

Study of the Reactions of Platinum Macrocyclic Complex Ions with Free Radicals Formed by Pulse Radiolysis of Aqueous Media

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The near-diffusion-controlled reactions of hydroxyl radical, hydrated electron, and hydrogen atom with platinum macrocyclic complex ions in aqueous media have been studied using pulse radiolysis in conjunction with UV–visible absorption and conductivity detection. The hydrated electron and hydrogen atom react with *trans*-[Pt(cyclam)(Cl)₂]²⁺ where cyclam is 1,4,8,11-tetraazacyclotetradecane to yield platinum(III) transients that exhibit intense absorption peaks in the 280–300 nm region; however in the case of the H-atom, the reaction involves a competition between chloride abstraction and a minor process, suggested to be attack on the organic ligand. The platinum(III) products are kinetically labile toward loss of chloro ligands, but these reactions are reversible in the presence of added KCl. The reactions of hydroxyl radical with [Pt(cyclam)]²⁺ and with [Pt(tmc)]²⁺, where tmc is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, lead to platinum(III) intermediates absorbing in the 250–300 nm region. Depending on the presence or absence of added KCl and on the pH, the platinum(III) cyclam systems can react to form a product(s) exhibiting absorption peaks near 330 and 455 nm, and this species is proposed to be a long-lived amidoplatinum(III) complex. In support of this proposal is the observation that the tmc system does not give rise to a similar visible-absorbing product. The interrelations of the cyclam-based transients through acid–base, chloro-substitution and water-elimination processes are discussed.

Introduction

The use of macrocyclic ligands such as 1,4,8,11-tetraazacyclotetradecane (cyclam or [14]aneN₄) has offered many opportunities in recent years to stabilize transition metal complexes in which the metal center is in the unusual oxidation state of plus three.^{2–6} A paradigmatic case is monometallic nickel(III) complexes where the species are generally low-spin d⁷ systems exhibiting tetragonal distortion from octahedral microsymmetry. While nickel(III) complexes are relatively stable in the solid state and in aprotic media, they are considerably less stable in aqueous solution. Pulse radiolysis of aqueous media has made possible the investigation of transitory nickel species formed by reactions of strong single-electron oxidizing agents (hydroxyl radical and dihalogen anion radicals) with nickel(II) macrocyclic complexes.^{7–15} Considerable discussion has arisen as to whether the initial reaction is metal-centered attack or involves reaction

at a ligand site, and in regard to the longer-lived transients absorbing near 540 nm, the question of their being nickel(III) hydrolysis products, amidonickel(III) species or nickel(II) ligand-based radicals has been under debate.^{9,10,12–18}

In contrast to the numerous studies of nickel(III) complex ions, little information exists on other monometallic members of the nickel triad, namely Pd(III) and Pt(III) macrocyclic complexes.^{2,19,20} Investigations undertaken on platinum(III) complex ions containing halogen and acyclic ammine ligands indicate that platinum(III) complexes can exhibit both octahedral and square-planar types of structures.^{21–30} One of our objectives has been to investigate platinum(III) macrocyclic species in order

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to compare their characteristics to platinum(III) acyclic amines. To do this, use has been made of pulse radiolysis to study the reactions of hydroxyl radical, a strong oxidizing agent ($E^{\circ} \cong 1.9$ V), with square-planar type $[\text{Pt}(\text{cyclam})]^{2+}$ and with $[\text{Pt}(\text{tmc})]^{2+}$; the ligand tmc (or [14]ane $\text{N}(\text{CH}_3)_4$) is the 1,4,8,11-tetramethyl analog of cyclam.³¹ A further objective in comparing these two complexes is to obtain insight into the possible occurrence of amidoplatinum(III) products. In the case of the platinum acyclic amines, the longer-lived platinum(III) intermediates which exhibit absorption bands with peaks in the 300–500 nm region have been proposed to be amido complexes.^{27,28,30} For cyclam, which is a secondary amine, the possible formation of amidoplatinum(III) species is feasible through loss of a hydrogen from an N–H group of cyclam; however in the case of $[\text{Pt}(\text{tmc})]^{2+}$, this group is absent and thus one does not expect here formation of an amido product. As additional routes to the generation of platinum(III) species, the reactions of octahedral-like $\text{trans}-[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ with strong reducing agents, the hydrated electron ($E^{\circ} \cong -2.8$ V) and hydrogen atom ($E^{\circ} \cong -2.2$), have been investigated.³¹

Experimental Section

Apparatus and Dosimetry. The pulse radiolysis system and the associated conductivity and UV-visible optical detection equipment are described elsewhere.^{8,30} The transient phenomena discussed in this work represent differences between the signal for the irradiated solution and that for the unirradiated media, recorded at 20–23 °C. The dosimeter was tetranitromethane media,^{32,33} and the following G values have been taken for the primary aqueous species: $G_{e^-} = G_{\text{H}^+} = 2.7$, $G_{\text{OH}} = 2.8$, and $G_{\text{H}} = 0.55$.^{34,35} The equivalent ionic conductivities of the hydrogen ion, hydroxide ion and hydrated electron are 350, 197 and 190 $\Omega^{-1} \text{cm}^2$, respectively, and those for the complex ions have been taken as 70 $\Omega^{-1} \text{cm}^2$.^{34,36} The estimated error in wavelength is ± 5 nm.

Materials and Solutions. The *trans*-dichlorobis(ethylenediamine)-platinum(IV) perchlorate, *trans*- $[\text{Pt}(\text{en})_2(\text{Cl})_2](\text{ClO}_4)_2$, was available from a previous study,²⁸ and the preparation of the analogous *trans*-dichloro-(1,4,8,11-tetraazacyclotetradecane)platinum(IV) perchlorate, *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2](\text{ClO}_4)_2$, was as follows. The compound $[\text{Pt}(\text{NH}_3)_4](\text{ClO}_4)_2$ (1.5 mmol), was dissolved into 17-mL of a solution of *N,N*-dimethylformamide (BDH, reagent) containing 1.9 mmol of 1,4,8,11-tetraazacyclotetradecane (Alpha Products) at ca. 90 °C and the mixture was refluxed for 7 h. The resulting brown-black solution was filtered to remove the black particles and then the solution was cooled in an ice-bath, followed by bubbling with chlorine gas (3–5 min). The golden yellow solution was allowed to stand overnight at 5 °C, and the resulting pale yellow precipitate was collected and dried overnight over P_2O_5 . NMR spectra for ^{13}C and ^{35}Cl run in D_2O on a Bruker AM-300 FT-NMR using a broad-band probe at 75.47 and 29.41 MHz, respectively, were consistent with a *trans*-configuration for the complex.

The complex ions 1,4,8,11-tetraazacyclotetradecaneplatinum(II) $[\text{Pt}(\text{cyclam})]^{2+}$ and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecaneplatinum(II) $[\text{Pt}(\text{tmc})]^{2+}$ were prepared according to procedures similar to those described in the literature.³⁷ Slow evaporation of acetonitrile solutions yielded crystalline $[\text{Pt}(\text{tmc})](\text{ClO}_4) \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ and its recrystallization from water gave $[\text{Pt}(\text{tmc})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. X-ray crystallographic results indicated that the acetonitrile molecule occupies a

lattice site,³⁸ and both this solvate and the diaqua hydrate gave identical results in the pulse-radiolysis experiments. As shown by NMR (^{13}C , J -modulation, D_2O -solvent), the complex $[\text{Pt}(\text{tmc})]^{2+}$ exists as a mixture of two isomeric forms; the major isomer being the form with three methyls above the plane defined by PtN_4 and one methyl below (*RSSR*, Bosnich Type II) whereas the minor component (ca. 15%) has all methyls on one side of the plane (*RSRS*, Bosnich Type I); the latter form is that found in the solid.^{38,39} XRD results show the meso-*RRSS* configuration for both *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ and $[\text{Pt}(\text{cyclam})]^{2+}$,³⁷ and NMR results indicate that these forms persist in solution. All of the platinum compounds exhibited satisfactory C, H, and N analysis.

Caution! The perchlorate salts prepared in this work are potentially explosive and must be handled with great care.

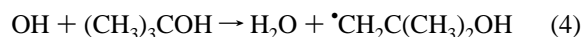
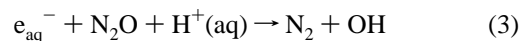
Other materials used in this study were of reagent quality. Because the hydrated electron and hydrogen atom formed on pulse irradiation of aqueous media are highly reactive toward dioxygen, solutions prepared from water obtained from a Millipore Super-Q system were deaerated by bubbling with argon or purified nitrous oxide. The latter reagent also reacts with e_{aq}^- to yield hydroxyl radical.³⁵ Solutions containing known amounts of dioxygen were prepared either by using a commercially available mixture of $\text{O}_2/\text{N}_2\text{O}$ (Linde AG, 19.9% O_2) or by adding aliquots of an oxygen-saturated aqueous solution to the matrix, and the concentration of oxygen was determined from the rate of the absorption decay of the hydrated electron in combination with the reported rate constant for its reaction with dioxygen.³¹ Changes to acidity or alkalinity were made by addition of perchloric acid or sodium hydroxide.

Results

Pulse irradiation of dilute aqueous solutions by 2–4 MeV electrons leads to the generation of aqueous free radicals, hydrogen ion, and small amounts of H_2 and H_2O_2 :

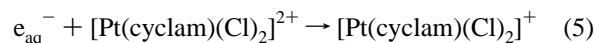


To minimize the possible occurrence of side reactions, use has been made of well-known scavenging agents to either interconvert the aqueous radicals or to form less reactive radicals as exemplified below for *tert*-butyl alcohol radical:



Apart from the e_{aq}^- , the above radicals do not contribute to conductivity changes nor do they absorb strongly at wavelengths used in this study.

Reaction of e_{aq}^- with *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$. Studies of the reactions of e_{aq}^- with other platinum(IV) complexes have shown that these processes occur very rapidly by electron transfer.^{8,27–31} The reaction of the platinum(IV)–cyclam complex is given by eq 5



for argon-saturated solutions at pH 4.0 to 10.7. Sufficient *tert*-butyl alcohol (*t*-BuOH) was added (0.042–0.21 M) to scavenge hydroxyl radical (eq 4) but not H-atom although the latter is a minor component (20% relative to e_{aq}^-). On the basis of the electron-decay rate at 600 nm for different concentrations of the platinum(IV) complex (20–200 μM), the calculated second-order rate constant for eq 5 is $(7.4 \pm 0.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$,

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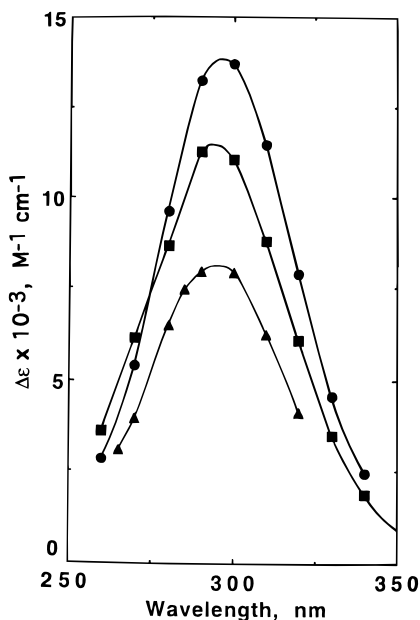
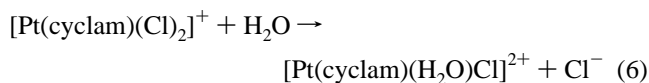


Figure 1. Absorption spectra arising from the reactions of e_{aq}^- and H-atom with $trans$ -[Pt(cyclam)Cl₂]²⁺. Key: (●) electron reaction with 199 μ M Pt complex at 3 μ s, 1.1 mM KCl, 3.8–4.8 μ M e_{aq}^- , 0.21 M *t*-BuOH, pH 4.2; (■) electron reaction with 201 μ M Pt complex at 5 μ s with no added chloride, ca. 1.4 μ M e_{aq}^- , 0.21 M *t*-BuOH, pH 4.3; (▲) H-atom reaction with 185 μ M Pt complex at 2 μ s, ca. 1.9 μ M H, 0.19 M *t*-BuOH, pH 2.0.

which is comparable to those found for other platinum(IV) complex ions.^{19,30} Concomitant with the decay of e_{aq}^- , a growth of an intense absorption band with a peak at 290 nm occurs as shown in Figure 1. In acidic media, the absorption change is accompanied by an increase in conductivity, associated in part with the generation of the hydrogen ion due to the irradiation process (eq 1). Saturation of the solutions with nitrous oxide reduces the initial absorption and conductivity changes by greater than 85% and no further alterations are found up to 1.5 ms, our longest observation period. This behavior confirms that the optical and conductivity signals are primarily associated with the reaction of e_{aq}^- and platinum(IV) complex.

Subsequent changes depend upon pH and the presence or absence of added chloride ion (KCl). In acidic solution without added KCl, the nascent growth of absorption in the 300 nm region is followed by a rapid decay of about 25%, with a first-order rate constant of $(2.7 \pm 0.2) \times 10^5 \text{ s}^{-1}$ ($\lambda = 290\text{--}330 \text{ nm}$). During this stage, the conductivity signal increases to a value of $420 \Omega^{-1} \text{ cm}^2$ which agrees with that predicted of $425 \Omega^{-1} \text{ cm}^2$ for the sequence of processes consisting of the generation of hydrogen ion (eq 1), reaction of e_{aq}^- (eq 5) and followed rapidly by eq 6.



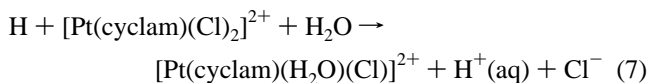
Addition of KCl (82 μ M to 2.47 mM) enhances the initial absorption level, and the subsequent aforementioned decay is suppressed. Above 1.1 mM added KCl, no further absorption growth occurs and the peak maximum is at 300 nm ($\Delta\epsilon = 13\,600 \text{ M}^{-1} \text{ cm}^{-1}$) as shown in Figure 1. The initial conductivity change is now $295 \Omega^{-1} \text{ cm}^2$ close to the value of $280 \Omega^{-1} \text{ cm}^2$ predicted for the combination of eqs 1 and 5. The foregoing features indicate that [Pt(cyclam)(Cl)₂]⁺ formed by the electron-reaction (eq 5) is labile toward loss of chloride as in eq 6 and this latter reaction is reversible. The intense absorption band at 300 nm (Figure 1, 1.1 mM added KCl) can be assigned

primarily to the absorption of [Pt(cyclam)(Cl)₂]⁺. In the absence of added chloride ion, a general long-term decrease in absorption occurs with an apparent first-order rate law ($t_{1/2} = 8 \text{ ms}$). At the same rate, a further conductivity increase takes place that by 35 ms attains a value of $680 \Omega^{-1} \text{ cm}^2$, indicating in part the release of the second chloro ligand to yield [Pt(cyclam)(H₂O)₂]³⁺.

The situation in basic media (pH 9.5–10.7) is remarkably different from that found in acidic solutions as now new absorption bands occur with peaks at 340 and 450 nm (Figure in Supporting Information). Concomitant with the growth in the 450 nm-absorption band, the band at 300 nm decays by a first-order process with the respective first-order rate constants being $(3.9 \pm 0.4) \times 10^5 \text{ s}^{-1}$ ($\lambda = 290\text{--}320 \text{ nm}$) and $(4.1 \pm 0.5) \times 10^5 \text{ s}^{-1}$ ($\lambda = 440\text{--}460 \text{ nm}$). These values are comparable to that found in acidic media for release of chloride ion (eq 6). While development of these new absorption bands (340 and 450 nm) requires a basic medium, the rate of formation at 450 nm is independent of hydroxide concentration. These features show the likelihood that release of chloride ligand(s) is rate controlling and is followed rapidly by the resulting aqua complex (eq 6) reacting with hydroxide ion to the generate 340/450-nm species. The intensities of the bands at 340 and 450 nm increase with pH, reaching at pH 10.0 a maximum: $\Delta\epsilon$ values of $1550 \text{ M}^{-1} \text{ cm}^{-1}$ (340 nm) and $1200 \text{ M}^{-1} \text{ cm}^{-1}$ (450 nm) with a $\Delta\epsilon$ ratio of $(1.3 \pm 0.2)/1$.

The subsequent decays of the 340/450 nm bands follow neither first- nor second-order rate laws, but both bands disappear with the same rate, indicating that these bands pertain to the same intermediate. The electron reaction with $trans$ -[Pt(en)₂(Cl)₂]²⁺ in basic media also shows behavior similar to that described above: the locations of the peaks in the visible region and their relative magnitudes closely parallel those found here for the cyclam complex. In the former case, the results are consistent with the species absorbing in the visible being [Pt(en)(en-H)]²⁺ where en-H designates an ethylenediamine ligand that has lost a proton from one of the coordinating nitrogen centers.^{23,30} We propose that the cyclam-intermediate is the analogous amido species [Pt(cyclam-H)]²⁺ (see below).

Reaction of Hydrogen Atom with $trans$ -[Pt(cyclam)(Cl)₂]²⁺. Investigations of H-atom reactions with [PtCl₆]²⁻ and $trans$ -[Pt(en)₂(Cl)₂]²⁺ show that these reactions proceed by chlorine-abstraction to yield platinum(III) products.^{28,29} The reaction of H-atom with $trans$ -[Pt(cyclam)(Cl)₂]²⁺ is thus anticipated to be that of eq 7 for acidified deaerated solutions



containing 51–185 μ M platinum(IV) complex and 0.05–0.2 M *t*-BuOH. At pHs of 2.0 to 2.7, the hydrated electron is converted into H-atom (eq 2), and *tert*-butyl alcohol will scavenge hydroxyl radical (eq 4) but not H-atom.³¹ Under these conditions, a rapid absorption growth occurs with a peak at 295 nm as shown in Figure 1. The rate is linearly proportional to the platinum(IV) concentration, and the calculated second-order rate constant is $(1.0 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Saturation of the solution with dioxygen to scavenge the H-atom decreases the absorption and conductivity signals by 80% and 95%, respectively, indicating the signals derive from the H-atom reaction: the small residual absorption is attributable to the peroxy radical formed by the reaction of dioxygen with *tert*-butyl alcohol radical.

The initial absorption growth is rapidly followed by decreases absorption with the peak shifting to 290 nm via an apparent

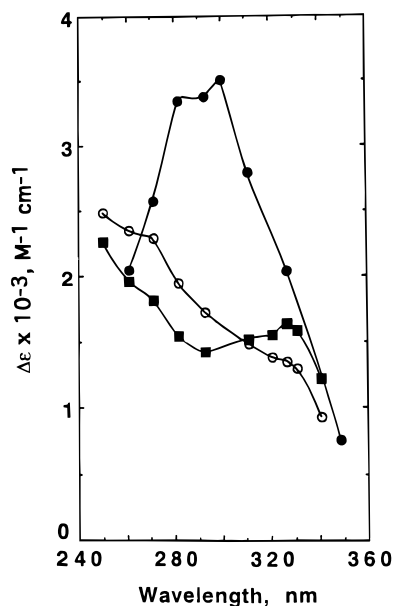
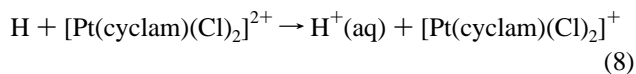


Figure 2. Absorption spectra arising from the reaction of OH and $[\text{Pt}(\text{cyclam})]^{2+}$ at pH 3.1 in N_2O -saturated solutions. Key: (○) 0.25 μs and (■) 3.5 μs , 846 μM Pt complex, 3 μM OH; (●) 1 ms, 290 μM Pt complex, 52 μM KCl, 1.6 μM OH.

first-order rate law ($k = (2.3 \pm 0.2) \times 10^5 \text{ s}^{-1}$). Accompanying the absorption growth and subsequent decay, two stages of conductivity increase occur; however, these stages could not be clearly resolved for kinetic measurements. Qualitatively, these changes are consistent with the occurrence of eq 7 followed by loss of chloride from the monochloro platinum(III) product, but quantitatively, the conductivity level was only about half that expected. To further investigate this aspect, the H-atom reaction was studied in the presence of 1.0 mM KCl where the expectation (based upon the electron-reaction results) is that the *net overall* reaction will be that of eq 8 with the



process of eq 7 being somewhat slower than the anation rate for the monochloro product. On irradiation, the absorption features are nearly identical to those shown in Figure 1 for the electron product, which is ascribed to $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^+$ in the presence of 1.1 mM KCl; however *both* the levels of absorbance and conductivity changes are only 75% of those anticipated for eq 8. These features indicate that while the major H-atom reaction is one of chloride abstraction as in eq 7, there is a minor process that is not associated with either a conductivity change or formation of a strongly absorbing product, and this may arise by H-atom attack on the organic ligand.

Reaction of Hydroxyl Radical with $[\text{Pt}(\text{cyclam})]^{2+}$. The reactions of hydroxyl radical have been studied in nitrous oxide saturated solutions to insure that the hydrated electron formed by the irradiation pulse is converted very rapidly into OH via eq 3.³¹ The following conditions were used: 164–846 μM $[\text{Pt}(\text{cyclam})]^{2+}$ at pHs 2.75–4.6 and 16–422 μM $[\text{Pt}(\text{cyclam})]^{2+}$ at pHs 8.7–10.0. On irradiation, absorption increases occurred in the near-UV–visible region as exemplified in Figures 2 and 3 with the specific change observed depending upon the pH and the presence or absence of added KCl. Addition of *tert*-butyl alcohol (0.23–0.52 M) eliminated the absorption changes, indicating that they arise from the reaction of OH and $[\text{Pt}(\text{cyclam})]^{2+}$.

At pH 4.4 and 846 μM platinum(II) complex, the initial absorption occurs with a maximum near 270 nm ($\Delta\epsilon$ ca. 2600

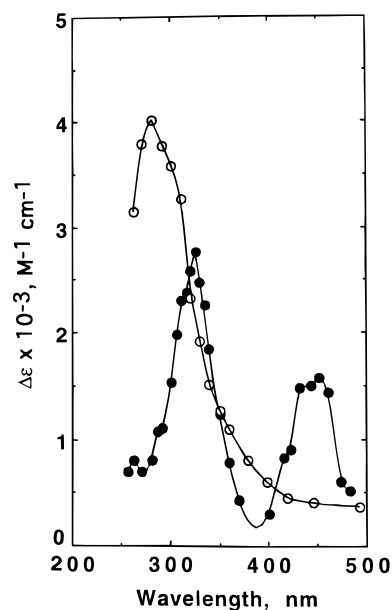
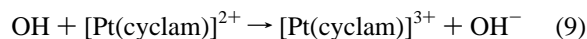


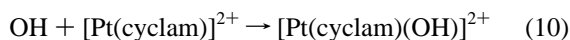
Figure 3. Absorption spectra arising from the OH-reaction of $[\text{Pt}(\text{cyclam})]^{2+}$ and $[\text{Pt}(\text{tmc})]^{2+}$ at pH 3.9–4.1 in N_2O saturated solutions at 5 μs . Key: (○) 249 μM $[\text{Pt}(\text{tmc})]^{2+}$, 2.5 μM OH; (●) 164 μM and 310 μM $[\text{Pt}(\text{cyclam})]^{2+}$, 1.5–2.5 μM OH.

$\text{M}^{-1} \text{ cm}^{-1}$) which decays very rapidly with a concomitant growth of new absorption bands with peaks at 325 nm ($\Delta\epsilon = 2760 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$) and at 455 nm ($\Delta\epsilon = 1580 \pm 70 \text{ M}^{-1} \text{ cm}^{-1}$) with a $\Delta\epsilon$ ratio of $(1.8 \pm 0.1)/1$ as shown in Figure 3. Both the decay and growth occur with the same first-order rate constant of $(1.6 \pm 0.1) \times 10^6 \text{ s}^{-1}$. In basic media, only the two visible bands are detectable, suggesting that the interconversion process may be base-catalyzed. At pH 9.7, the peak locations are now at 330 nm ($\Delta\epsilon = 2700 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$) and at 455 nm ($\Delta\epsilon = 1900 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$) with a $\Delta\epsilon$ ratio of $(1.4 \pm 0.2)/1$. These features are very similar to those encountered in basic media from the reaction of e_{aq}^- and *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$, suggesting that the same or very similar species are being observed (see Discussion). The foregoing absorption bands remained unchanged for times up to 0.5 s in the pH-interval of 4.1–9.7. Because of the very short lifetime of the nascent OH-product absorbing near 270 nm, the rate constant of the reaction between OH and $[\text{Pt}(\text{cyclam})]^{2+}$ was measured at pH 8.8 by monitoring the growths of the 330 and 455 nm bands but at low complex concentrations (16 and 32 μM) where the nascent reaction would be slower than the interconversion process. These measurements yield a calculated second-order rate constant of $(7 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ that is close to the OH-rate constants reported for $[\text{Pt}(\text{en})_2]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$.^{15,30}

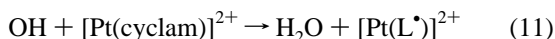
A salient feature associated with the absorption changes is that there was *no accompanying change in conductivity* ($\Delta\Delta \leq |40| \Omega^{-1} \text{ cm}^2$) in the pH-range of 4.1–9.7 either at short times or at longer times (up to 18 ms, our longest observation period). The *absence* of a conductivity change rules out a charge transfer process as in eq 9 because if this was to occur



then major changes in conductivity would occur. Two possible OH-processes consistent with no conductivity change are OH-bond formation to the metal center (eq 10) or H-abstraction from

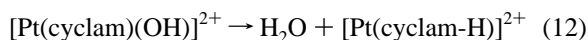


a carbon center of the ligand to yield a ligand-based radical as in eq 11 ($\text{L}^\bullet = \text{ligand radical}$).



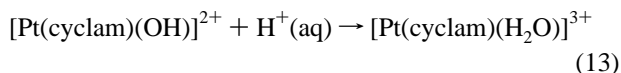
Two considerations suggest that the ligand-abstraction mode (eq 11) is at most a minor pathway. Firstly, the absorption and conductivity patterns encountered in the reaction of OH with $[\text{Pt}(\text{NH}_3)_4]^{2+}$ where no potential carbon-center exists strongly parallel the behaviors described above for the platinum(II)-cyclam complex.²⁷ Furthermore, one anticipates carbon-based radicals to be highly reactive towards molecular oxygen.^{12,40} To investigate this latter possibility, a solution at pH 9.7 and saturated with a mixture of 20% O₂/80% N₂O was irradiated, and the decay of the 330/455-nm species measured on the 100 ms time scale. Because of the longevity of this change, it was not feasible experimentally to measure the rate law; however, the time scale suggests a small dioxygen rate constant, one below $1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.⁴¹ This lack of reactivity towards oxygen is *not* supportive of the 330/455 nm species being a carbon-based free radical but it is consistent with a platinum(III) complex (eq 10).

We propose that the initially observed product absorbing below 300 nm at pH 4.4 is the species $[\text{Pt}(\text{cyclam})(\text{OH})]^{2+}$ (or $[\text{Pt}(\text{cyclam})(\text{H}_2\text{O})(\text{OH})]^{2+}$ as described in the Discussion). Since its interconversion to the 330/455-nm species takes place *without a change in conductivity*, this process is consistent with a reaction involving water-elimination as in eq 12. The product



with absorption maxima at 330 nm and 455 nm is the same or very similar species to that encountered in the reaction of the hydrated electron with *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$.

Between pHs 3.9 and 2.75, a number of major changes occur relative to the situation for pHs >4.0. The initial absorption in the near-UV shifts to the blue and as shown in Figure 2; the peak appears to be at or below 250 nm whereas at pH 4.4, a broad peak occurs near 270 nm. The formation of the amido complex as represented by the two absorption bands (Figure 3) takes place in two stages in contrast to only one discernible stage at pH ≥ 4.4 , and these stages become better resolved in time as the concentration of hydrogen ion is increased. The first stage is characterized by increased rate of formation of the visible absorption bands but at the same time, the maximum absorbance-level decreases (Figure 2) and these optical changes are accompanied by a progressive decrease in conductivity. A plot of the ratio of the maximum absorption at pH 4.4 to the absorption values at lower pHs (2.75–3.9) vs the hydrogen ion concentration is linear. This behavior, which is analogous to those reported for platinum(III) ammonia and ethylenediamine complexes,^{27,30} is consistent with the water-elimination process (eq 12) being in competition with protonation of the hydroxo ligand (eq 13) with the latter being responsible for the decrease

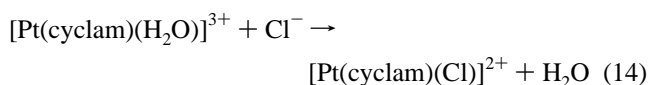


in conductivity with increasing hydrogen ion concentration. The slope of the aforementioned plot gives the ratio of k_{13}/k_{12} as 840 M^{-1} . Assuming that the maximum conductivity change (eq 13) will be ca. $-280 \text{ } \Omega^{-1} \text{ cm}^2$, a second estimate of the k_{13}/k_{12} ratio is 740 M^{-1} . Using an average ratio of 790 M^{-1}

and the value for k_{12} ($=1.6 \times 10^6 \text{ s}^{-1}$), the value of k_{13} is calculated to be $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The second stage in the development of the 330/455-nm species is accompanied by a partial recovery of conductivity toward the zero-level, and these changes become smaller and slower in time as the hydrogen-ion concentration increases. The fact that the development of absorption does not attain the values found at pH 4.4 indicates the reverse reaction of eq 13 is itself in competition with a decay process that does not lead to an observed product(s).

With added chloride ion (10–52 μM ; pH 3.0), this second stage of growth in the 330/455-nm absorption bands is eliminated and one now sees a new absorption band centered around 290 nm (Figure 2), accompanied by a slight further decrease in conductivity. The absorption level increases with increasing chloride-ion concentration, and a plot of the associated first-order rate constant versus added-chloride concentration is linear: $k_{\text{obs}} = 600 + (1.7 \times 10^8)[\text{Cl}^-]$. This growth plus the slight decrease in conductivity show the occurrence of an anation process, eq 14. Because of the need to restrict the KCl



concentrations to avoid the reaction of OH and Cl^- , it was not possible to determine if the reaction of eq 14 reached completion.³¹ However, based upon the level of conductivity change that provides a measure of the extent to which eqs 13 and 14 occur, one anticipates the actual absorption coefficient of the 290 nm peak to be about twice that shown in Figure 2. This level would be slightly larger than the value found for the hydrogen atom reaction but considerably less than the absorption attributed to $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^+$ in Figure 1, suggesting that, at 50 μM added KCl, one is observing predominately the monochloro species.

Reaction of Hydroxyl Radical with $[\text{Pt}(\text{tmc})]^{2+}$. The results for $[\text{Pt}(\text{cyclam})]^{2+}$ implicate the loss of hydrogen from one of the secondary amine groups as an essential feature for the water-elimination process (eq 12). To investigate further this key aspect, studies have been undertaken on the complex $[\text{Pt}(\text{tmc})]^{2+}$ where four *N*-methyl groups exist in place of the four *N*-H groups of cyclam and complex concentrations ranged from 30 to 542 μM for the pH ranges 2.9–4.1 and 9.85–10.5. On irradiation, an absorption band appears with a peak at 290 nm ($\Delta\epsilon = 3800 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$; pH 3.8–9.9) as shown in Figure 3. Its rate of growth ($\lambda = 270$ –330 nm) leads to a calculated second-order rate constant of $(3.9 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Addition of 0.21 M *tert*-butyl alcohol decreases the absorption at 290 and 350 nm by greater than 90%, indicating that the absorption change is due primarily to the reaction of OH with $[\text{Pt}(\text{tmc})]^{2+}$. Subsequently very little further change occurs; however, at longer periods ($> 1 \text{ ms}$), a general decay takes place, obeying a second-order rate law with $2k \cong 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (pH 4.0). In basic media at 290 nm and 300 nm, the $2k$ value increases linearly with hydroxide ion concentration, giving an apparent third-order rate constant of $(9 \pm 1) \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$. As no conductivity changes ($\Delta\Lambda \leq \Omega [40] \text{ } \Omega^{-1} \text{ cm}^2$) are associated with the absorption measurements, the OH reaction involves either HO–Pt bond formation or ligand attack in analogy to eqs 10 and 11, respectively. Addition of O₂ at pH 9.9 does cause a slight decrease in the absorption band at shorter times ($< 1 \text{ ms}$), but the change is not uniform with wavelength; the largest relative decrease ($< 20\%$) occurs at wavelengths above 300 nm. The major effect of dioxygen (141–327 μM) is to enhance the long-term general decrease in absorption, but

(40) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 413.

(41) On the tens of microsecond scale, a small wavelength-independent decrease occurred and this can be attributed at least partly to the reaction of the complex with a small amount of O₂^{•-} formed via the reaction of the H atom with O₂.³¹

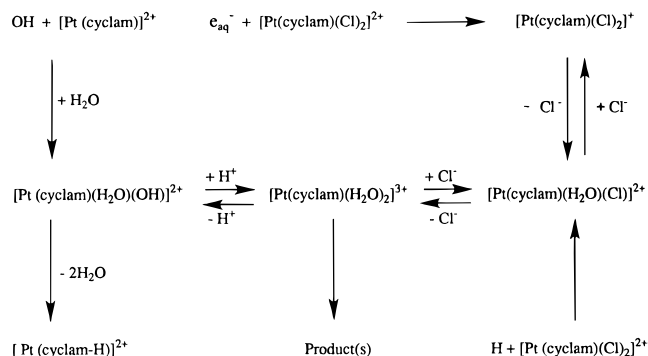
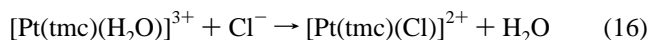
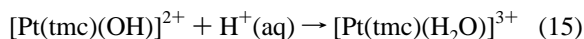


Figure 4. Mechanism for platinum(III) cyclam intermediates.

as this enhancement is not easily resolved from the decay rate found in the absence of dioxygen, one can only set an upper limit to the rate constant of ca. $1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for an oxygen reaction.

In contrast to the above circumstances where no conductivity change is detected, a progressive decrease in conductivity occurs with increasing hydrogen-ion concentration (pH 3.8–2.6), reaching an observed value of $-225 \Omega^{-1} \text{ cm}^2$ at pH 2.6. The absorption spectra remain relatively unchanged in comparison to Figure 3. Addition of KCl at pH 2.9 ($10\text{--}52 \mu\text{M}$) causes a shift of the peak to 300 nm ($\Delta\epsilon = 4200 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$) accompanied by a further small decrease in conductivity ($\Delta(\Delta\epsilon)$ ca. $-45 \Omega^{-1} \text{ cm}^2$). These effects seem qualitatively similar to the features found for the cyclam case (eqs 13 and 14):



Since the absorption level at 300 nm remains the same at $52 \mu\text{M}$ KCl as at $26 \mu\text{M}$ KCl, one presumes that the reaction of eq 16 went to completion. The expected conductivity change for the sum of eqs 15 and 16 is $-425 \Omega^{-1} \text{ cm}^2$ whereas the observed change is $-270 \pm 20 \Omega^{-1} \text{ cm}^2$. This discrepancy together with the small absorption decrease in the presence of O_2 described above suggest that the possible occurrence of ligand attack by hydroxyl radical but the major process involves OH-bond formation to the metal center to give a platinum(III) complex ion. Unlike the cyclam case, the results in both acidic and basic media for the reaction of $[\text{Pt}(\text{tmc})]^{2+}$ with hydroxyl radical give *no* discernible evidence for an interconversion process analogous to that of eq 12.

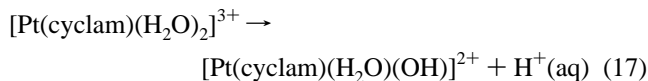
Discussion

The mechanism proposed to interrelate the various platinum(III)–cyclam species is given in Figure 4, and it parallels the pathways found for platinum(III) ions containing ammonia and ethylenediamine ligand systems.^{27,28,30} The reactions of e_{aq}^- and H atom with *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ and that of hydroxyl radical with $[\text{Pt}(\text{cyclam})]^{2+}$ serve as three different entry points to the scheme. The platinum(III) transients can be grouped into two categories based upon their absorption features. One category is represented by the long-lived species having peaks near 330 nm and 450 nm. The initial reaction products are characterized by a single-intense near-UV absorption band as exemplified by $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ with a peak at 300 nm (Figure 1).

The products of eqs 10, 13, and 14 have been presented as five-coordinated complex ions $[\text{Pt}(\text{cyclam})(\text{OH})]^{2+}$, $[\text{Pt}(\text{cyclam})(\text{H}_2\text{O})]^{3+}$, and $[\text{Pt}(\text{cyclam})(\text{Cl})]^{2+}$, respectively, based upon the

kinetic findings; however, these species also exhibit intense absorption bands in the 250–300 nm region. In view of this similarity to $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$, these complexes are likely to be tetragonally distorted octahedral systems with the sixth coordination position being occupied by a water molecule. This supposition is in keeping with earlier findings on related platinum(III) amine systems and with the results of a recent single-crystal EPR study of X-irradiated bis(ethylenediamine)-platinum(II) bis(hydrogen squarate) where the platinum(III) product is a low-spin d^7 complex.^{24,27,28,30}

In the reaction of OH and $[\text{Pt}(\text{cyclam})]^{2+}$, the fate of the initial product $[\text{Pt}(\text{cyclam})(\text{H}_2\text{O})(\text{OH})]^{2+}$ depends upon the relative rates of the two competitive pathways, water-elimination (eq 12) versus protonation (eq 13). At pHs below 4, the rate of protonation increases with increasing hydrogen-ion concentration whereas the competitiveness of eq 12 in forming the product $[\text{Pt}(\text{cyclam}-\text{H})]^{2+}$ with peaks near 330 and 450 nm decreases. This product is also formed at a second stage but this becomes slower and lesser in amount with decreasing pH. The presence of this stage indicates not only that the protonation process is reversible (eq 17) but also that the diaqua complex can decay



by another route to an unobserved product(s). As the latter process seems minor, then the apparent first-order rate constant k_{obs} describing the second stage is given approximately by $(k_{12})(k_{17}/k_{13})\{1/[\text{H}^+(\text{aq})]\}$.²³ At pH 3.0, k_{obs} equals $(1.9 \pm 0.3) \times 10^3 \text{ s}^{-1}$ as measured at 330 nm and 445 nm, and this value in combination with k_{12} ($1.6 \times 10^6 \text{ s}^{-1}$) yields for the diaqua complex the first $\text{p}K_{\text{a}}$ of ca. 5.9. This value is close to those found for $[\text{Pt}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ ($\text{p}K_{\text{a}}$ 6.4) and for $[\text{Pt}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$ ($\text{p}K_{\text{a}}$ 6.8).²⁷

With added chloride ion ($11\text{--}52 \mu\text{M}$ KCl) at pH 3.0, *no* second-stage of growth stage for the 330/450-nm species takes place but instead a new intense absorption band with a peak near 290 nm occurs (Figure 2) involving in part the formation of $[\text{Pt}(\text{cyclam})(\text{H}_2\text{O})(\text{Cl})]^{2+}$ via eq 14. The observed first-order rate constant for the formation of the monochloro complex is given by a two-term rate expression (Results). Assuming that this situation approximates an approach to equilibrium, the formation constant K_{f} for the monochloro complex (eq 14) is calculated to be about $3 \times 10^5 \text{ M}^{-1}$. Due in part the overlapping spectra in the region of 250–300 nm, the value of K'_{f} for the dichloro complex (reverse reaction of eq 6) is problematical; however as the absorption derived from the reaction of e_{aq}^- and $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ (Figure 1) does not change between 1.1 and 2.47 mM added KCl, one surmises that K'_{f} is about 10^3 M^{-1} . Furthermore, the slow decays of the monochloro and dichloro complex ions in acidic media (steps not shown in Figure 4) presumably involve in part reactions between these species and between like-species. When the electron reaction with *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ is carried out in *basic* media, one observes at the secondary level the formation of $[\text{Pt}(\text{cyclam}-\text{H})]^{2+}$. As portrayed in Figure 4, this route involves the sequence from $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ to $[\text{Pt}(\text{cyclam})(\text{H}_2\text{O})(\text{OH})]^{2+}$; however, a more direct route to $[\text{Pt}(\text{cyclam}-\text{H})]^{2+}$ occurs in the reaction of hydroxyl radical with $[\text{Pt}(\text{cyclam})]^{2+}$ at pH > 4 where eq 10 is followed by eq 12. A key feature of this pathway is that it occurs *without* a change in conductivity. This absence is consistent with the proposed water-elimination reaction, and it distinguishes this process from other possible candidates, e.g. formation of $[\text{Pt}(\text{cyclam})(\text{OH})_2]^{2+}$ or of $[\text{Pt}(\text{cyclam})]^{3+}$, either of which would entail major changes in conductivity. The

importance of the N–H group to the proposed water-elimination reaction is further demonstrated by the *absence* of a process analogous to eq 12 for $[\text{Pt}(\text{tmc})]^{2+}$ where the N–H group has been replaced by a N–CH₃ combination.

These features, plus the fact that, in basic media, *both* the electron reaction with *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ (a reduction process) and the OH-reaction with $[\text{Pt}(\text{cyclam})]^{2+}$ (an oxidation path) give similar, if not identical species, lead us to propose that this species is an amidoplatinum(III) complex $[\text{Pt}(\text{cyclam-H})]^{2+}$. Its very different spectral properties and greater longevity from those of the UV-absorbing octahedral-type complexes implicate a different structure and one likely to be a limiting square planar form.^{27,29,30} Only a few monometallic platinum(III) complexes have been structurally characterized, and these have limiting square-planar forms.^{2,21} Recently De Santis and co-workers have proposed that the red intermediate encountered in the pulse radiolysis and electrochemistry of nickel(II) cyclam is an analogous amidonickel(III), $[\text{Ni}(\text{cyclam-H})]^{2+}$.¹⁷ Others have proposed, however, for the nickel cyclam and related macrocyclic systems that species absorbing near 540 nm are nickel(III) hydrolysis products of the form $\text{NiL}(\text{OH})^{2+}$ (L = macrocycle) or nickel(II) ligand-based free radicals.^{10–16} Moliere and Patterson in their studies of the reactions of hydroxyl radical with the nickel(II) macrocyclic complexes $\text{Ni}(\text{CR}+4\text{H})$, $\text{Ni}(\text{CR}-2\text{H})$, and $\text{Ni}(\text{CR})(\text{H}_2\text{O})_2$ found the formation of a ligand radical product for the latter complex and mixtures of ligand radical and nickel(III) species for the first two complexes.¹² These ligand-radical species exhibit very high reactivity toward dioxygen with rate constants of ca. $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In the present study, one can not entirely discount some formation of Pt(II) ligand-radical species formed via eq 11, particularly for $[\text{Pt}(\text{tmc})]^{2+}$; however, the major products $[\text{Pt}(\text{cyclam-H})]^{2+}$ and $[\text{Pt}(\text{tmc})(\text{OH})]^{2+}$ are orders of magnitude lower in reactivity toward O₂ (rate constants $\ll 10^5 \text{ M}^{-1} \text{ s}^{-1}$) than the nickel ligand-radical products. This comparison suggests that the platinum intermediates can reasonably be described as metal-centered d⁷ systems.

The comparison of the absorption spectra obtained for $[\text{Pt}(\text{cyclam-H})]^{2+}$ in acidic solution (Figure 3) with that for basic media (Figure in Supporting Information) suggests some difference which is outside of experimental error. For the OH-reaction with $[\text{Pt}(\text{cyclam})]^{2+}$, the peak molar absorption coefficient ratio in acidic solution is $(1.8 \pm 0.1/1)$ for $\epsilon_{325}/\epsilon_{455}$ whereas in basic solution $\epsilon_{330}/\epsilon_{455}$ is $(1.4 \pm 0.2/1)$. By contrast, in the case of $[\text{Pt}(\text{en})(\text{en-H})]^{2+}$, the ratios of the corresponding two bands ($\epsilon_{340}/\epsilon_{480} = (1.9 \pm 0.1)/1$) are the same in acidic and basic media.³⁰ A possible explanation for the cyclam case, which would not apply for the ethylenediamine system, is the occurrence of invertomers. In *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ and $[\text{Pt}(\text{cyclam})]^{2+}$, the cyclam conformation is in the *meso-RRSS* form (see Experimental Section). The formation of $[\text{Pt}(\text{cyclam-H})]^{2+}$ with its amido site offers through proton exchange, a possible means to interconvert the different isomeric forms. One presumes that in basic media (pH 10), hydroxide ion may rapidly catalyze the exchange so that $[\text{Pt}(\text{cyclam-H})]^{2+}$ is representative of a mixture of isomers whereas in acidic media (pH 4) exchange may be too slow to observe on the pulse radiolysis

time scale with the consequence that the conformation of $[\text{Pt}(\text{cyclam})]^{2+}$ is retained by the amidoplatinum(III) species.

The $[\text{Pt}(\text{cyclam-H})]^{2+}$ species formed via the OH-reaction with $[\text{Pt}(\text{cyclam})]^{2+}$ (eqs 10 and 12) is unreactive to added 56 μM KCl in contrast to the high reactivity of the proposed octahedral-type complex $[\text{Pt}(\text{cyclam})(\text{H}_2\text{O})(\text{OH})]^{2+}$ (eq 14). Furthermore in the pH range 4–9.7, the amidoplatinum(III) complex appears to be stable for periods of up to 0.5 s and its greater stability relative to those of the platinum(III) octahedral-types ions may be due in part to some degree of π -bonding between the metal and the amido ligand.¹⁸ In the case of $[\text{Pt}(\text{cyclam-H})]^{2+}$ generated through the reaction of e_{aq}^- and *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ at pH 10, the amidoplatinum(III) decays faster with dose-dependent mixed-order kinetics (first $t_{1/2}$ 80–160 μs); however, *tert*-butyl alcohol radical is now present (eq 4), so the decay of $[\text{Pt}(\text{cyclam-H})]^{2+}$ likely occurs by its reaction with the alcohol radical as found for other platinum(III) amine intermediates.^{27,30}

The ion $[\text{Pt}(\text{tmc})]^{2+}$ is in solution a mixture of two isomers (see Experimental Section), and thus the reaction of hydroxyl radical is expected to give rise to more than one product although only one broad absorption peak occurs (Figure 3). At short times, the presence of oxygen does lead to some absorption decrease, and while the change is small, it implicates the possible occurrence of ligand radical products, and the findings obtained at pH 3.0 with added KCl lend support to this possibility. In this latter context, chloride substitution can occur (eq 16), and because the absorption-level at 300 nm is approximately the same for 26 and 52 μM added KCl, one presumes that this reaction has gone to completion. On the basis of this assumption and also that the acid–base reaction of eq 15 is reversible, one anticipates the overall conductivity change for eqs 15 and 16 to be about $-425 \Omega^{-1} \text{ cm}^2$ whereas the experimental value is $-270 \pm 20 \Omega^{-1} \text{ cm}^2$. This difference suggests that perhaps 30% of the OH reaction may give rise to ligand-radical product(s), and consequently the estimation of the $\text{p}K_{\text{a}}$ for $[\text{Pt}(\text{tmc})(\text{H}_2\text{O})]^{2+}$ becomes problematical. On the millisecond time scale, a general absorption decay occurs (Figure 3), and the rate law obeys second-order kinetics. In basic media (pH 9.85–10.5) the values of the measured second-order rate constant increase linearly with hydroxide ion concentration. Because no net conductivity accompanies the optical decay, hydroxide ion is acting as a catalyst. The overall third-order character implies a multiple-step mechanism. Several processes can potentially explain the results, including base-catalyzed disproportionation or dimerization with the latter perhaps forming an oxo-dimer $\{[\text{Pt}(\text{tmc})]_2\text{O}\}^{4+}$; however, in the absence of product information, no clear choice can be made between such possibilities.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Figure of the absorption spectrum of the products arising in basic, aqueous media from the reaction of e_{aq}^- and *trans*- $[\text{Pt}(\text{cyclam})(\text{Cl})_2]^{2+}$ (1 page). Ordering information is given on any current masthead page.

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