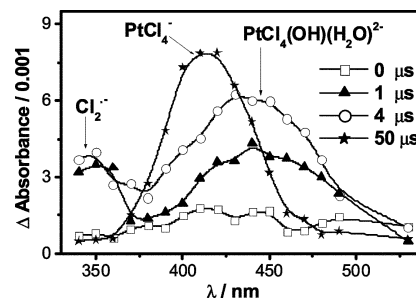


### Intermediates formed by laser flash photolysis of $[\text{PtCl}_6]^{2-}$ in aqueous solutions

Irene V. Znakovskaya, Yulia A. Sosedova,  
Evgeni M. Glebov, Vjacheslav P. Grivin and  
Victor F. Plyusnin

Laser flash photolysis (308 nm) of the  $\text{PtCl}_6^{2-}$  complex in aqueous solutions results in three types of intermediates,  $\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})^{2-}$  and  $\text{PtCl}_4^-$  complexes and  $\text{Cl}_2^{\cdot-}$  radical anions.



Please check the proof of your paper carefully. **Your proof will not be read in detail by staff after you have returned it to us.** It is your responsibility to ensure that the proof has been read carefully.

Translation errors between word-processor files and typesetting systems can occur so the whole proof needs to be read even if an electronic file has been supplied. Please pay particular attention to: tabulated material (this may have been rekeyed); equations; numerical data; figures and graphics; and references. If you have not already indicated the corresponding author(s) please mark their name(s) with an asterisk. Please fax or e-mail your corrections to us. When returning the proof by fax please also include a list detailing the corrections to be made. If responding by e-mail please send only a list of corrections – do not make any changes directly to the pdf file.

**This proof reflects the content and general style of the paper without the stylistic complexity of the final printed page; however, the only differences should be minor layout changes such as different line breaks, tables being double column instead of single column and improvements in graphic placement.**

We will endeavour to publish the article electronically on the RSC web site as soon as possible after we receive your corrections. **NB: No late corrections can be made hence please ensure that only your final corrections are notified to us.**

Please return your **final** corrections, where possible within **48 hours** of receipt to:

Serials Production, The Royal Society of Chemistry,  
Tel: +44 (0)1223 432345; Fax: +44 (0)1223 432160; E-mail: proofs@rsc.org

Reprints—Electronic (PDF) reprints will be provided free of charge to the corresponding author. Enquiries about purchasing paper reprints should be addressed to: Production Operations Department (prodops@rsc.org). Costs for reprints are below:

#### Reprint costs

No of pages	Cost for 50 copies	Cost for each additional 50 copies
2–4	£180	£115
5–8	£300	£230
9–20	£600	£480
21–40	£1100	£870
>40	£1700	£1455

*Cost for including cover of journal issue:*  
£50 per 50 copies

## Q2 Intermediates formed by laser flash photolysis of $[\text{PtCl}_6]^{2-}$ in aqueous solutions

Irene V. Znakovskaya,<sup>a</sup> Yulia A. Sosedova,<sup>a</sup> Evgeni M. Glebov,<sup>\*b</sup> Vjacheslav P. Grivin<sup>b</sup> and Victor F. Plyusnin<sup>b</sup>

<sup>a</sup> Department of Natural Sciences, Novosibirsk State University, 630090, Novosibirsk, Russian Federation

<sup>b</sup> Institute of Chemical Kinetics and Combustion, 630090, Novosibirsk, Russian Federation.  
E-mail: glebov@ns.kinetics.nsc.ru

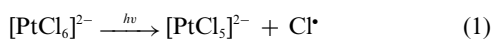
Received 6th July 2005, Accepted 14th September 2005  
First published as an Advance Article on the web ??????

The stationary photolysis of  $[\text{PtCl}_6]^{2-}$  in aqueous solutions ( $10^{-5}$ – $10^{-4}$  M) at the region of 313 nm leads to its photoaquation with a quantum yield of 0.19. Laser flash photolysis experiments (308 nm) provided evidence of the formation of Pt(III) intermediates, namely  $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{2-}$  and  $[\text{PtCl}_4]^-$ , and  $\text{Cl}_2^{\cdot-}$  radical anions. The Pt(III) complexes formed as a result of an intrasphere electron transfer from  $\text{Cl}^-$  ligands to the excited Pt(IV) ion. However, the main (~90%) photolysis channel was not accompanied by the transfer of Cl atoms to the solvent bulk. The photoaquation of  $[\text{PtCl}_6]^{2-}$  results from the back electron transfer in the secondary geminate pair,  $[\text{PtCl}_5(\text{H}_2\text{O})]^{2-}\text{--Cl}$ . The relative yield of Pt(III) intermediates, recorded after the completion of all processes in the geminate pair, was less than 10% of the number of disappearing initial  $[\text{PtCl}_6]^{2-}$  complexes.

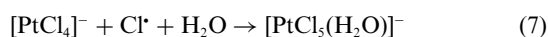
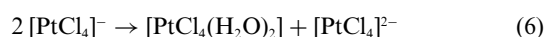
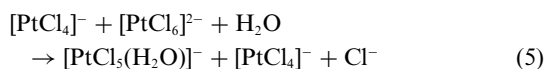
Q1

### 1 Introduction

Although the photochemistry of  $[\text{PtCl}_6]^{2-}$  in aqueous solutions has been the object of investigation for 50 years,<sup>1–7</sup> the pattern of photolysis is not clearly understood. Rich and Taube<sup>1</sup> have established that the isotopic exchange between a free  $\text{Cl}^-$  ion and an ion in the coordination sphere of Pt(IV) is catalyzed by light. The process obeys the following reaction scheme:



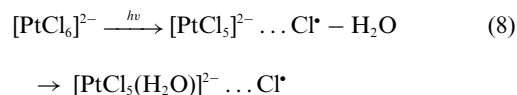
In 1, and subsequently in most papers devoted to the photochemistry of aqueous solutions of  $[\text{PtCl}_6]^{2-}$ , a homolytic cleavage of the Pt–Cl bond and the escape of a Cl atom into the bulk (eqn (1)) was considered a primary photochemical process. At the same time, the integral photoprocess for  $[\text{PtCl}_6]^{2-}$  is photoaquation, which gives rise to  $[\text{PtCl}_5(\text{H}_2\text{O})]^{2-}$ .<sup>4–6</sup> When the primary process (eqn (1)) is realized, photoaquation can follow a chain mechanism. A feasible variant of chain development is proposed in 5 and includes reactions (4)–(7).



The main argument in favor of this chain mechanism is the quantum yield of the  $[\text{PtCl}_6]^{2-}$  photoaquation, which can substantially exceed unity.<sup>5</sup> In the framework of this mechanism, the quantum yield depends on irradiation wavelength, initial concentration of the complex, light intensity, and pH of the medium.<sup>3,5</sup> An additional argument supporting this mechanism is that flash photolysis experiments with a microsecond time

resolution have demonstrated intermediates of trivalent platinum (probably,  $[\text{PtCl}_4]^-$ ).<sup>4,6</sup>

A direct (non-chain) mechanism of photoaquation can be related to the back electron transfer in the geminate pair, Pt(III) ion–Cl atom.



Wright and Laurence<sup>4</sup> have established that only *ca.* 10% of the excited  $[\text{PtCl}_6]^{2-}$  is subjected to photoreduction (the Cl atom escapes into the solvent bulk). They, however, assumed that a basic process leading to the formation of the final product ( $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ ) is a heterolytic cleavage of the Pt–Cl bond. It is worth noting that the heterolytic cleavage of the Pt–Br bond is assumed to be the only primary process in the photochemistry of  $[\text{PtBr}_6]^{2-}$ , which is similar in structure.<sup>2,8</sup>

It should be noted that the photochemistry of  $[\text{PtCl}_6]^{2-}$  in organic solvents<sup>9–15</sup> is now better understood than the photochemistry in aqueous solutions.

The goal of the present work is to use nanosecond laser flash photolysis to determine the nature of the intermediates arising from  $[\text{PtCl}_6]^{2-}$  photolysis in aqueous solutions. It is expected that both a quantitative determination of spectral and kinetic properties of unstable Pt(III) species and data on the quantum yield of the photolysis would allow one to choose between the direct and chain mechanisms of  $[\text{PtCl}_6]^{2-}$  photoaquation.

### Experimental

As a source of  $[\text{PtCl}_6]^{2-}$  ions,  $\text{Na}_2\text{PtCl}_6$  (Aldrich) was used. Solutions were prepared using either bidistilled or deionized water. The results obtained with the samples prepared from bidistilled and deionized water were identical. Initially, the pH values of the solutions were 6.5. During stationary photolysis, these decreased to 5.5–4.5 (depending on the initial concentration of the Pt complex).

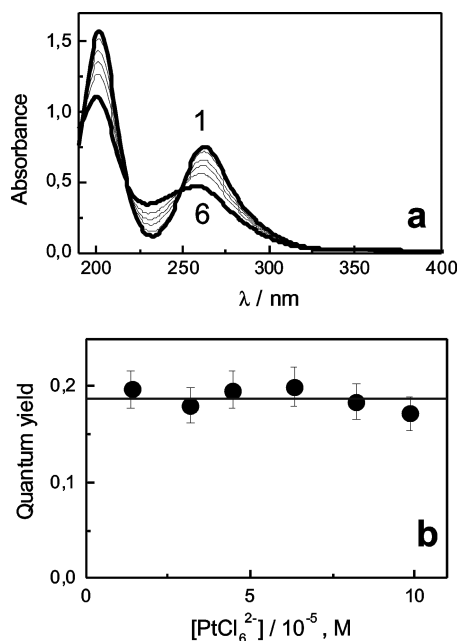
The optical absorption spectra were recorded using an HP 8354 (Hewlett Packard) spectrophotometer. The stationary photolysis was performed using an excimer laser (XeCl, 308 nm) or a high pressure mercury lamp with a set of glass filters to separate light with the necessary wavelength. The quantum yields were measured by means of a ferrioxalate actinometer.<sup>16</sup>

Laser flash photolysis experiments were performed using a setup (XeCl laser, 308 nm, 15 ns pulse duration, *ca.* 30 mJ pulse energy) described elsewhere.<sup>9</sup> Each kinetic curve was a result of 30–50 accumulations. The intensities of the laser pulses were measured by the value of anthracene T–T absorption (431 nm) in oxygen-free benzene solutions (the quantum yield of triplet state formation was taken to be 0.53, and the absorption coefficient of T–T absorption band as 42 000 M<sup>-1</sup> cm<sup>-1</sup><sup>17</sup>).

## 15 Results and discussion

### 3.1. Stationary photolysis of [PtCl<sub>6</sub>]<sup>2-</sup> (313 nm)

Changes in optical spectrum due to the stationary photolysis (313 nm) of the aqueous [PtCl<sub>6</sub>]<sup>2-</sup> solution are shown in Fig. 1a. The existence of two isosbestic points (218 and 249 nm) indicates the appearance of only one photolysis product. Adding free Cl<sup>-</sup> ions to the irradiated solution causes almost complete recovery of the initial [PtCl<sub>6</sub>]<sup>2-</sup> spectrum. This indicates that the final photolysis product is the aquated [PtCl<sub>5</sub>(H<sub>2</sub>O)]<sup>-</sup> complex, which manifests acidic properties (pK<sub>a</sub> = 3.8<sup>18</sup>). When the concentration is of the order of 10<sup>-5</sup> M, the main form existing in solution (~90%) is [PtCl<sub>5</sub>(OH)]<sup>2-</sup>.

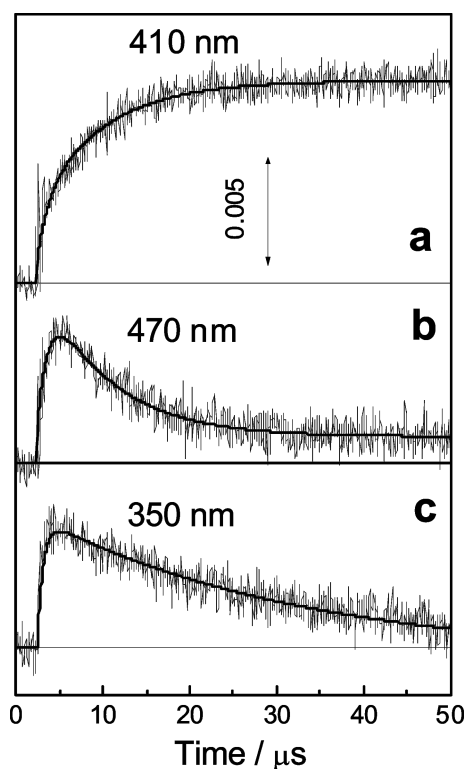


**Fig. 1** Change in UV spectrum (a) of the aqueous solution of [PtCl<sub>6</sub>]<sup>2-</sup> (3.2 × 10<sup>-5</sup> M) in a 1 cm cuvette upon stationary photolysis at 313 nm (the line of the high pressure mercury lamp with a light intensity of -1.6 × 10<sup>-6</sup> E L<sup>-1</sup>) and the dependence of the quantum yield of photolysis (b) on initial PtCl<sub>6</sub><sup>2-</sup> concentration. Curves 1–6 correspond to irradiation times of 0, 10, 30, 50, 75, and 130 s.

The quantum yield of photoaquation ( $\phi = 0.19$ ) is independent of the concentration of the initial complex over the range of 10<sup>-5</sup>–10<sup>-4</sup> M (Fig. 1b). The value of the quantum yield is close to the value of 0.15 (365 nm) obtained in ref 5 over a range of low [PtCl<sub>6</sub>]<sup>2-</sup> concentrations.

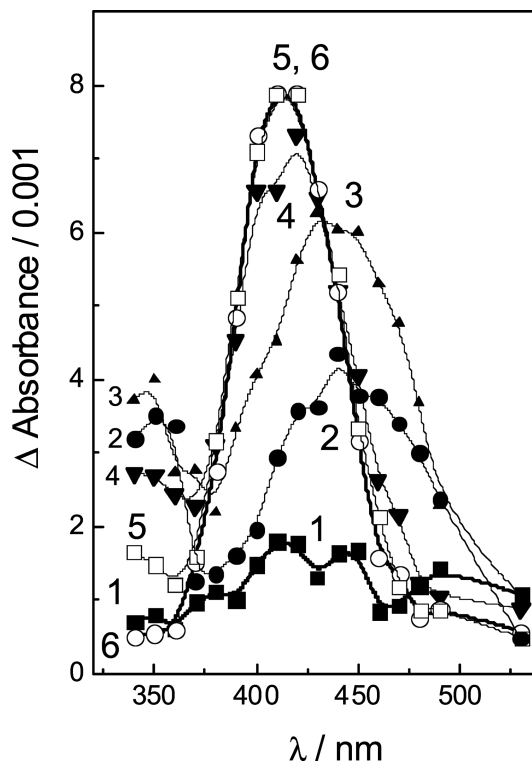
### 3.2. Laser flash photolysis of [PtCl<sub>6</sub>]<sup>2-</sup>: identification of intermediates

Fig. 2 shows the kinetic curves of absorption by the intermediates at several wavelengths upon the laser flash photolysis



**Fig. 2** Kinetic curves of changes in the absorption of the intermediates after a laser pulse (308 nm) of the aqueous solution of [PtCl<sub>6</sub>]<sup>2-</sup> (9.5 × 10<sup>-5</sup> M). The solid black lines are calculated by a two-exponential model (see text).

(308 nm) of the aqueous [PtCl<sub>6</sub>]<sup>2-</sup> solutions. The evolution of the absorption spectra of the intermediates after a laser pulse is demonstrated in Fig. 3. A new absorption band is formed shortly after the laser pulse (~0.7 μs) in the range of 340–380 nm. Another intermediate with a wide absorption



**Fig. 3** Absorption spectra of the intermediates calculated from kinetic curves, some of which are shown in Fig. 2. Curves 1–6 denote the spectra recorded 0, 0.8, 4, 14, 30, and 49 μs after the laser pulse, respectively.

band with a maximum at 450 nm is formed a bit more slowly (*ca.* 1.2  $\mu$ s). It transforms with a characteristic time of *ca.* 20  $\mu$ s into a new species having an absorption band with a maximum at 410 nm. The intensity of the latter remains almost constant over the range up to 1 ms.

The band in the range of 340–380 nm almost completely vanishes by about 50  $\mu$ s (the kinetic curve for 350 nm in Fig. 2 and spectra 3–6 in Fig. 3). The essentially different rates of absorption disappearance in the range of 450 and 350 nm indicate that these bands belong to different intermediates. The water-dissolved oxygen has no effect on the yield and kinetics of intermediate absorption.

The absorption band with a maximum at 410 nm has been recorded in microsecond (lamp) flash photolysis<sup>3,6</sup> and pulse radiolysis<sup>19–21</sup> experiments of  $[\text{PtCl}_6]^{2-}$  in aqueous solutions. An intermediate with an absorption band at 450 nm was revealed during both the lamp flash photolysis of  $[\text{PtCl}_4(\text{OH})_2]^{2-}$  and the pulse radiolysis of  $[\text{PtCl}_4]^{2-}$  and  $[\text{PtCl}_6]^{2-}$ .<sup>21</sup> The ratio between the intensities of the bands at 410 and 450 nm is equal to 1.4 (Fig. 3) and is in agreement with the measured absorption coefficients of these bands ( $\epsilon_{450} = 2800$ ,<sup>19</sup>  $2500 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{410} = 3700$ ,<sup>19</sup>  $3500 \text{ M}^{-1} \text{ cm}^{-1}$ ).

In the literature, both these bands are attributed to Pt(III) intermediates. Based on the calculations of Goursot *et al.*,<sup>22,23</sup> the band at 410 nm could be assigned to  $[\text{PtCl}_4]^-$ , which has a square-planar structure. The intermediate at 450 nm most probably has a distorted octahedral structure with the composition  $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{2-}$ .

This interpretation should be compared with the literature assignment of Pt(III) bands from lamp flash photolysis<sup>4,6</sup> and the pulse radiolysis<sup>19–21,24</sup> of Pt(IV) and Pt(II) chloride complexes in aqueous solutions. Wright and Laurence<sup>4</sup> and Shagisultanova *et al.*<sup>6</sup> attributed the band with a maximum at 410 nm formed by the lamp flash photolysis of  $[\text{PtCl}_6]^{2-}$  to the planar  $[\text{PtCl}_4]^-$ , and assigned the band with a maximum at 450 nm formed from  $[\text{PtCl}_4(\text{OH})_2]^{2-}$  to the  $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{2-}$  species.

It should be noted that two other possible identities of intermediates with absorption bands at 410 and 450 nm exist, both based on the experiments of Broszkiewicz *et al.*<sup>19–21</sup> The results of refs. 19 and 21 seem contradictory (see Appendix). We believe that additional experiments on the pulse radiolysis of  $[\text{PtCl}_6]^{2-}$  should be performed to understand this contradiction.

In experiments on the flash photolysis of  $[\text{PtCl}_6]^{2-}$  in alcohols<sup>9,11–13</sup> and acetonitrile,<sup>10</sup> absorption bands with maxima at 530 and 410 nm belonging to a single intermediate species were recorded. These bands refer to  $[\text{PtCl}_5]^{2-}$  formed by the dissociation of the primary complex of trivalent platinum,  $[\text{PtCl}_6]^{3-}$ . The spectrum of  $[\text{PtCl}_5]^{2-}$ , which has a square pyramidal structure ( $C_{4v}$ ) and not a trigonal bipyramid ( $D_{3h}$ ), is also in agreement with the theoretical predictions of Goursot *et al.*<sup>22</sup>

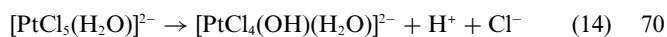
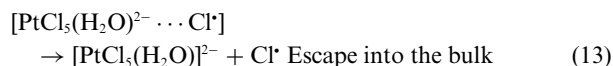
The band at 350 nm (Fig. 2) is likely to refer to the radical anion  $\text{Cl}_2^{\cdot-}$  formed by the reaction of a Cl atom with a Cl ion. In this case, both are the products of the photolysis of a parental  $[\text{PtCl}_6]^{2-}$  complex. The spectroscopy and kinetics of the reactions of this particle will be discussed below.

### 3.3. Yield and kinetic characteristics of intermediate Pt(III) complexes

The value of the absorption at 410 nm was used to estimate a relative yield of  $[\text{PtCl}_4]^-$ . When the absorption coefficient is  $3700 \text{ M}^{-1} \text{ cm}^{-1}$ <sup>19</sup> and the quantum yield of the  $[\text{PtCl}_6]^{2-}$  photolysis is 0.19 (this work), the yield of  $[\text{PtCl}_4]^-$  ( $\sim 2 \times 10^{-6} \text{ M}$ ) does not exceed 10% of the number of disappearing  $[\text{PtCl}_6]^{2-}$  complexes ( $\sim 3 \times 10^{-5} \text{ M}$ ). This estimate is in agreement with the conclusion of Wright and Laurence<sup>4</sup> on a small ( $\sim 10\%$ ) contribution of  $[\text{PtCl}_6]^{2-}$  photoreduction.

The laser flash photolysis experimental data for  $[\text{PtCl}_6]^{2-}$  can be explained in the framework of the Adamson mechanism of

radical pairs.<sup>25</sup> Similar concepts were applied for describing the mechanism of  $[\text{IrCl}_6]^{2-}$  photolysis in aqueous solutions.<sup>26,27</sup>



The mechanism of radical pairs assumes a homolytic cleavage of the metal–ligand bond in the excited state and a successive formation of two intermediates, *primary*  $[\text{PtCl}_5^{2-} \dots \text{Cl}^*]$  and *secondary*  $[\text{PtCl}_5(\text{H}_2\text{O})^{2-} \dots \text{Cl}^*]$  radical pairs. The products of photoaquation (reaction (12)) and photoreduction (reaction (13)) result from the transformation of the secondary radical pair. A particular feature of the system studied is the dissociation of  $[\text{PtCl}_5(\text{H}_2\text{O})]^{2-}$ , which gives rise to the  $[\text{PtCl}_4(\text{OH})]^{2-}$  intermediate including a hydroxide ion (reaction (14)).

In the framework of the kinetic scheme proposed, the intermediates of trivalent platinum,  $[\text{PtCl}_5(\text{H}_2\text{O})]^{2-}$ ,  $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{2-}$ , and  $[\text{PtCl}_4]^-$  convert successively into each other. In this case, the kinetics of a change in the  $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{2-}$  (450 nm) and  $[\text{PtCl}_4]^-$  (410 nm) absorption should be described by two-exponential curves. Approximating experimental kinetic curves at 470 and 410 nm by the sum of two exponents (Fig. 2), one can obtain the rate constants of reactions (14) and (15):  $k_{14} = (8 \pm 1) \times 10^5 \text{ s}^{-1}$  and  $k_{15} = (1.3 \pm 0.2) \times 10^5 \text{ s}^{-1}$ . The latter is close to the rate constant of the transformation of the “450 nm” band into the “410 nm” band reported in ref. 19, ( $1.8 \times 10^5 \text{ s}^{-1}$ ).

The trivalent platinum complex  $[\text{PtCl}_4]^-$  is known to vanish in the reaction of disproportionation (eqn (16)) with the rate constant  $2k_{16} = (4.6 \pm 0.4) \times 10^6 \text{ s}^{-1}$ .<sup>4</sup>



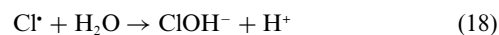
When the initial concentration is about  $2 \times 10^{-6} \text{ M}$ , this rate constant provides a characteristic lifetime of the complex of about 0.1 s. This is in fair agreement with the stability of  $[\text{PtCl}_4]^-$  absorption (410 nm) over the time domain up to 1 ms (Fig. 2).

### 3.4. Formation and disappearance of the $\text{Cl}_2^{\cdot-}$ radical anion

The appearance of a Cl atom in the reaction system is followed by its fast conversion into the  $\text{Cl}_2^{\cdot-}$  radical anion in the reaction with  $\text{Cl}^-$  (reaction (17)).  $\text{Cl}_2^{\cdot-}$  displays the absorption band at 350 nm with the absorption coefficient of  $9600 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>28</sup>



The  $\text{Cl}^-$  ion results from the general process of  $[\text{PtCl}_6]^{2-}$  photoaquation (reaction (12)). Its concentration after the laser pulse is *ca.*  $2 \times 10^{-5} \text{ M}$ . Reaction (17) is diffusion-controlled ( $k_{17} = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>29</sup>  $6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ <sup>30</sup>) and can provide a characteristic time of  $\text{Cl}_2^{\cdot-}$  formation of about 6  $\mu$ s. Fig. 2 shows that the formation of absorption at 350 nm takes about 0.7  $\mu$ s and its yield is smaller than that calculated from reaction (17). Thus, the Cl atom not only reacts with the  $\text{Cl}^-$  ion but also disappears in alternative reactions, one of which can be the reaction with water molecules (reaction 18).



The available rate constants for reaction (18) are  $1.6 \times 10^5 \text{ s}^{-1}$ <sup>30</sup> and  $2.5 \times 10^5 \text{ s}^{-1}$ <sup>31</sup>, which indicate that the reaction can not substantially accelerate the  $\text{Cl}_2^{\bullet-}$  formation. The recombination of Cl atoms with the rate constant of  $8.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ <sup>32</sup> at the initial concentration of  $2 \times 10^{-6} \text{ M}$  can not compete even with reactions (17) and (18).

In principle, the presence of undefined organic impurities in water could accelerate the disappearance of the Cl atoms and the appearance of  $\text{Cl}_2^{\bullet-}$ . However, the concentration of the impurities should not be less than  $10^{-4} \text{ M}$ , which is improbable. Only two species in solution have high enough concentration to accelerate Cl atom disappearance, the initial  $[\text{PtCl}_6]^{2-}$  ( $\sim 10^{-4} \text{ M}$ ) and aquated  $[\text{PtCl}_5(\text{OH})]^{2-}$  ( $\sim 2 \times 10^{-5} \text{ M}$  after the pulse). The fast disappearance of the Cl atom in the reaction with these Pt(IV) complexes can provide the observed time of  $\text{Cl}_2^{\bullet-}$  formation (reaction (19))



If the rate constant of reaction (19) is diffusion-controlled ( $k_{19} = k_{\text{diff}} = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), for concentrations of the Pt(IV) complexes of about  $10^{-4} \text{ M}$ , the competition of reactions (17)–(19) leads to the yield  $[\text{Cl}_2^{\bullet-}]_{\text{max}} = 0.2 \times [\text{Cl}^\bullet]_0$ , which is in fair agreement with the experimental data ( $[\text{Cl}_2^{\bullet-}]_{\text{max}} = 4 \times 10^{-7} \text{ M}$ ;  $[\text{Cl}^\bullet]_0 = [\text{PtCl}_4]_{\text{max}} = 2 \times 10^{-6} \text{ M}$ ).

The kinetics of the change in  $\text{Cl}_2^{\bullet-}$  absorption (Fig. 2) depends on both its formation in reactions (17)–(19) and the disappearance with the observed first-order rate constant  $k_d \approx 3 \times 10^4 \text{ s}^{-1}$ . When the initial concentration is  $4 \times 10^{-7} \text{ M}$ , the reaction of  $\text{Cl}_2^{\bullet-}$  disproportionation (for zero ionic strength  $2k_{\text{dispr}} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ <sup>27</sup>) does not contribute much to the disappearance of radical anions (because the corresponding characteristic time is ca. 1 ms). The  $\text{Cl}_2^{\bullet-}$  disappearance reaction will be discussed below.

When the Cl atom disappears in reactions (17)–(19), the time dependence of the  $\text{Cl}_2^{\bullet-}$  concentration obeys the equation

$$[\text{Cl}_2^{\bullet-}](t) = [\text{Cl}^\bullet]_0 \frac{k_{23}[\text{Cl}^\bullet]}{k_f - k_d} (e^{-k_d t} - e^{-k_f t}), \quad (20)$$

where  $k_f = k_{17}[\text{Cl}^\bullet] + k_{18} + k_{19}[\text{Pt}^{\text{IV}}]$  and  $k_d$  are the rate constants of the formation and decay of the radical anion. In Fig. 2, the solid lines denote the calculations of kinetics from eqn (20) with constants  $k_f = 1.5 \times 10^6 \text{ s}^{-1}$  and  $k_d = 3.3 \times 10^4 \text{ s}^{-1}$ , which is in fair agreement with the experimental curve. The  $k_f$  value is fully determined by the aforementioned rate constants of reactions (17)–(19) and reagent concentrations.

The kinetics of  $\text{Cl}_2^{\bullet-}$  disappearance with the observed rate constant  $k_d = 3.3 \times 10^4 \text{ s}^{-1}$  can not be provided by the reaction with water and the complexes of either trivalent or bivalent platinum. The rate constant of the reaction between  $\text{Cl}_2^{\bullet-}$  and water ( $1.3 \times 10^3 \text{ s}^{-1}$ )<sup>31</sup> gives a characteristic reaction time of 800  $\mu\text{s}$ , which is much longer than the observed one. For the concentration of Pt(III) and Pt(II) complexes of about  $2 \times 10^{-6} \text{ M}$ , the rate constant, which can give the necessary rate, should be  $\geq 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . This value substantially exceeds the rate constant of the diffusion-controlled reaction of charged particles (all platinum complexes carry a negative charge) which obeys the equation<sup>33</sup>

$$k_{\text{diff}} = \frac{4\pi R_0 D}{\exp\left(\frac{R_0}{R} - 1\right)}, \quad (21)$$

where  $R_0 = q_1 q_2 e^2 / (\epsilon k T)$  is the Onsager radius,  $q_1$  and  $q_2$  are the charges,  $R$  is the total radius of reacting particles, and  $D$  is the coefficient of the mutual diffusion of reagents. For the pairs  $\text{Cl}_2^{\bullet-}$ – $[\text{PtCl}_4]^-$  or  $\text{Cl}_2^{\bullet-}$ – $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{2-}$ , the total reaction radius is estimated to be 5.6 Å (the length of the Cl–Cl bond in  $\text{Cl}_2^{\bullet-}$  is 2.6 Å,<sup>34</sup> the  $\text{Cl}^-$  radius is 1.8 Å,<sup>35</sup> and the typical length of the Pt–Cl bond is 2.3 Å<sup>36</sup>). The  $R_0$  in water at room temperature amounts to 7 and 14 Å for  $q_1 = -1$ ,  $q_2 = -1$ ,  $q_1 = -1$ , and  $q_2 = -2$ , respectively. Thus, the value of the rate constant of the reaction between the  $\text{Cl}_2^{\bullet-}$  radical anions and the Pt(III) ions

(single- or double-charged) does not exceed  $(2-4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and fails to provide the observed rate of  $\text{Cl}_2^{\bullet-}$  decay.

The only reaction which can give the observed rate of  $\text{Cl}_2^{\bullet-}$  decay is its reaction with the Pt(IV) complexes ( $[\text{PtCl}_6]^{2-}$  and  $[\text{PtCl}_5(\text{OH})]^{2-}$ ),



similarly to the aforementioned reaction between the Cl atom and the same complexes. The value  $k_d = 3.3 \times 10^4 \text{ s}^{-1}$  and the total concentration of tetravalent platinum ( $\sim 10^{-4} \text{ M}$ ) allows one to estimate the rate constant of reaction (22) as  $k_{22} \approx 3.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which is an order of magnitude smaller than the rate constant of the diffusion-controlled reaction. No spectral manifestations of Pt(V) complexes were obtained as these species are likely to have no substantial absorption in the nearest UV and visible regions.

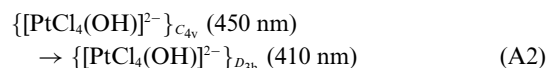
## Conclusions

Spectral and kinetic characteristics of intermediates arising from laser flash photolysis of aqueous solutions of  $[\text{PtCl}_6]^{2-}$ , namely Pt(III) complexes— $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{2-}$  and  $[\text{PtCl}_4]^-$ —and  $\text{Cl}_2^{\bullet-}$  radical anions were obtained. About 90% of  $[\text{PtCl}_6]^{2-}$  photoaquation at 308 nm over the concentration range of  $10^{-5}$ – $10^{-4} \text{ M}$  and with  $\text{pH} \approx 5$ – $6$  occurs without the escape of a chlorine atom from the secondary radical pair ( $[\text{PtCl}_5(\text{H}_2\text{O})]^{2-}$ –Cl) into the solvent bulk. The contribution of chain processes to photoaquation could be assigned to both the appearance of Cl atoms in the bulk and the formation of trivalent platinum intermediates. Under the experimental conditions of the current work, the chain processes are of minor importance, which is confirmed by a low quantum yield of photoaquation. The reasons for a substantial increase in the quantum yield of  $\text{PtCl}_6^{2-}$  photoaquation with increasing pH, concentration of the complex (over the range of  $10^{-4}$ – $10^{-2} \text{ M}$ ), and excitation wavelength<sup>3-6</sup> should be established in further investigations.

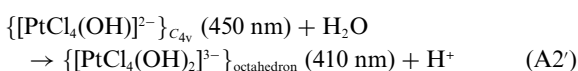
## Appendix: Pulse radiolysis of $[\text{PtCl}_4]^{2-}$ and $[\text{PtCl}_6]^{2-}$ in aqueous solutions

In this Appendix, we comment the works by Broszkiewicz *et al.*<sup>19-21</sup> on the pulse radiolysis of  $[\text{PtCl}_4]^{2-}$  and  $[\text{PtCl}_6]^{2-}$ . The results of refs. 19 and 21 concerning  $[\text{PtCl}_6]^{2-}$  seems to be rather contradictory.

In refs. 19, 20 and 21, the pulse radiolysis of  $[\text{PtCl}_4]^{2-}$  in water saturated with  $\text{N}_2\text{O}$  leads to the formation of the band with a maximum at 450 nm followed by its transformation to the band with a maximum at 410 nm. In ref. 19 and 20 these bands were assigned to the pentacoordinated complexes of Pt(III) with the composition  $[\text{PtCl}_4(\text{OH})]^{2-}$  and a square pyramid structure ( $C_{4v}$ ) for the “450 nm” band and a trigonal bipyramid ( $D_{3h}$ ) for the “410 nm” band:

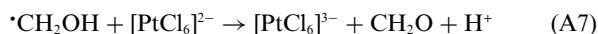
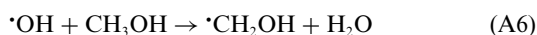
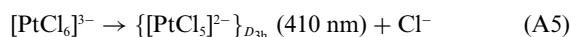
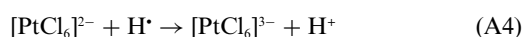
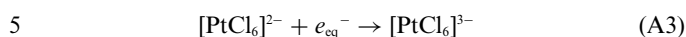


In a more recent work,<sup>21</sup> the “410 nm” band was attributed (based on the conductivity measurements) to  $[\text{PtCl}_4(\text{OH})_2]^{3-}$  with a distorted octahedron structure:



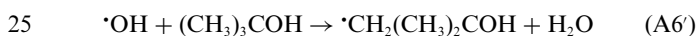
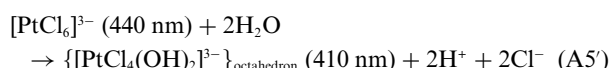
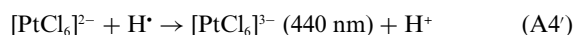
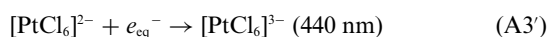
Pulse radiolysis of  $[\text{PtCl}_6]^{2-}$  was performed in refs. 19 and 21. In both cases, alcohols (methanol in ref. 19 and *tert*-butyl alcohol in ref. 21) were used to scavenge  $\bullet\text{OH}$  radicals. The temporal resolution of the pulse radiolysis setup in both cases was ca. 1  $\mu\text{s}$ . The results were different, as in ref. 19 only a band in the region of 410 nm was recorded. This band was assigned

to  $[\text{PtCl}_5]^{2-}$  with a trigonal bipyramidal structure ( $D_{3h}$ ). It was proposed that the UV spectra of  $[\text{PtCl}_5]^{2-}$  and  $[\text{PtCl}_4(\text{OH})]^{2-}$   $D_{3h}$  complexes are almost the same. The reaction pathway (A3–A7) was put forward:



10 It was proposed that  $[\text{PtCl}_6]^{3-}$  does not absorb in near UV and visible spectral regions.

In ref. 21, the initial formation of an absorption band with a maximum at 440 nm was recorded followed by its transformation to the 410 nm band. Based on both UV spectra and conductivity measurements, the 410 nm band (as in the case of  $[\text{PtCl}_4]^{2-}$  radiolysis) was attributed to  $[\text{PtCl}_4(\text{OH})_2]^{3-}$ , and the 440 nm band (considered to be different from the 450 nm band in the case of  $[\text{PtCl}_4]^{2-}$ ) was assigned to  $[\text{PtCl}_6]^{3-}$ . Correspondingly, the radiolysis mechanism A3–A7 was changed to A3'–A6' (the reaction between the butoxy radical and Pt(IV) was proposed to be negligible):



The principal question is why the change of the  $\bullet\text{OH}$  scavenger (*tert*-butyl alcohol instead of methanol) leads to the dramatic change in the mechanism of radiolysis displayed by the occurrence of the 440 nm band. This problem is not discussed in ref. 21.

30 Assuming that both refs. 19 and 21 are correct, the following comments could be made:

(i) To achieve the formation of the 440 nm intermediate with the characteristic time of *ca.* 1  $\mu\text{s}$ , the reaction between  $[\text{PtCl}_6]^{2-}$  and  $\bullet\text{CH}_2(\text{CH}_3)_2\text{COH}$  radical should exist. Its rate constant should be *ca.*  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . For the case of the  $\bullet\text{CH}_2\text{OH}$  radical, the rate constant should be at least two orders of magnitude smaller.

(ii) The 410 nm complex may be either the planar  $[\text{PtCl}_4]^{2-}$  itself or a square-planar structure with weakly coordinating ligands in the apical position.<sup>23</sup>

(iii) The assignment of the 440 nm band to  $[\text{PtCl}_6]^{3-}$  contradicts the theoretical predictions.<sup>22,23</sup>

(iv) Both 440 nm and 450 nm bands could be the same band belonging to the six-coordinated  $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{2-}$  complex.

45 In conclusion, the data of pulse radiolysis seems to be unclear. Particularly, the dependence of the reaction pathway on the nature of an  $\bullet\text{OH}$  radical scavenger should be reproduced.

## Acknowledgements

50 The work was supported by the Russian Foundation for Fundamental Research (grants 03-03-33134, 03-03-39008 GFEN, and 05-03-32474) and the program of the Ministry of Education of RF "Universities of Russia" (grant UR. 05.01.020).

## References

55 1 R. L. Rich and H. Taube, Catalysis by Pt(III) of exchange reactions of  $\text{PtCl}_4^{2-}$  and  $\text{PtCl}_6^{2-}$ , *J. Am. Chem. Soc.*, 1954, **76**, 2608–2611.

- 2 V. Balzani and V. Carassiti, *Photochemistry of coordination compounds*, Acad. Press, New York, 1970, pp. 258–262.
- 3 L. E. Cox, D. G. Peters and E. L. Wehry, Photoaquation of hexachloroplatinate(IV), *J. Inorg. Nucl. Chem.*, 1972, **14**, 297–305. 60
- 4 R. C. Wright and G. S. Laurence, Production of Pt(III) by flash photolysis of  $\text{PtCl}_6^{2-}$ , *J. Chem. Soc., Chem. Commun.*, 1972, 132–133.
- 5 K. P. Balashev, V. V. Vasil'ev, A. M. Zimnyakov and G. A. Shagisultanova, Kinetics of chain reactions of photoaquation involving platinum(III) complexes, *Koord. Khim.*, 1984, **10**, 976–980 (in Russian). 65
- 6 K. P. Balashev, I. I. Blinov and G. A. Shagisultanova, Acidic-basic properties of platinum(III) chloride complexes, *Zh. Neorg. Khim.*, 1987, **32**, 2470–2474 (in Russian). 70
- 7 A. Goursot, A. D. Kirk, W. L. Waltz, G. B. Porter and D. K. Sharma, Experimental and theoretical study of the nascent photoredox behavior of the aqueous hexachloroplatinate(IV) ion, *Inorg. Chem.*, 1987, **26**, 14–18.
- 8 V. Balzani, M. F. Manfrin and L. Moggi, Photochemistry of coordination compounds. XVI. Hexabromoplatinate(IV) and hexaiodoplatinate(IV) ions, *Inorg. Chem.*, 1967, **6**, 354–358.
- 9 V. P. Grivin, I. V. Khmelinski, V. F. Plyusnin, I. I. Blinov and K. P. Balashev, Photochemistry of  $\text{PtCl}_6^{2-}$  complex in methanol solution, *J. Photochem. Photobiol., A*, 1990, **51**, 167–178. 80
- 10 K. P. Balashev, I. I. Blinov and G. A. Shagisultanova, Kinetics and mechanism of the photosubstitution of  $[\text{PtCl}_6^{2-}]$  ion in acetonitrile, *Kinet. Katal.*, 1987, **28**, 801–804 (in Russian).
- 11 K. P. Balashev, I. I. Blinov and G. A. Shagisultanova, Kinetics and mechanism of photoinduced reactions of haloid complexes of platinum(III) in methyl alcohol, *Koord. Khim.*, 1987, **12**, 1674–1678 (in Russian). 85
- 12 V. P. Grivin, I. V. Khmelinski and V. F. Plyusnin, Intermediates in the photoreduction of  $\text{PtCl}_6^{2-}$  in methanol, *J. Photochem. Photobiol., A*, 1990, **51**, 379–389. 90
- 13 V. P. Grivin, I. V. Khmelinski and V. F. Plyusnin, Primary photochemical processes of the  $\text{PtCl}_6^{2-}$  complex in alcohols, *J. Photochem. Photobiol., A*, 1991, **59**, 153–161.
- 14 P. E. Hoggard and A. Vogler, The photooxidation of tetrachloroplatinate(II) in chloroform, *Inorg. Chim. Acta*, 2003, **348**, 229–232. 95
- 15 O. Montreal, T. Esmaeli and P. E. Hoggard, A kinetic study of the photoreduction of hexachloroplatinate(IV) in chloroform, *Inorg. Chim. Acta*, 1997, **265**, 279–282.
- 16 K. C. Kurien, A modification to the ferrioxalate actinometer, *J. Chem. Soc. B*, 1971, 2081–2082. 100
- 17 R. H. Compton, K. T. V. Grattan and T. J. Morrow, Extinction coefficients and quantum yields for triplet–triplet absorption using laser flash photolysis, *J. Photochem.*, 1980, **14**, 61–66.
- 18 C. M. Davidson and R. F. Jameson, Complexes formed between the platinum metals and halide ions. Part 3. -Hydrolysis of haloplatinates-potentiometric and spectrophotometric studies, *Trans. Faraday Soc.*, 1965, **61**, 2462–2467. 105
- 19 G. E. Adams, R. K. Broszkiewicz and B. D. Michael, Pulse radiolysis studies on stable and transient complexes of platinum, *Trans. Faraday Soc.*, 1968, **64**, 1256–1264.
- 20 R. K. Broszkiewicz and J. Grodkowski, Pulse radiolysis studies on aqueous systems  $\text{PtCl}_4^{2-} - \text{Cl}^-$  and  $\text{PtCl}_4^{2-} - \text{Br}^-$ , *Int. J. Radiat. Phys. Chem.*, 1976, **8**, 359–365.
- 21 E. Bothe and R. K. Broszkiewicz, Platinum(III) in the REOA mechanism of  $\text{PtCl}_4^{2-}$  and  $\text{PtCl}_6^{2-}$ . A pulse-radiolysis study, *Inorg. Chem.*, 1989, **28**, 2988–2991. 115
- 22 A. Goursot, H. Chermette, E. Peigault, M. Chanon and W. L. Waltz,  $X_u$  method as a tool for structure elucidation of short-lived transients generated by pulse radiolysis or flash photolysis. I. Reductive reactions of  $\text{PtCl}_6^{2-}$ , *Inorg. Chem.*, 1984, **23**, 3618–3625. 120
- 23 A. Goursot, H. Chermette, E. Peigault, M. Chanon and W. L. Waltz,  $X_u$  method as a tool for structure elucidation of short-lived transients generated by pulse radiolysis or flash photolysis. II. Oxidative reactions of  $\text{PtCl}_4^{2-}$ , *Inorg. Chem.*, 1985, **24**, 1042–1047. 125
- 24 A. S. Ghosh-Mazumdar and E. J. Hart, Electron pulse radiolysis of aqueous tetrachloro and tetracyano complexes of  $\text{Pt}^{\text{II}}$ , *Int. J. Radiat. Phys. Chem.*, 1969, **1**, 165–176.
- 25 A. W. Adamson and A. H. Sporer, Photochemistry of complex ions. I. Some photochemical reactions of aqueous  $\text{PtBr}_6^{2-}$ ,  $\text{Mo}(\text{CN})_6^{4-}$ , and various Co(III) and Cr(III) complex ions, *J. Am. Chem. Soc.*, 1958, **80**, 3865–3870. 130
- 26 L. Moggi, G. Varani, M. F. Manfrin and V. Balzani, Photochemical reactions of hexachloroiridate(IV) ion, *Inorg. Chim. Acta*, 1970, **4**, 335–341. 135
- 27 E. M. Glebov, V. F. Plyusnin, N. V. Tkachenko and H. Lemmetyinen,

- Laser flash photolysis of  $\text{IrCl}_6^{2-}$  in aqueous solutions, *Chem. Phys.*, 2000, **257**, 79–89.
- 28 D. J. Adams, S. Barlow, G. V. Buxton, T. M. Malone and G. A. Salmon, Evaluation of the stability constants of  $\text{Cl}_2^{\cdot-}$  in neutral aqueous solutions, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3303–3305.
- 5 29 V. Nataranjan and R. W. Fessenden, Flash photolysis of transient radicals. I.  $\text{X}_2^{\cdot-}$  with X = Cl, Br, I and SCN, *J. Phys. Chem.*, 1985, **89**, 2330–2335.
- 10 30 U. K. Klaining and T. Wolff, Laser flash photolysis of  $\text{HClO}$ ,  $\text{ClO}^-$ ,  $\text{HBrO}$  and  $\text{BrO}^-$  in aqueous solutions, *Ber. Bunsen-Ges. Phys. Chem.*, 1985, **89**, 243–245.
- 15 31 W. J. McElroy, A laser flash photolysis study of the reaction of  $\text{SO}_4^{\cdot-}$  and subsequent decay of  $\text{Cl}_2^{\cdot-}$  in aqueous solution, *J. Phys. Chem.*, 1990, **94**, 2435–2441.
- 32 D. Wu, D. Wong and B. DiBartolo, Evolution of  $\text{Cl}_2^{\cdot-}$  in aqueous NaCl solutions, *J. Photochem.*, 1980, **14**, 303–310.
- 33 S. G. Entelis and R. P. Tiger, *Kinetika reaktsii v rastvorakh. Kolichestvenny uchet vliyaniya sredy (Kinetics of Reactions in Solutions. Qualitative account for the Medium Effects)*, Khimiya, Moscow, 1973, p. 34 (in Russian). 20
- 34 W. B. Person, Electron affinities of some halogen molecules and the charge-transfer frequency, *J. Chem. Phys.*, 1963, **38**, 109–116.
- 35 F. Basolo and R. G. Pearson, *Mechanism of Inorganic Reactions. A Study of Metal Complexes in Solution*, John Wiley & Sons, New York, 1967, p. 78. 25
- 36 R. J. Williams, D. R. Dillin and W. O. Milligan, Structure refinement of potassium chloroplatinate by powder and single-crystal methods, *Acta Crystallogr., Sect. B*, 1973, **29**, 1369–1372.

Dear Author,

Paper No. b509587e

Please check the proofs of your paper carefully, paying particular attention to the numerical data, tables, figures and references.

When answering the queries below please ensure that any changes required are clearly marked **on the proof**. There is no need to e-mail your answers to the queries separately from the rest of your proof corrections.

Editor's queries are marked like this [Q1, Q2, ...], and for your convenience line numbers are indicated like this [5, 10, 15, ...].

Many thanks for your assistance.

Query	Remarks
Q1 Please check that changes to the English in this sentence have not affected the meaning.	
Q2 Square brackets have been placed around all complex formulae in this paper to be consistent with our house style.	
Q3 Do you mean an escape of a Cl radical here?	
Q4 Do you mean Einsteins per litre as the units for this light intensity?	
Q5 The word black has been inserted after solid to give solid black lines in this sentence for clarity. Is this correct?	
Q6 Please check that changes to the English in these sentences have not affected the meaning.	
Q7 Please check that changes to the English in this sentence have not affected the meaning.	
Q8 Please check that changes to the English in this sentence have not affected the meaning.	
Q9 The meaning of this point is not clear - please clarify. Do you mean apical positions in the plane- for a square planar complex- or do you mean a distorted octahedral structure eg like a tetragonal structure?	
Q10 In references 19, 20 and 21, the authors name changes from Broszkiewicz to Broszkewich- which is correct?	