

# Photochemical Reductive *trans*-Elimination from *trans*-Diacidotetracyanoplatinate(IV) Complexes

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*Dedicated to Prof. Dr. Dr. h. c. mult. E. O. Fischer on the occasion of his sixtieth birthday*

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Photochemical Reductive *trans*-Elimination, *trans*-Diacidotetracyanoplatinate(IV) Complexes

Upon CT excitation the complex ions *trans*-[Pt(CN)<sub>4</sub>N<sub>3</sub>X]<sup>2-</sup> and *trans*-[Pt(CN)<sub>4</sub>X<sub>2</sub>]<sup>2-</sup> (X = Cl and Br) undergo a reductive *trans*-elimination with formation of [Pt(CN)<sub>4</sub>]<sup>2-</sup> and two ligand radicals in the photoprimary step. The formation of a Pt(III) intermediate is not observed. Due to the stability of [Pt(CN)<sub>4</sub>]<sup>2-</sup>, recombination reactions regenerating the starting complex are efficient if the ligand radicals are not scavenged. For the azide complexes the high quantum yields for the production of [Pt(CN)<sub>4</sub>]<sup>2-</sup> are explained by the instability of azide radicals. For *trans*-[Pt(CN)<sub>4</sub>X<sub>2</sub>]<sup>2-</sup>, the recombination is efficient in aqueous solution, while in ethanol the halogen atoms are scavenged by hydrogen abstraction. The sequence of steps following CT excitation can be explained by a potential energy diagram.

## Introduction

It has been shown recently that CT-excitation of *trans*-[Pt(IV)(CN)<sub>4</sub>(N<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> in the primary photochemical step leads to a reductive *trans*-elimination with the formation of [Pt(II)(CN)<sub>4</sub>]<sup>2-</sup> and two azide radicals [1]. While in aqueous solution the azide radicals yield only molecular nitrogen, in ethanol they are also able to abstract hydrogen atoms from the solvent with formation of CH<sub>3</sub>CHOH radicals and HN<sub>3</sub>. The present investigation was an extension of this work to see if reductive *trans*-elimination is a general rule for other tetracyanoplatinate(IV) complexes.

## Experimental

### Materials

K<sub>2</sub>-*trans*-[Pt(CN)<sub>4</sub>Cl<sub>2</sub>] and K<sub>2</sub>-*trans*-[Pt(CN)<sub>4</sub>Br<sub>2</sub>] were prepared according to published procedures [2] and shown to be of good spectroscopic purity. The complexes K<sub>2</sub>-*trans*-[Pt(CN)<sub>4</sub>N<sub>3</sub>X] (X = Cl and Br) were prepared by adding a slight excess of potassium azide to an aqueous solution of K<sub>2</sub>-*trans*-[Pt(CN)<sub>4</sub>X<sub>2</sub>]. After stirring for 3 h, the solution was evaporated to half the volume. Addition of ethanol and ether gave a precipitate which was recrystallized several times from acetone. The *trans*-assignment is sup-

ported by the occurrence of only one IR band [3] (2157 for X = Cl and 2159 cm<sup>-1</sup> for X = Br) in the region of cyanide stretching vibrations. For elemental analyses the complexes were precipitated from aqueous solution as tetraphenylarsonium salts which are not as explosive as alkali salts of azide complexes [4].

*Analysis for* [As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[Pt(CN)<sub>4</sub>N<sub>3</sub>Cl]

Calcd C 54.51 H 3.51 N 8.56,

Found C 54.85 H 3.42 N 8.42.

[As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[Pt(CN)<sub>4</sub>N<sub>3</sub>Br]

Calcd C 51.72 H 3.35 N 8.25,

Found C 52.12 H 3.38 N 8.12.

### Photolysis Procedures

The light sources used were a 1000 W Hanovia-Xe/Hg lamp or an Osram 100 W high-pressure mercury lamp. A Schoeffel monochromator GM 250-1 was used for irradiation at 254 nm and 342 nm. Schott interference filters UV-IL 300 and UV-IL 282 were used for irradiation at 300 nm and 282 nm. Cut-off filters were used on some experiments. For quantum-yield measurements the complex concentrations were such as to have complete light absorption. Absorbed light intensities were determined by ferrioxalate actinometry.

### Measurements

Visible and ultraviolet spectra were measured with a Varian Techtron Super Scan 3 recording spectrophotometer and a Zeiss PMQ II spectrophotometer was used for measurements at selected wavelengths. ESR spectra were recorded either on a Varian E 9 or a Bruker 420 ESR spectrometer.

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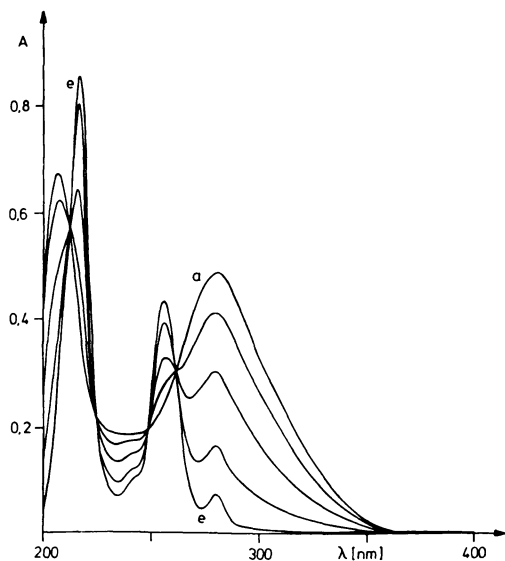


Fig. 1. Spectral changes observed upon irradiating a  $4.04 \cdot 10^{-5}$  M solution of  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Cl}]^{2-}$  in ethanol with  $\lambda = 280$  nm. Cell length = 1 cm. Total irradiation time between (a) initial and (e) final is 12 minutes.

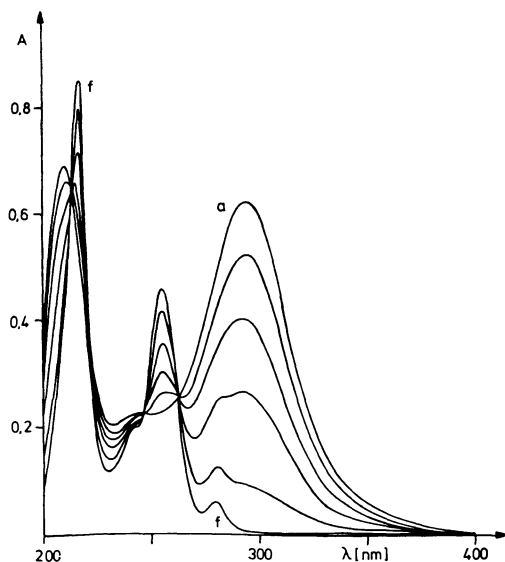


Fig. 2. Spectral changes of the photochemical conversion of a  $4.06 \cdot 10^{-5}$  M ethanolic solution of  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Br}]^{2-}$  (a) to  $[\text{Pt}(\text{CN})_4]^{2-}$  (f). 300 nm irradiating wavelength, 1.0 cm cell. Time elapsed between (a) initial and (f) final spectra is 10 minutes.

## Results

The electronic absorption spectra of *trans*- $[\text{Pt}(\text{CN})_4(\text{N}_3)\text{Cl}]^{2-}$  and *trans*- $[\text{Pt}(\text{CN})_4(\text{N}_3)\text{Br}]^{2-}$  are shown in Figs. 1 and 2, respectively. Upon irradiation with light of wavelengths longer than 280 nm, both complexes underwent a clean conversion to  $[\text{Pt}(\text{CN})_4]^{2-}$  in water and in ethanol as indicated by the spectral changes during the photolyses (Figs. 1 and 2). The final spectra were identical with that of  $[\text{Pt}(\text{CN})_4]^{2-}$  [5]. The quantum yields (Table I) were determined by measuring the change of extinction at 279 nm for  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Cl}]^{2-}$  and at 294 nm for  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Br}]^{2-}$ . In ethanol and water, the photolyses were accompanied by the evolution of  $\text{N}_2$ . While in aqueous solution free azide was not formed, some free azide was detected [6] when the photolyses were carried out in ethanol.

The electronic absorption spectra of *trans*- $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  and *trans*- $[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$  are shown in Figs. 3 and 4, respectively. Upon irradiating  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  ( $\lambda_{\text{irr}} = 230, 280, \text{ or } 340$  nm) and

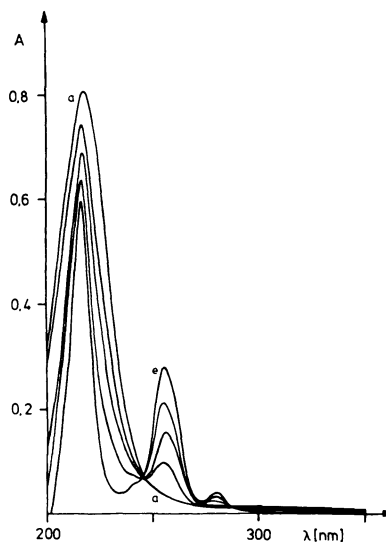


Fig. 3. Spectral changes during the photolysis of a solution of  $2.94 \cdot 10^{-5}$  M  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  in ethanol in a 1 cm cell with  $\lambda > 230$  nm; duration of irradiation between (a) initial and (e) final is 10 minutes.

Table I. Quantum yields for the formation of  $[\text{Pt}(\text{CN})_4]^{2-}$ .

Complex	$[\text{Pt}(\text{CN})_4\text{N}_3\text{Cl}]^{2-}$		$[\text{Pt}(\text{CN})_4\text{N}_3\text{Br}]^{2-}$		$[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$	$[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$
	ethanol	water	ethanol	water	ethanol	ethanol
irradiation wavelength	300 nm	300 nm	300 nm	300 nm	254 nm	254 nm
quantum yield $\phi$	$0.35 \pm 0.02$	$0.22 \pm 0.02$	$0.42 \pm 0.02$	$0.26 \pm 0.02$	$0.34 \pm 0.02$	$0.25 \pm 0.03$

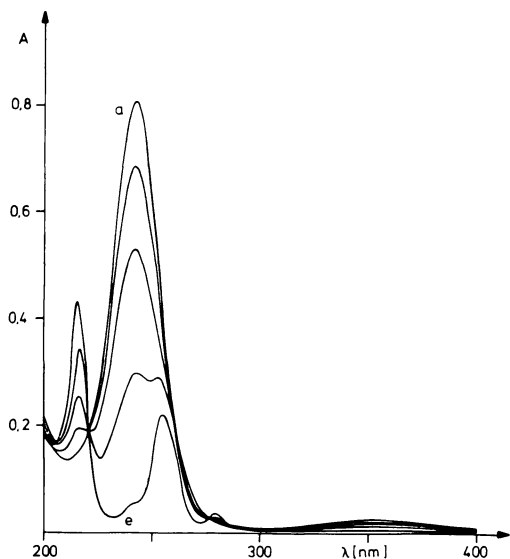


Fig. 4. Change in absorption spectrum during the photolysis of a solution of  $[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$  ( $1.81 \cdot 10^{-5} \text{ M}$ ) in ethanol in a 1 cm cell. Excitation wavelength:  $\lambda > 230 \text{ nm}$ ; duration of irradiation between (a) initial and (e) final is 10 minutes.

$[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$  ( $\lambda_{\text{irr}} > 230 \text{ nm}$ ) in ethanol, both complexes underwent an efficient conversion to  $[\text{Pt}(\text{CN})_4]^{2-}$  as indicated by the spectral variations during the photolyses (Figs. 3 and 4). Complete photoconversions to  $[\text{Pt}(\text{CN})_4]^{2-}$  were achieved. The final spectra were identical with that of  $[\text{Pt}(\text{CN})_4]^{2-}$  [5]. Quantum yields for the formation of  $[\text{Pt}(\text{CN})_4]^{2-}$  (Table I) were determined by measuring the change of extinction at 254 nm for  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  and at 243 nm for  $[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$ . Upon irradiation of  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  and  $[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$  in water, photolyses of both complexes took place. The formation of  $[\text{Pt}(\text{CN})_4]^{2-}$ , which was identified by its absorption maxima at 280 nm and 254 nm, was observed. However, the absence of isosbestic points indicated the occurrence of secondary thermal or photochemical reactions. In addition, the photolyses in water were apparently much less efficient than those in ethanol, since the spectral changes were much smaller than those in ethanol when the experimental conditions were the same.

For the identification of primary photoredox products by ESR spectroscopy, photolyses were carried out at 77 K in ethanol glasses. The irradiation of  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  yielded ESR signals which are assigned to  $\text{CH}_3\text{CHOH}$  radicals [7]. A five-line spectrum was obtained. Computer-simulation yield-

ed good agreement with experimental data using typical methyl-proton coupling (19 G) and an  $\alpha$ -proton tensor of  $-10$ ,  $-20$  and  $-30 \text{ G}$ . The  $g$ -tensor was assumed to be  $g_{\parallel} = 2.0025$  and  $g_{\perp} = 2.0040$ .

In the case of azide complexes additional signals appeared. These signals, which were most clearly seen for  $[\text{Pt}(\text{CN})_4(\text{N}_3)_2]^{2-}$  [1], are characteristic for N-atoms. The ESR spectrum shows a well resolved 1:1:1 triplet with  $g = 2.0026$  and a hyperfine coupling of 5.1 G. These data correlate with those given by Symons [8–10] for irradiated sodium azide. An analysis of the D-term was, however, impossible since the weak outer satellites expected for N-atoms were obscured by the ethanol radicals. N-atoms are known to be decomposition products of azide radicals [8–10]. A spectrum characteristic for Pt(III) [11, 12] species was not obtained for any of the complexes investigated.

## Discussion

The intense long-wavelength absorption bands of  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Cl}]^{2-}$  (Fig. 1) ( $\lambda_{\text{max}} = 279 \text{ nm}$ ;  $\epsilon = 12800$ ) and  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Br}]^{2-}$  (Fig. 2) ( $\lambda_{\text{max}} = 294 \text{ nm}$ ;  $\epsilon = 15200$ ) are assigned to CT (ligand to metal) transitions in analogy to  $[\text{Pt}(\text{CN})_4(\text{N}_3)_2]^{2-}$  [1]. This is also consistent with the photochemical behavior of both complexes.

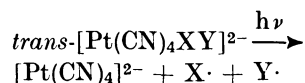
The electronic spectrum of  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  shows absorption maxima at 218 nm ( $\epsilon = 27500$ ), 284 nm ( $\epsilon = 522$ ), 333 nm ( $\epsilon = 220$ ) and that of  $[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$  at 243 nm ( $\epsilon = 44000$ ) and at 350 nm ( $\epsilon = 1200$ ). The assignment of these bands is less straightforward compared to the intense long wavelength absorptions of  $[\text{Pt}(\text{CN})_4\text{N}_3\text{X}]^{2-}$ . The less intense bands of  $[\text{Pt}(\text{CN})_4\text{X}_2]^{2-}$  and particularly the absorption maximum of  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  at 333 nm may also be assigned to LF transitions. However, the exact assignments are not crucial for the discussion of the photochemical results since the observed photochemical reactions were only of the redox type. It follows that the reactive excited states are CT (ligand to metal) states. If the longest-wavelength absorptions are indeed LF bands, the initially excited LF states would then undergo an efficient radiationless transition to a lower-lying reactive CT-state [13], since the redox reaction also took place upon irradiation of the longest-wavelength bands of  $[\text{Pt}(\text{CN})_4\text{X}_2]^{2-}$ .

Upon CT excitation aqueous and ethanolic solutions of  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Cl}]^{2-}$  and  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Br}]^{2-}$  were

completely reduced to  $[\text{Pt}(\text{CN})_4]^{2-}$ . Upon irradiation of  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  and  $[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$ , an efficient reduction to  $[\text{Pt}(\text{CN})_4]^{2-}$  was only observed in ethanol.

In ethanol glasses at 77 °K the irradiation of *trans*- $[\text{Pt}(\text{CN})_4\text{N}_3\text{Cl}]^{2-}$  and  $[\text{Pt}(\text{CN})_4\text{Cl}_2]^{2-}$  did not produce any Pt(III) species as indicated by the absence of ESR signals characteristic of Pt(III) [11, 12]. It follows that the photoreduction of Pt(IV) to Pt(II) should occur by a simultaneous two-electron transfer from the ligands to be eliminated. This is in agreement with an investigation of thermal redox reactions of *trans*- $[\text{Pt}(\text{CN})_4\text{X}_2]^{2-}$  complexes which apparently do not proceed via Pt(III) intermediates [2].

The mechanism of these photochemical reductive *trans*-eliminations is assumed to be analogous to that of  $[\text{Pt}(\text{CN})_4(\text{N}_3)_2]^{2-}$  [1]. The primary photochemical step should then proceed for all four complexes according to the equation



Generally efficient photoredox reactions of transition metal complexes, resulting in the reduction of the metal and oxidation of ligands, occur only if the photoreduced metal complex is kinetically very labile or if the oxidized ligand radicals are efficiently scavenged by secondary reactions [14, 15]. Otherwise recombination reactions regenerating the starting complex are frequently observed. Since  $[\text{Pt}(\text{CN})_4]^{2-}$  as a photoreduction product is very stable, the photoeliminated ligand radicals must be scavenged to prevent a recombination. Azide radicals formed in the primary photochemical step of the photolysis of  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Cl}]^{2-}$  and  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Br}]^{2-}$  are very unstable [8–10]. In water they decompose rapidly to yield molecular nitrogen. This instability of azide radicals seems to determine the light sensitivity of these complexes in aqueous solution, preventing an efficient regeneration of the starting complex.

In ethanol the decomposition of azide radicals yielding molecular nitrogen also took place. N-atoms as a decomposition product of azide radicals were observed in the low temperature photolysis. In addition, azide radicals in ethanol can also abstract H-atoms from the solvent with the formation of  $\text{HN}_3$  and ethanol radicals in a competing reaction as has been shown for  $[\text{Pt}(\text{CN})_4(\text{N}_3)_2]^{2-}$  [1]. This additional

scavenging reaction may explain the increase of the quantum yield of  $[\text{Pt}(\text{CN})_4]^{2-}$  formation in ethanol compared to water.

The fate of the halogen atoms which are also formed in the primary photochemical step with  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Cl}]^{2-}$  and  $[\text{Pt}(\text{CN})_4\text{N}_3\text{Br}]^{2-}$  in aqueous solution was not investigated further. However, as soon as the azide radicals are decomposed a regeneration of the starting complex is no longer possible. The halogen atoms may then yield halogen molecules  $\text{X}_2$  which at the low concentration used are not able to re-oxidize  $[\text{Pt}(\text{CN})_4]^{2-}$ . Alternatively, the halogen atoms may undergo secondary reactions with the solvent.

The photochemical behavior of  $[\text{Pt}(\text{CN})_4\text{X}_2]^{2-}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) is distinctly different, although there is no reason to expect any other mechanism for the primary photochemical step compared to the azide complexes. Hence  $[\text{Pt}(\text{CN})_4]^{2-}$  and two halogen atoms should be formed. However, in aqueous solution the  $[\text{Pt}(\text{CN})_4\text{X}_2]^{2-}$  complexes do not undergo an efficient photoredox reaction. In contrast to azide radicals which decompose rapidly in water no such decomposition path is available to halogen atoms. As a consequence, an efficient recombination regenerating the starting complex takes place. In ethanol the halogen atoms are scavenged by hydrogen abstraction from the solvent as indicated by the formation of ethanol radicals. This process can compete successfully with the recombination reactions as shown by the high quantum yields for the formation of  $[\text{Pt}(\text{CN})_4]^{2-}$  in ethanol.

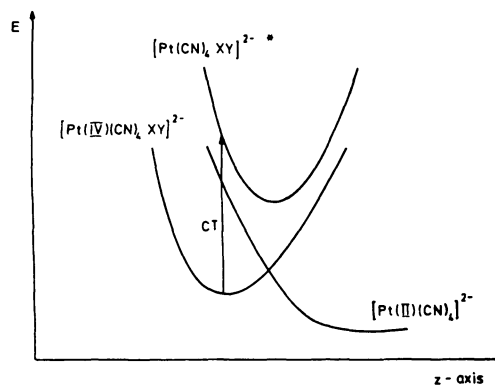


Fig. 5. Potential curve diagram of the electronic states participating in the photochemical reductive elimination of *trans*- $[\text{Pt}(\text{CN})_4\text{XY}]^{2-}$ . The X–Pt–Y axis is taken as z-axis.

The excited state processes of these photochemical reductive *trans*-eliminations may be explained by a qualitative potential energy diagram (Fig. 5) which has been applied to the electrochemical interconversion of  $[\text{Pt}(\text{CN})_4\text{X}_2]^{2-}/[\text{Pt}(\text{CN})_4]^{2-}$  [16]. The axial *z*-axis is taken as reaction coordinate since the geometrical changes which accompany the photo-reduction of *trans*-diacydotetracyanoplatinates(IV) of the general formula  $\text{trans}-[\text{Pt}(\text{CN})_4\text{XY}]^{2-}$  are mainly associated with variations of the axial X–Pt–Y bond lengths. The CT excitation of the pseudooctahedral  $d^6$  complexes  $\text{trans}-[\text{Pt}(\text{CN})_4\text{XY}]^{2-}$  leads to a CT excited state which by a very rough description contains Pt(III) with a  $d^7$  electron configuration. The potential curve of this excited state should be shifted to increased axial metal ligand distances due to the Jahn-Teller distortion which is expected for  $d^7$  systems. From this CT excited state, a radiationless transition may occur to the potential curve of the square planar  $d^8$  complex  $[\text{Pt}(\text{CN})_4]^{2-}$  leading to the final loss of the

axial ligands as radicals. The energy of the CT excited state relative to the  $d^6$  and  $d^8$  ground states is not known. If the CT state would be lowered in energy its potential curve may cross the  $d^6$  as well as the  $d^8$  curve and could then have a minimum outside of the  $d^6$  and  $d^8$  curves. In this case the CT excitation of the  $d^6$  complexes  $[\text{Pt}(\text{CN})_4\text{X}_2]^{2-}$  should lead to the existence of Pt(III) intermediates. The lifetime of these intermediates would be determined by the difference in energy between the minimum of the  $d^7$  state and the crossing points with the  $d^6$  and  $d^8$  potential curves. When this energy difference is sufficiently small an experimental distinction between a Pt(III) intermediate and a true CT excited state may become impossible. Since even at low temperatures Pt(III) species were not identified as photoproducts, the lifetime of such an intermediate must be very short, provided it is formed at all.

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