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Ultrafast photochemical processes in the complex *trans,trans,trans*-[$Pt^{IV}(py)_2(N_3)_2(OH)_2$]

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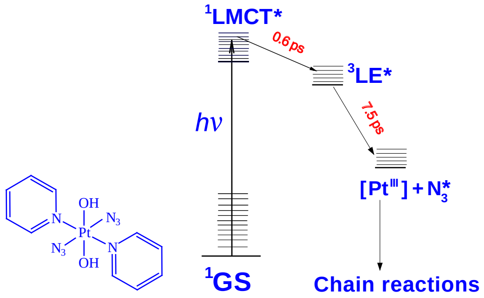
Using ultrafast transient absorption spectroscopy, primary photophysical processes in aqueous and acetonitrile solutions of the *trans,trans,trans*-[$Pt^{IV}(N_3)_2(py)_2(OH)_2$] complex, which is interesting as a potential light-activated anticancer drug, were investigated. A mechanism for early photoprocesses has been proposed, including ultrafast intersystem crossing and reductive dissociation.



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Chemotherapy with cisplatin and its analogues is one of the most important strategies for the treatment of cancer.[1–3] These complexes act as prodrugs. Hydrolytic reactions lead to the formation of reactive mono- and diaqua complexes of Pt^{II}, which bind to various cellular components such as DNA and proteins.[4] However, the use of Pt^{II} complexes is often accompanied by severe side effects and the development of resistance, which leads to disease progression.[3] Another drawback of chemotherapy with these complexes is the lack of selectivity.

An alternative strategy in oncology is photodynamic therapy (PDT), which involves selective damage of target tissues using a photosensitizing drug and light.[5,6] The most popular PDT strategy is based on the use of triplet sensitizers and, consequently, on the action of singlet oxygen.[5,7] However, many tumors are hypoxic,[8] which is a fundamental limitation of oxygen-based PDT strategy. This drawback of PDT has stimulated the development of photochemotherapy, or photoactivated chemotherapy (PACT), as a promising cancer treatment method based on phototransformations, usually of platinum metals complexes.[9–15] In the PACT method, the biologically active compound is protected from interaction with the cellular environment by a light-cleavable protecting group, which is removed by light irradiation. The first drug based on this principle of action, a monometallic Ru^{II} complex known as TLD1433,[16] is currently in phase II clinical trials.[17]

In the case of platinum, photoactive Pt^{IV} complexes, which produce cytotoxic Pt^{II} species upon irradiation, are of interest.[18–22] The initial photochemical process is inner-sphere electron transfer in a light-excited complex, which is characteristic of Pt^{IV}.[23–28] Diazido complexes of Pt^{IV} are among the most promising PACT prodrugs.[9,15,29,30] Complex *trans,trans,trans*-[$Pt^{IV}(py)_2(N_3)_2(OH)_2$] **1** (Figure 1, inset), synthesized using a known procedure,[20] demonstrated light-induced cytotoxicity comparable to the thermal cytotoxicity of cisplatin.[21,31] The light-induced cytotoxicity of complex **1** occurs through three mechanisms: (i) platination of DNA by reduced Pt^{II} species, similar to the effect of cisplatin;[21,32] (ii) damage of tissue cells by $N_3^{\bullet}$ radicals released by light-excited complexes;[33] and (iii) the effect of photolysis products on peptides.[34,35]

The mechanism of photolysis of complex **1** has been studied previously.[33,36,37] In the work of Vernooij *et al.*,[36] the complexes *trans*-[$Pt^{II}(N_3)(py)_2(OH/H_2O)$] and *trans*-[$Pt^{II}(py)_2(OH/H_2O)_2$] (ligands can be both OH^- and H_2O) were identified as the intermediate and final products of two-electron photoreduction, respectively. The authors of that work put forward the idea that both $N_3^{\bullet}$ and $OH^{\bullet}$ radicals can be released during photolysis. While the azidyl radical was captured by Butler *et al.*[33] by the spin trap method, the formation of hydroxyl radicals was never directly observed. We recently[37] applied stationary photolysis and nanosecond laser flash photolysis to study the photochemistry of complex **1**. It was found that the first stage of photolysis is a chain photoaquation, which occurs through a mechanism involving reactions (1)–(6):

chain initiation

$$[Pt^{IV}(py)_2(N_3)_2(OH)_2] \xrightarrow{h\nu} [Pt^{III}(py)_2(N_3)(OH)_2] + N_3^{\bullet}, \quad (1)$$

chain propagation

$$[Pt^{III}(py)_2(N_3)(OH)_2] \longrightarrow [Pt^{III}(py)_2(OH)_2]^+ + N_3^-, \quad (2)$$

$$[\mathrm{Pt^{III}(py)_2(OH)_2}]^+ + [\mathrm{Pt^{IV}(py)_2(N_3)_2(OH)_2}] \xrightarrow{\mathrm{H_2O}}$$

$$[\mathrm{Pt^{III}(py)_2(N_3)(OH)_2}] + [\mathrm{Pt^{IV}(py)_2(N_3)(OH)_2\,(H_2O)}]^+, \qquad (3)$$

chain termination

$$\mathrm{Pt^{III}} + \mathrm{Pt^{III}} \longrightarrow \mathrm{Pt^{IV}} + \mathrm{Pt^{II}}, \qquad (4)$$

$$\mathrm{Pt^{III}} + \mathrm{N_3^{\bullet}} \longrightarrow \mathrm{Pt^{IV}} + \mathrm{N_3^{-}}, \qquad (5)$$

$$\mathrm{Pt^{III}} \xrightarrow{k_{\mathrm{1app}}} \mathrm{Pt^{II}}\ \text{and/or}\ \mathrm{Pt^{IV}}. \qquad (6)$$

The early processes caused by photoexcitation of complex **1** still remain poorly understood. Vernooij *et al.*[36] used ultrafast transient absorption (TA) spectroscopy to study the photophysics of complex **1** in acetonitrile. However, the results obtained in acetonitrile should be used with caution in the case of aqueous solutions due to the possible strong solvent effect on the photochemistry of $\mathrm{Pt^{IV}}$ complexes.[38,39] In this work, we conducted experiments with complex **1** on ultrafast TA both in aqueous solutions and, for comparison with published data,[36] in acetonitrile solutions.[†]

Experiments on ultrafast kinetic spectroscopy of complex **1** were carried out with excitation at a wavelength of 320 nm. Excitation at 320 nm falls into the tail of the $\mathrm{N_3^-} \rightarrow \mathrm{Pt^{IV}}$ LMCT band (Figure 1).[37] Time-dependent intermediate absorption spectra were recorded in the range 400–750 nm. Time profiles of intermediate absorption are shown in Figure 2(*a*). Examples of kinetic curves at selected detection wavelengths are shown in Figure 2(*b*).

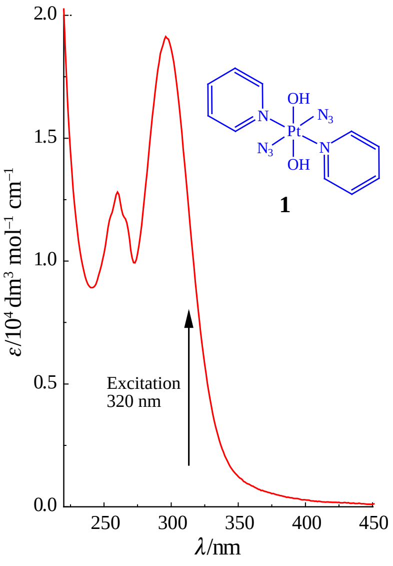

Figure 1 Structure of the $[\mathrm{Pt^{IV}(py)_2(N_3)_2(OH)_2}]$ complex and its UV spectrum in aqueous solutions. The arrow indicates the excitation wavelength in ultrafast TA experiments.

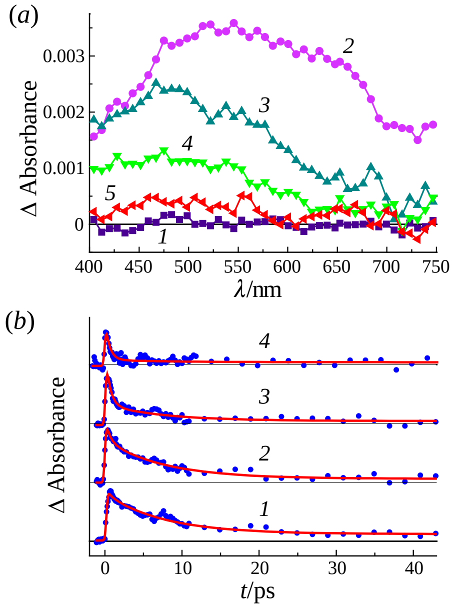

Figure 2 Results of ultrafast TA spectroscopy experiments (excitation at 320 nm) with complex **1** in aqueous solutions (1.0 mM, 1 mm cell): (*a*) time-dependent intermediate absorption spectra at (*1*) 1 ps before and (*2*) 0.4, (*3*) 3, (*4*) 10 and (*5*) 35 ps after excitation; (*b*) experimental kinetic curves (dots) at detection wavelengths of (*1*) 460, (*2*) 538, (*3*) 631 and (*4*) 715 nm, as well as curves obtained by global fitting with a 3-exponental function (red lines).

Kinetic curves obtained from ultrafast pump-probe spectroscopy experiments at 320 nm excitation were globally fitted using a 3-exponential function:

$$\Delta A(\lambda, t) = A_1(\lambda)\exp\left(-\frac{t}{\tau_1}\right) + A_2(\lambda)\exp\left(-\frac{t}{\tau_2}\right) + A_3(\lambda)\exp\left(-\frac{t}{\tau_3}\right). \quad (7)$$

The best fit curves are shown as red lines in Figure 2(*b*). The extracted characteristic lifetimes were $\tau_1 = 0.62 \pm 0.22$, $\tau_2 = 7.5 \pm 1.4$ and $\tau_3 \geqslant 10^4$ ps, respectively. In fact, the longest characteristic lifetime is equal to infinity on the experimental time scale. The amplitude spectra $A_i(\lambda)$ are shown in Figure S1 (see Online Supplementary Materials).

When kinetic curves are fitted using equation (7), the decay of TA is usually proposed as the sequence **A** → **B** → **C**. Here **C** can include both the ground state of the initial complex and the photolysis products. Species-associated difference spectra (SADS) of individual components were calculated using equations (8)–(10).[45] If the characteristic lifetimes are sufficiently different (as in our case), SADS can be represented as the sum of the corresponding amplitudes $A_i(\lambda)$:

$$S_{\mathrm{A}}(\lambda) = A_1(\lambda) + A_2(\lambda) + A_3(\lambda), \qquad (8)$$

$$S_{\mathrm{B}}(\lambda) = A_2(\lambda)\frac{\tau_2 - \tau_1}{\tau_2} + A_3(\lambda), \qquad (9)$$

$$S_{\mathrm{C}}(\lambda) = A_3(\lambda). \qquad (10)$$

SADS obtained from equations (8)–(10) are shown in Figure 3(*a*). Immediately after excitation of complex **1** at 320 nm, the TA spectrum appears as a broad band with a flat maximum in the region 475–670 nm [Figure 3(*a*), curve *1*]. The initial absorption band transforms into another band with a maximum around 490 nm [Figure 3(*a*), curve *2*] with a characteristic lifetime of 0.6 ps. The second intermediate decays with a characteristic lifetime of 7.5 ps. The final SADS [Figure 3(*a*), curve *3*; Figure 3(*b*), curve *1*] obtained in ultrafast TA spectroscopy experiments should be compared with the spectrum of the initial intermediate recorded in nanosecond laser flash photolysis experiments [Figure 3(*b*), curve *2*]. The shapes of these two SADS are similar. This means that species **C** in the **A** → **B** → **C** sequence used to analyze ultrafast TA spectroscopy

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[†] Complex **1** was synthesized and characterized as previously described.[20,37] Solutions were prepared in deionized water and spectrally pure grade acetonitrile (Cryochrom, Russia). UV absorption spectra were recorded using a Varian Cary 50 spectrophotometer. Laser flash photolysis experiments were carried out using excitation by the 4th harmonic of an Nd:YAG laser (Lotis TII, Belarus, 355 nm, pulse duration 5 ns, pulse energy up to 10 mJ). The setup has been described in detail in published papers.[40,41] Ultrafast TA spectroscopy experiments were carried out using a setup described in detail in previous works.[42,43] For more details, see Online Supplementary Materials. The experimental kinetic curves were globally fitted to a single set of kinetic parameters using approach described earlier.[44]

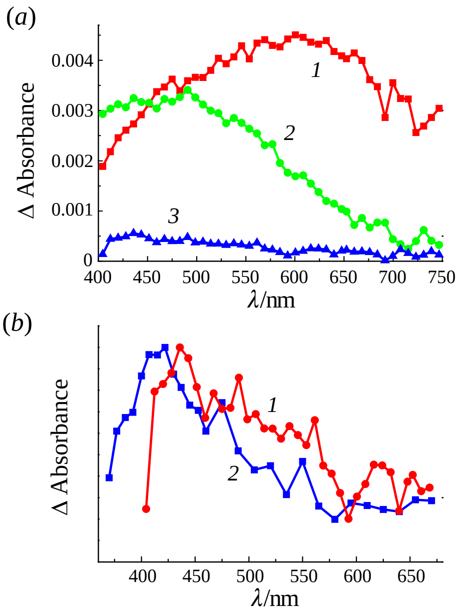

Figure 3 Results of the ultrafast kinetic spectroscopy experiment (excitation at 320 nm) with complex **1** in aqueous solutions (1.0 mM, 1 mm cell): (*a*) SADS of (*1*) species **A**, (*2*) species **B** and (*3*) species **C**, obtained by global fitting with equations (8)–(10); (*b*) comparison of the intermediate absorption spectra (*1*) of species **C** found in the ultrafast TA spectroscopy experiment and (*2*) of the initial intermediate detected in a nanosecond laser flash photolysis experiment with excitation at 355 nm (spectra normalized to maximum absorption).

data is indeed the same as the initial intermediate observed in the nanosecond time domain.

To compare the results obtained for complex **1** in aqueous solutions with those obtained by Vernooij *et al.*,[36] we performed ultrafast TA experiments in acetonitrile. The excitation wavelengths were similar: 310 nm in their work and 320 nm in our case (see Online Supplementary Materials). It was found that the dynamics of intermediate absorption in acetonitrile are similar to that observed in aqueous solutions. The experimental kinetic curves (Figure S2) were globally fitted by the 3-exponential function [equation (7)] with characteristic lifetimes $\tau_1 = 0.7 \pm 0.3$, $\tau_2 = 6.9 \pm 1.6$ and $\tau_3 = 10000$ ps (infinity). The SADS profiles corresponding to the absorption decay of successive intermediates **A** → **B** → **C** (Figure S3) are very similar to those obtained in aqueous solutions. The lifetimes are close to those obtained by Vernooij *et al.*[36] These authors, however, also reported a shorter lifetime of 195 ± 40 fs, which was not resolved in our experiments. It should be noted that the raw experimental data in their work[36] are presented in the form of color maps, which does not allow assessing their quality.

Our interpretation of the ultrafast TA data in both aqueous and acetonitrile solutions is as follows. The initial SADS of species **A** corresponds to the Franck–Condon (FC) state spectrum. The first observed process with a characteristic time of 0.62 ± 0.22 ps corresponds to intersystem crossing (ISC). As follows from a comparison of the spectra in Figure 3(*b*), the second process with a characteristic time of 7.5 ± 1.4 ps is a reductive dissociation, consisting in the transfer of an electron from the azide ligand to Pt^{IV} and the release of the azidyl radical into the bulk of the solvent. The scheme of processes corresponding to the described model is represented by reactions (11)–(13):

$$[Pt^{IV}(py)_2(N_3)_2(OH)_2] \xrightarrow{h\nu} {}^1[Pt^{IV}(py)_2(N_3)_2(OH)_2]^*, \qquad (11)$$

$${}^1[Pt^{IV}(py)_2(N_3)_2(OH)_2]^* \xrightarrow{\tau_1} {}^3[Pt^{IV}(py)_2(N_3)_2(OH)_2]^*, \qquad (12)$$

$${}^3[Pt^{IV}(py)_2(N_3)_2(OH)_2]^* \xrightarrow{\tau_2} [Pt^{III}(py)_2(N_3)(OH)_2] + N_3^{\bullet}. \qquad (13)$$

The proposed ISC characteristic time (0.6 ps) is quite typical for ISC in transition metal complexes, where it could vary from tens of femtoseconds to one nanosecond.[46] The second characteristic lifetime (7.5 ps), corresponding to the release of the azidyl radical, is also reliable, since it is comparable to the time of diffusion divergence of the complex $[Pt^{III}(py)_2(N_3)(OH)_2]$ and $N_3^{\bullet}$ over a distance of *ca.* 1 Å, amounting to *ca.* 10 ps. Note that the experimental data presented do not contain evidence of the presence of relaxation processes such as vibratiional cooling and solvent relaxation. This is explained by the proximity of the characteristic lifetimes of different processes, which can manifest themselves as a single convoluted process.[47] In our case, the vibrational cooling of ${}^3[Pt^{IV}(py)_2(N_3)_2(OH)_2]^*$ and its reductive dissociation seem not to be resolved.

An alternative hypothesis describing the primary photophysical processes is reductive dissociation from a singlet excited state, represented by reactions (11a)–(13a). In this case, the primary process [reaction (11a)] is considered as a radial electron transfer from the azide ligand to Pt^{IV} with the formation of the Pt^{III} intermediate ${}^1[Pt^{III}(py)_2(N_3^-)(N_3^{\bullet})(OH)_2]^*$, the differential spectrum of which corresponds to curve *1* in Figure 3(*a*). The first observed kinetic process [reaction (12a)] is the formation of the radical complex (RC) ${}^1[Pt^{III}(py)_2(N_3^-)(OH)_2\cdots(N_3^{\bullet})]_{cage}$, consisting of two species, namely a pentacoordinated Pt^{III} intermediate and azidyl radical, separated by a few nanometers and stabilized in a solvent cage. Its differential spectrum corresponds to curve *2* in Figure 3(*a*). The second observed process [reaction (13a)] is the dissociation of the RC.

$$[Pt^{IV}(py)_2(N_3)_2(OH)_2] \xrightarrow{h\nu} {}^1[Pt^{III}(py)_2(N_3^-)(N_3^{\bullet})(OH)_2]^* \qquad (11a)$$

$${}^1[Pt^{III}(py)_2(N_3^-)(N_3^{\bullet})(OH)_2]^* \xrightarrow{\tau_1} {}^1[Pt^{III}(py)_2(N_3^-)(OH)_2\cdots(N_3^{\bullet})]_{cage} \qquad (12a)$$

$${}^1[Pt^{III}(py)_2(N_3^-)(OH)_2\cdots(N_3^{\bullet})]_{cage} \xrightarrow{\tau_2} [Pt^{III}(py)_2(N_3)(OH)_2] + N_3^{\bullet} \qquad (13a)$$

The formation of RCs has been repeatedly proposed in the photochemistry of Pt^{IV} complexes.[38,39] However, in those cases the RC was always formed by an ion and a radical. In our case, both partners are electrically neutral. We doubt that the weak interaction between two electrically neutral species can explain the large difference in the spectra of the RC and completely separated partners [Figure 3(*a*), curves *2* and *3*]. That is why we believe that the mechanism involving reactions (11)–(13) is more reliable than the mechanism based on reactions (11a)–(13a).

In summary, in this work, we conducted experiments on ultrafast TA spectroscopy of complex **1** in aqueous and acetonitrile solutions. The results are in satisfactory agreement with previously published data on nanosecond laser flash photolysis[37] and data reported[36] for acetonitrile solutions. The proposed interpretation of the intermediates is tentative and requires further verification using additional ultrafast experimental techniques, such as fluorescence upconversion[46] and ultrafast TA spectroscopy with IR registration,[48] as well as quantum chemical calculations of the electronic absorption spectra of the proposed intermediates.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.06.006.

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