2^{\cdot-}$ formation and decay is described by the following reaction scheme:



The primary photochemical process is electron transfer from a free thiocyanate anion to the light-excited complex [(reaction (3))]. The characteristic times of reactions (3) and (4) are obviously less than the resolution of the experimental setup. Both the $(\text{SCN})_2^{\cdot-}$ radical anion and the $\text{Pt}(\text{SCN})_6^{2-}$ complex could be responsible for the initial intermediate absorption [curve 1 in Figure 3(b)]. $(\text{SCN})_2^{\cdot-}$ decays in disproportionation reaction (5). In addition, the oxidation of a Pt^{III} intermediate by $(\text{SCN})_2^{\cdot-}$ [reaction (6)] is possible. Reaction (7) describes the possible pseudo-first-order processes of $(\text{SCN})_2^{\cdot-}$ disappearance, *i.e.*, reactions with the initial $\text{Pt}(\text{SCN})_6^{2-}$ complex and, probably, impurities in the NaSCN salt. Equilibrium between thiocyanogen and trithiocyanate (8) was thoroughly considered.¹⁸ Reaction (9) is written by analogy with published data,¹⁹ in which the long-living Pt^{III} intermediate formed by the photolysis of PtCl_6^{2-} was assigned as the PtCl_4 complex. The $\text{Pt}(\text{SCN})_4$ complex could be responsible for the residual absorption observed in the laser flash photolysis experiments [curve 3 in Figure 3(b)]. Disproportionation of Pt^{III} complexes (10) results in the formation of final Pt^{II} products.

Thus, photoaquation is the only process caused by $\text{Pt}(\text{SCN})_6^{2-}$ irradiation in the near UV region. The mechanism of photoaquation is similar to that for PtBr_6^{2-} rather than the PtCl_6^{2-} complex. In the presence of free thiocyanate anions in high

concentrations, electron transfer from an outer-sphere SCN^- anion to the light-excited complex becomes sufficient.

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