

Primary Photochemical Processes For Pt(IV) Diiodine and Diazido Complexes Prospective As Prodrugs In PDT Processes

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Synthesis and investigation of photochemical properties of platinum (IV) metal complexes prospective as prodrugs in PDT processes is an attractive task in modern chemistry. The important condition of application of these complexes is a photoreduction of Pt(IV) to Pt(II). Among of the prospective candidates are the diazido and diiodine Pt(IV) complexes containing ethylenediamine fragment^[1,2]. It was shown that products of these complexes photolysis can platinate DNA analogously to well-known Cisplatin.

In this work four mixed-ligand complexes of Pt(IV) (Fig. 1) - *cis, trans*-[Pt(en)(I)₂(OH)₂] (**1**), *cis, trans*-[Pt(en)(I)₂(CH₃COO)₂] (**2**), *cis, trans, cis*-[Pt(N₃)₂(OH)₂(NH₃)₂] (**3**) and *trans, trans, trans*-[Pt(N₃)₂(OH)₂(NH₃)₂] (**4**) prospective as prodrugs in PDT processes were synthesized and investigated by ultrafast kinetic spectroscopy method (Ti:Sapphire laser, λ_{ex} = 320 and 400 nm, E_{pulse} ≈ 2.5 μJ/pulse, τ_{pulse} ≈ 100 fs), laser flash photolysis (Nd:YAG laser, λ_{ex} = 266 and 355 nm, E_{pulse} is up to 10 mJ/pulse, τ_{pulse} ≈ 5 ns), stationary photolysis (XeBr exilamp, λ_{ex} = 282 nm) and NMR spectroscopy.

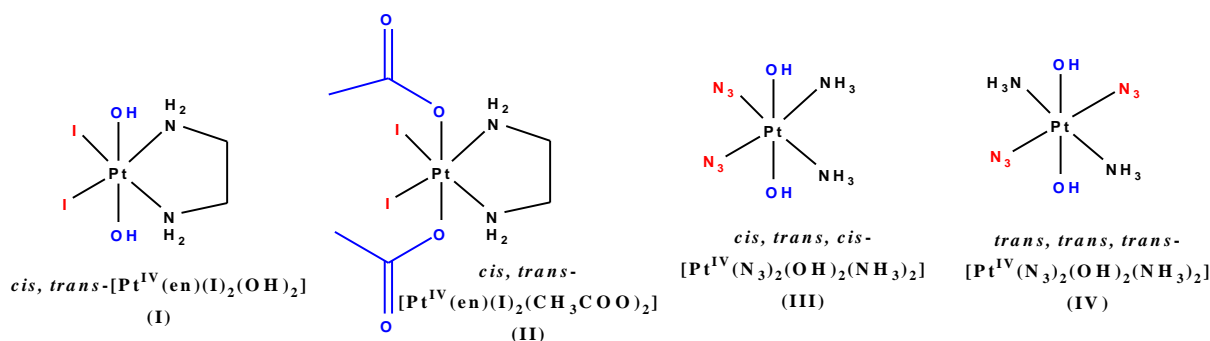


Figure 1. Pt(IV) Diiodine and Diazido complexes under study

For diiodine Pt(IV) complexes photolysis leads mainly to a multistage photoaquation in agreement with previous investigations. On the first stage, *mer*-[Pt^{IV}(en)(I)(OH)₃] complex is formed for (1) with the quantum yield of 0.06. Further ligand exchange and photoreduction

occur with much lower quantum yield. The characteristic lifetime of ligand exchange is about 90 ps for both diiodine complexes (Fig. 1). The spectrum of the key intermediate (KI) was recorded in the picosecond time domain. Depending on the attribution of the KI (the triplet ligand field state or the ion pair formed by a pentacoordinated Pt(IV) complex and an iodide anion) two tentative schemes of the primary photophysical and photochemical processes are proposed. The postulated intermediates should be verified against high-level quantum chemical calculations of their electronic absorption spectra.

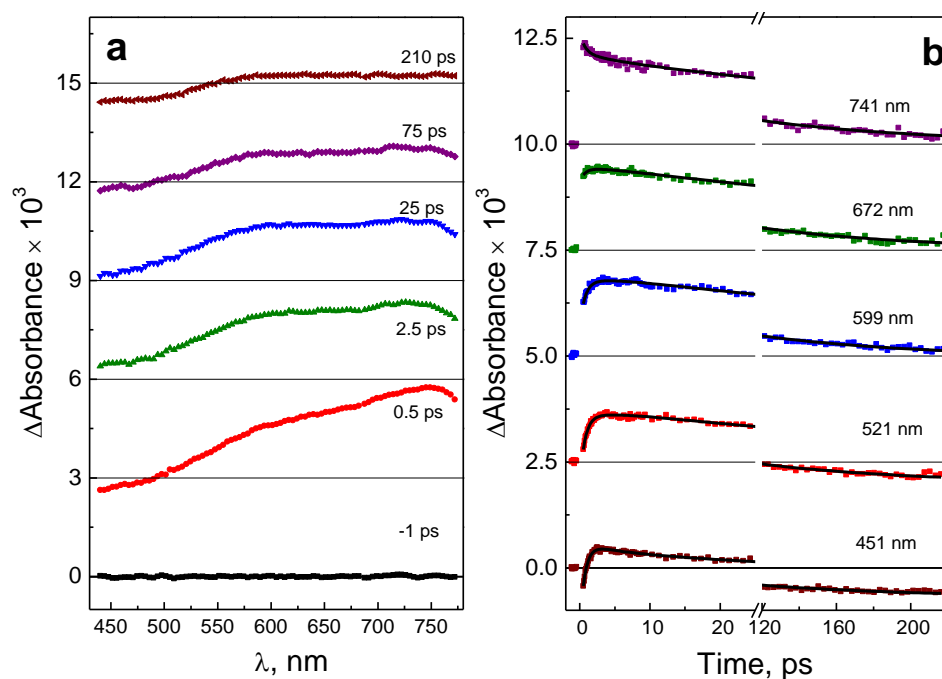


Figure 2. Results of ultrafast kinetic spectroscopy experiments (400 nm) with complex **1** (7.9×10^{-5} M) pH 6.0, 1 mm cell) in aqueous solution. **a** – intermediate absorption spectra at different time delay between exciting and probing pulses; **b** – experimental kinetic curves (dots) and the best three-exponential fits (solid lines)

For diazido Pt(IV) complexes the first stage of photolysis was found to be photoexchange of an azide anion to a water molecule with a quantum yield of about 0.2 for both complexes. The chain mechanism of photoaquation was proposed in consistent with the concentration dependence of quantum yields obtained in the stationary experiments and with the observation of two successive Pt(III) intermediates in the laser flash photolysis experiments. Details of mechanism (including direct observation of azide radicals) are the subjects of further study. Deep photolysis leads to complete photoreduction of Pt(IV) to Pt(II) which is important for application of these complexes in PDT processes.

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