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Formation and Characterization of Platinum(III)–Ethylenediamine Complex Ions Using Pulse Radiolysis

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Pulse radiolysis experiments using conductivity, polarographic and UV–visible absorption detection techniques have been carried out on the reaction of hydroxyl radical with bis(ethylenediamine)platinum(II) perchlorate in aqueous media. This reaction is shown to proceed by OH addition to the platinum center to yield a nascent product where the metal is in a formal oxidation state of III. The subsequent behavior of this Pt(III) transient generates three additional transients, whose formations are dependent upon the pH and presence of free chloride ion. A mechanism is proposed whereby these transients are interrelated through acid–base, chloride substitution, and water elimination processes. Evidence is presented to support the classification of the Pt(III) species into two groups having the compositions of $Pt(en)_2(X)^{n+}$ ($X = OH, H_2O, Cl$; $n = 2, 3$) and $Pt(en)(en\text{-}H)^{2+}$ ($en\text{-}H = {}^-NHCH_2CH_2NH_2$). For the former group, the respective wavelength maxima and molar absorption coefficients are 270 nm, ca. 4500 M^{-1} cm^{-1} ($X = OH$), <250 nm ($X = H_2O$), and 260 nm, 8000 M^{-1} cm^{-1} ($X = Cl$). For $Pt(en)(en\text{-}H)^{2+}$, two absorption bands are found with peaks at 340 nm (2900 M^{-1} cm^{-1}) and 480 nm (1500 M^{-1} cm^{-1}). This latter species is also the major product of the reaction of the hydrated electron and *trans*-dihydroxobis(ethylenediamine)platinum(IV) perchlorate which was investigated by absorption and conductivity techniques. The possible structures of these intermediates are discussed.

Introduction

A considerable number of reports have now appeared concerning the occurrence of platinum complexes where the metal center is formally in the unusual oxidation state of III.[2–19] Such occurrence has been associated with electrochemical, photolytic, thermal noncomplementary, and radiolytic reactions of platinum(II) and platinum(IV) compounds which involve 1-equiv electron changes. For complex ions containing halides, pseudohalides, NH_3, glycine, and amines such as ethylenediamine (en) as ligands, the platinum(III) species have a transitory existence. Consequently the application of the fast-reaction technique of pulse radiolysis (and to a lesser extent flash photolysis) has proven useful in generating and characterizing in a direct fashion these substances in aqueous media. Results of such studies not only have confirmed earlier suggestions as to their substitutional lability but also have introduced new facets, one being the possibility that the transients can exhibit different structures.[2,5,6,8,13,17,19]

Notwithstanding such recent developments, progress in characterizing Pt(III) transients has been restricted due to the presence of more than one transient, the limited number of different chemical routes employed to generate these species, and the reliance to date on only one detection technique, namely, UV–visible absorption spectroscopy. The complexity of the situation is exemplified by our earlier investigation of the reaction of hydroxyl radical with bis(ethylenediamine)platinum(II), $Pt(en)_2^{2+}$, where four transients were observed.[5] While these results clearly implied that the Pt(III) intermediates were interrelated by acid–base and substitution processes and that they might have different structural properties, there was insufficient information to delineate between various possible kinetic compositions for the transients, in particular one having absorption peaks at 340 and 480 nm. Contributing to this uncertainty was the question as to whether the reaction of OH involved an addition process or one of electron transfer. The former mode had been proposed in studies on the reactions of OH with platinum(II) complexes.[2,5,6,8] In contrast, OH reactions with nickel(II)– and copper(II)–ethylenediamine complex ions have been formulated as ones of electron transfer.[20,21]

The present pulse radiolysis investigation was undertaken to broaden the basis for examining the reactions of OH and $Pt(en)_2^{2+}$ and of the resultant transients in part through the use of conductivity and polarographic detection techniques. One particular advantage of the present approach was that the conductivity measurements could be performed simultaneously with those involving absorption This approach has provided decisive information on the nature and behavior of the transients as well as confirmation of the previous absorption results. In addition, a new route was found for the formation of the species with peaks at 340 and 480 nm via the reaction of the hydrated electron, e_{aq}^-, with *trans*-dihydroxobis(ethylenediamine)platinum(IV) ion, $Pt(en)_2(OH)_2^{2+}$. These efforts in conjunction with earlier ones have provided the opportunity to generate two of the transients by three separate chemical routes for each and to characterize their kinetic behavior by using different detection techniques. This has allowed for reasonable assignments to be made as to the

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(1) (a) University of Saskatchewan. (b) Hahn-Meitner-Institut.
(2) Adams, G. E.; Broskiewicz, R. K.; Michael, B. D. *Trans. Faraday Soc.* **1968**, *64*, 1256.
(3) Amano, C.; Fujiwara, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1437.
(4) Belluco, U. "Organometallic and Coordination Chemistry of Platinum"; Academic Press: New York, 1974; pp 166–170.
(5) Brodovitch, J. C.; Storer, D. K.; Waltz, W. L.; Eager, R. L. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 465.
(6) Broszkiewciz, R. K.; Grodkowski, J. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 359.
(7) Buxton, G. V.; Sellers, R. M. *Coord. Chem. Rev.* **1977**, *22*, 195.
(8) Ghosh-Mazumdar, A. S.; Hart, E. J. *Int. J. Radiat. Phys. Chem.* **1969**, *1*, 165.
(9) Hall, J. R.; Plowman, R. A. *Aust. J. Chem.* **1955**, *8*, 158.
(10) Krigas, T.; Rogers, M. T. *J. Chem. Phys.* **1971**, *55*, 3035.
(11) (a) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1. (b) Eisenberg, R. *Ibid.* **1970**, *12*, 295. (c) McCleverty, J. A. *Ibid.* **1968**, *10*, 49.
(12) Peloso, A. *Coord. Chem. Rev.* **1973**, *10*, 123.
(13) Rich, R. L.; Taube, H. *J. Am. Chem. Soc.* **1954**, *76*, 2608.
(14) (a) Shagisultanova, G. A.; Karaban, A. A.; Poznyak, A. L. *Khim. Vys. Energ.* **1971**, *5*, 368. (b) Shagisultanova, G. A.; Karaban, A. A. *Zh. Fiz. Chim.* **1971**, *45*, 2918. (c) Loginov, A. V.; Shagisultanova, G. A. *Zh. Prikl. Khim.* **1976**, *49*, 2353.
(15) Stasicka, A.; Marchaj, A. *Coord. Chem. Rev.* **1977**, *23*, 131.
(16) Storer, D. K.; Waltz, W. L.; Brodovitch, J. C.; Eager, R. L., *Int. J. Radiat. Phys. Chem.* **1975**, *7*, 693.
(17) Waltz, W. L.; Brodovitch, J. C.; Kundu, K. P. *Radiat. Phys. Chem.* **1977**, *10*, 77.
(18) Waltz, W. L.; Woods, R. J.; Whitburn, K. D. *Photochem. Photobiol.* **1978**, *28*, 681.
(19) Wright, J. C.; Laurence, G. S. *J. Chem. Soc., Chem. Commun.* **1972**, 132.
(20) Meyerstein, D. *Inorg. Chem.* **1971**, *10*, 2244.
(21) Lati, J.; Meyerstein, D. *Inorg. Chem.* **1972**, *11*, 2397.

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Table I. Rate Constants for Reactions of Aqueous Free Radicals with Complexes

complex ion	hydrated electron $k \times 10^{-10}$, M^{-1} s^{-1}	H atom $k \times 10^{-10}$, M^{-1} s^{-1}	hydroxyl radical $k \times 10^{-9}$, M^{-1} s^{-1}
$Pt(en)_2^{2+}$	1.2 ± 0.1[a]	1.4 ± 0.2[a]	4.8 ± 1.0[b]
trans-$Pt(en)_2(OH)_2^{2+}$	5.8 ± 1.0[c]	<0.05[c]	
trans-$Pt(en)_2(Cl)_2^{2+}$	6.6 ± 0.6[a]	0.43 ± 0.10[a]	0.14 ± 0.05[d]

[a] Reference 16. [b] Reference 5. [c] This work. [d] Reference 18.

compositions of the intermediates. In so doing, this lends further credence to proposals that these species can exhibit different structures.

Experimental Section

Materials and Solutions. The preparation of bis(ethylenediamine)platinum(II) perchlorate, $[Pt(en)_2](ClO_4)_2$, has been described previously,[16] and that for *trans*-dihydroxobis(ethylenediamine)platinum(IV) perchlorate, *trans*-$[Pt(en)_2(OH)_2](ClO_4)_2$, was as follows. $[Pt(en)_2](ClO_4)_2$ (0.64 g) was dissolved in 10 mL of water containing 10% H_2O_2 and 0.01 M $HClO_4$, and the mixture was heated for 1 h at 70 °C. The pH was adjusted to 6, and a 1:1 by volume solution of ethanol and diethyl ether was added until a white cloudy precipitate formed. The crude product was filtered and recrystallized from a minimum amount of aqueous $NaClO_4$ (60 °C), followed by cooling in an ice bath (yield ca. 40%). Anal. Calcd for $[Pt(en)_2(OH)_2](ClO_4)_2$: N, 10.2; C, 8.8; H, 3.3. Found: N, 10.2; C, 8.9; H, 3.4. The UV absorption spectrum, recorded on a Cary 118C spectrophotometer, exhibited a general increase from ca. 350 to 230 nm without peaks. The ^{1}H NMR spectra were measured at ambient temperature with a Varian T-60 spectrometer. The chemical shifts are given in ppm downfield from internal Me_4Si in Me_2SO-d_6 and internal DDS in D_2O. In D_2O, the spectrum of $[Pt(en)_2(OH)_2](ClO_4)_2$ exhibited a singlet at δ 2.97 (CH_2) with ^{195}Pt satellites, J(Pt–H) = 13 Hz. In Me_2SO-d_6, there was a broad multiplet centered at δ 6.6 (NH_2), a singlet at δ 2.65 (CH_2) with ^{195}Pt satellites (J(Pt–H) = 13 Hz), and a broadened singlet at δ 0.7 (OH). These features are consistent with a trans configuration for the dihydroxo groups.

All solutions used for the pulse radiolysis experiments, which were carried out at about 23 °C, were prepared just prior to use with triply distilled water or water purified by a Millipore Super-Q system. The pH of such solutions was adjusted with reagent grade $HClO_4$ or NaOH. Solutions were deaerated by bubbling with argon, helium, or N_2O or by a syringe-degassing bulb technique.[16] All other materials were of reagent quality.

Pulse Radiolysis Apparatus and Dosimetry. The apparatus employing conductivity, optical, and polarographic detection techniques has been described elsewhere.[16,22,23] Of note is that, in the use of these detection techniques, the transient signal represented a difference between that of the unirradiated and the pulsed solutions. Such differences were calibrated against one of the following dosimetry solutions: $Fe(CN)_6^{4-}$,[23] $(SCN)_2^-$,[23b,24] or tetranitromethane.[22a]

Results and Discussion

Primary Reactions of Aqueous Free Radicals with Platinum Complexes. Pulse irradiation of dilute aqueous solutions by high-energy electrons (2–20 MeV) leads initially to the generation of aqueous free radicals, hydrogen ion, and small amounts of H_2 and H_2O_2

$$H_2O \overset{e^-}{\rightsquigarrow} e_{aq}^-, H, OH, H^+, H_2, H_2O_2 \qquad (1)$$

The following G values (number of a given species formed per 100 eV of energy absorbed) were in general used: $G_{e^-} = G_{H^+} = 2.66$, $G_{OH} = 2.69$, $G_H = 0.55$.[25,26] The rate constants for the reactions of these radicals with *trans*-$Pt(en)_2(OH)_2^{2+}$ and $Pt(en)_2^{2+}$ are given in Table I, and for comparative purposes the corresponding values for *trans*-$Pt(en)_2(Cl)_2^{2+}$ are included. The rate constant for the reaction of e_{aq}^- with $Pt(en)_2(OH)_2^{2+}$ was determined from the decay of the electron's absorption at 578 nm in solutions at pH 9.8 containing 1 M *tert*-butyl alcohol (*t*-BuOH) and 10–25 μM platinum complex. A plot of the apparent first-order rate constants vs. complex concentrations was linear, and the second-order rate constant (Table I) was calculated from the slope of this plot. An attempt was made to measure the reaction of H atom with $Pt(en)_2(OH)_2^{2+}$ (300 μM) in solutions saturated with N_2O and containing 0.2 M *t*-BuOH at pH 3.95. For these conditions, e_{aq}^- will be efficiently scavenged by N_2O

$$N_2O + e_{aq}^- \xrightarrow{H^+} N_2 + OH \qquad (2)$$

to yield hydroxyl radical.[27] In turn, the presence of *tert*-butyl alcohol ensured the rapid scavenging of OH to give *t*-BuOH radical; however, the rate of reaction of the alcohol with H atom would be sufficiently slow to allow for detection of a moderately rapid reaction of H atom with the complex.[24,28] Under these circumstances only the weak optical absorption in the UV attributable primarily to the presence of *tert*-butyl alcohol radical formed by the end of the pulse was observed.[29] Based upon the decay of this absorption, an estimate of the upper limit to the rate constant for the H atom reaction is given in Table I. This and a series of experiments carried out in the absence of N_2O (pH 3.9–9.2; 0.2, 1.0 M *t*-BuOH; 100, 250 μM $Pt(en)_2(OH)_2^{2+}$) also served to show that *tert*-butyl alcohol radical was unreactive toward the platinum(IV) complex ($k < 2 \times 10^7$ M^{-1} s^{-1}). Such lack of reactivity has been previously noted in the case of *trans*-$Pt(en)_2(Cl)_2^{2+}$.[16] The situation was complicated in the absence of N_2O by the interaction of the alcohol radical with a platinum transient as described below.

The reaction of OH with *trans*-$Pt(en)_2(OH)_2^{2+}$ was not studied; however this process is not expected to be facile on the basis of the low reactivity of *trans*-$Pt(en)_2(Cl)_2^{2+}$ toward OH (Table I).[18] In any event, sufficient *t*-BuOH (0.2–1.0 M) was always present in the investigations of the reaction of e_{aq}^- and $Pt(en)_2(OH)_2^{2+}$ to ensure complete scavenging of OH by the alcohol. In the study of the reaction of OH and $Pt(en)_2^{2+}$ and the transients arising from this reaction, the high reactivities of e_{aq}^- and H atoms toward $Pt(en)_2^{2+}$ could potentially serve to complicate these experiments. However, we believe that these processes were not a source of concern for the following reasons. Previous work has shown that the electron and H atom products absorb only weakly below 350 nm.[16] Our studies were carried out in N_2O-saturated media where N_2O would have scavenged the electrons in excess of 90%. While some H atoms were present (less than 16% relative to OH), conductivity experiments at pH 2.5, 2.8, and 8.9 with 0.1 M *t*-BuOH indicated that signals associated with H atom processes were of negligible concern ($\Delta\Lambda \ll |50|$ Ω^{-1} cm^2 $equiv^{-1}$). This conclusion was substantiated by studies undertaken in the presence of 2-propanol (0.1–1.0 M) where

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(22) (a) Asmus, K.-D. *Int. J. Radiat. Phys. Chem.* **1972**, *4*, 417. (b) Beck, G. *Int. J. Radiat. Phys. Chem.* **1969**, *1*, 361. (c) Kelm, M.; Lilie, J.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1974**, *78*, 882. (d) Kelm, M.; Lilie, J.; Henglein, A. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1132. (e) Lilie, J.; Beck, G.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1971**, *74*, 458. (f) Janata, E. *Radiat. Phys. Chem.*, in press.

(23) (a) Waltz, W. L.; Akhtar, S. S.; Eager, R. L. *Can. J. Chem.* **1973**, *51*, 2525. (b) Spinks, J. W. T.; Woods, R. J. "An Introduction to Radiation Chemistry", 2nd ed.; Wiley: New York, 1976; p 105.

(24) Dorfman, L. M.; Adams, G. E. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1973**, *NSRDS-NBS46*.

(25) Reference 23b, p 258.

(26) Sehested, K.; Corfitzen, H.; Fricke, H. *J. Phys. Chem.* **1970**, *74*, 211.

(27) Anbar, M.; Bambenek, M.; Ross, A. B. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1973**, *NSRDS-NBS43*.

(28) Anbar, M.; Farhataziz; Ross, A. B. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1975**, *NSRDS-NBS51*.

(29) Simic, M.; Neta, P.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 3794.

Table II. Absorption Spectra Features and Kinetic Compositions of Transients

kinetic compn	peak wavelength, nm (ϵ, M^{-1} cm^{-1})[a]	ϵ(340 nm)/ϵ (480 nm)	associated reacn[b]
$Pt(en)_2(OH)^{2+}$	270 (ca. 4500)		OH + I
$Pt(en)(en\text{-}H)^{2+}$	340 (2900), 480 (1500)	1.91 ± 0.15	OH + I[c]
	340 (2400), 480 (1250)	1.92 ± 0.15	e_{aq}^- + II
	340, 480	1.95 ± 0.08	flash photolysis of III[d]
$Pt(en)_2(H_2O)^{3+}$	<250		OH + I
$Pt(en)_2(Cl)^{2+}$	260 (8000)		OH + I, acid, 10–20 μM Cl^-
	260		flash photolysis of III[d]
	265 (7120)		H + III[e]

[a] The precisions of peak wavelengths and ϵ values are ±5 nm and ±20%, respectively. [b] Symbols: I, $Pt(en)_2{}^{2+}$; II, *trans*-$Pt(en)_2(OH)_2{}^{2+}$; III, *trans*-$Pt(en)_2(Cl)_2{}^{2+}$. [c] This work plus data from ref 5. [d] Reference 5. [e] Reference 16.

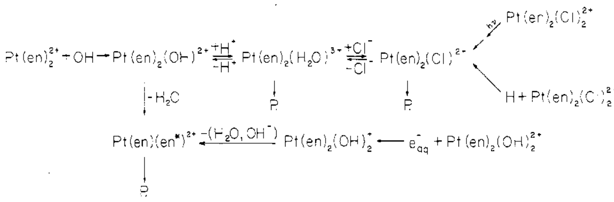

Figure 1. Proposed reaction scheme for the platinum–ethylenediamine systems. Symbols: en, ethylenediamine; en*, en-H; P·, products (see text).

similar results were obtained. Under these conditions, this alcohol would be expected to scavenge H atoms.[28]

Transient Species. The principal focus of this report is on the transitory products arising from the reactions of e_{aq}^- and $Pt(en)_2(OH)_2{}^{2+}$ and of OH with $Pt(en)_2{}^{2+}$. For the latter case, four species are identified. One of these (peaks at 340 and 480 nm) is also the major product of the electron reaction. In Table II, are presented the spectral properties of these transients and their kinetic compositions, i.e., their compositions as deduced from kinetic results to be given subsequently. Two of these transients have been reported previously in the context of the flash photolysis of *trans*-$Pt(en)_2(Cl)_2{}^{2+}$ and in this complex's reaction with H atoms,[5,16] and this information is included for comparative purposes. A proposed mechanism for the interrelationship between these entities is given in Figure 1. The evidence in support of this mechanism will be presented below by first considering results associated with reaction of OH with $Pt(en)_2{}^{2+}$ (proceeding from left to right in Figure 1) and subsequently those for the electron reaction with $Pt(en)_2(OH)_2{}^{2+}$.

This mechanism is based in part on the conclusion that these transients are *not* associated with the loss and/or degradation of the coordinated ethylenediamine ligands.[30] An earlier pulse radiolysis study has shown that no detectable amount of free ethylenediamine or NH_3 results from reaction of OH and $Pt(en)_2{}^{2+}$ (pHs ca. 5 and 9).[5] In contrast, free ethylenediamine reacts readily with OH to yield NH_3 as one of the major final products.[21,32] The mechanism of OH attack is believed to involve initial abstraction of an H atom from a methylene group. In a study of the reaction of OH and $Pt(NH_3)_4{}^{2+}$ where this group is absent, transients with spectral and kinetic properties very similar to those described here are observed.[33] This implies that ligand attack at the methylene group of ethylenediamine probably does not occur. This interpretation is reinforced by the observation that the same transient (peaks at 340 and 480 nm) as shown in Table II and Figure 2 is encountered in the reactions of OH with $Pt(en)_2{}^{2+}$ and of e_{aq}^- with $Pt(en)_2(OH)_2{}^{2+}$. In the latter instance, the process is expected to involve electron transfer with concomitant reduction of the metal center.[34] Furthermore, others have concluded that the transients from the reactions of hydroxyl radical with copper(II)– and nickel(II)–ethylenediamine complexes are not those involving ligand attack by OH but are instead Cu(III) and Ni(III) intermediates derived from interaction at the metal centers.[20,21] On the basis of these features, we propose that the species under consideration arise from metal-centered attack and are indicative of the platinum center being in a formal oxidation state of III.

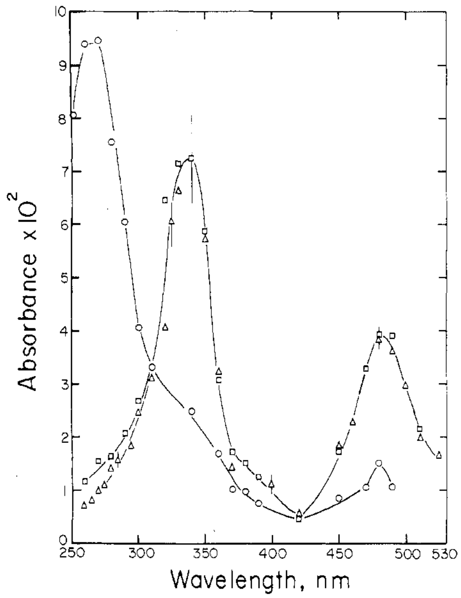

Figure 2. Absorption spectra arising from the reactions of OH and $Pt(en)_2{}^{2+}$ and of e_{aq}^- and $Pt(en)_2(OH)_2{}^{2+}$: (○) at end of pulse; (□) at 20 μs for 986 μM $Pt(en)_2{}^{2+}$ at natural pH of ca. 5.5 (after ref 5); (△) at 2 μs for 100–300 μM $Pt(en)_2(OH)_2{}^{2+}$. Conditions: pH 9.5, 9.8, 1.0 M *tert*-butyl alcohol; data normalized at 340 nm to that for the spectrum of $Pt(en)_2{}^{2+}$ at 20 μs. Error bars represent standard deviations for at least three separate determinations.

Reactions Associated with OH and $Pt(en)_2{}^{2+}$. In N_2O-saturated solutions (100 μM–1 mM $Pt(en)_2{}^{2+}$; pH 4.0–9.5), the initially observed product after irradiation has an absorption band with a peak at 270 nm (Figure 2 and Table II). Addition of methanol, 2-propanol, or *tert*-butyl alcohol eliminated the formation of this transient and subsequent species, showing that the transients are ones derived from the reaction of OH and $Pt(en)_2{}^{2+}$. No changes in conductivity were observed at pH 8.9 and 10.5 even for times approaching 1 ms after the irradiation pulse.[35] In acidic media (pH 4.0–4.5),

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(30) While the possible occurrence of ring opening of the bidentate ethylenediamine system, particularly in acid media, cannot entirely be excluded, such might lead to loss of ethylenediamine whereas none is observed. Furthermore, our conductivity results would imply that subsequent closure of the ring occurred. For closure, its rate would be required to be considerably faster than that reported[31] for such processes in the case of platinum(II) ethylenediamine complex and this seems somewhat unlikely.

(31) Carter, M. J.; Beattie, J. K. *Inorg. Chem.* **1970**, *9*, 1233.

(32) Anbar, M.; Munoz, R. A.; Rona, P. *J. Phys. Chem.* **1963**, *67*, 2708.

(33) Khan, H. M.; Lilie, J.; Waltz, W. L.; Woods, R. J., manuscript in preparation. Portions of this work were presented at the 62nd Canadian Chemical Conference, Vancouver, B.C., June 1979 (see paper PH-32 in the abstracts).

(34) Hart, E. J.; Anbar, M. "The Hydrated Electron"; Wiley-Interscience: New York, 1970; Chapter 5.

(35) While both e_{aq}^- and H^+ are formed upon irradiation, they are rapidly consumed via eq 2.

the initial conductivity changes were less than $-60\ \Omega^{-1}\ cm^2\ equiv^{-1}$, and they appeared to be associated with the beginning phases of subsequent reactions. The equivalent ionic conductivities of the proton and hydroxide ion are 350 and 198 $\Omega^{-1}\ cm^2\ equiv^{-1}$ at 25 °C, and those for platinum complex ions are anticipated to be about 50 $\Omega^{-1}\ cm^2\ equiv^{-1}$.[36,37] From these values, the conductivity changes in acidic and basic solutions are expected to be about -300 and $+240\ \Omega^{-1}\ cm^2\ equiv^{-1}$ respectively for an electron-transfer process

$$Pt(en)_2^{2+} + OH \rightarrow Pt(en)_2^{3+} + OH^- \qquad (3)$$

Clearly the experimental results are not in accord with this reaction. They are consistent with that for an addition reaction involving no net change of charge

$$Pt(en)_2^{2+} + OH \rightarrow Pt(en)_2(OH)^{2+} \qquad (4)$$

with $Pt(en)_2(OH)^{2+}$ being identified as the species absorbing at 270 nm.

The subsequent behavior of $Pt(en)_2(OH)^{2+}$ is strongly dependent upon the pH. Between pH 5 and 10.5, the decay of its absorption peak at 270 nm was first order, and this correlated with the formation of a transient having peaks at 340 and 480 nm (Figure 2, isosbestic point ca. 310 nm). The observed first-order rate constant had a first-order dependence upon the concentration of hydroxide ion.[5] This feature had previously been interpreted to indicate that the transformation is accompanied by release of proton,[5] suggesting that the transient might be a five-coordinate oxo or amido species, or $Pt(en)_2(OH)_2^+$ if $Pt(en)_2(OH)^{2+}$ was in fact $Pt(en)_2(H_2O)(OH)^{2+}$. The formation of any of these species would necessitate a change in conductivity; however, we observed no conductivity change. Consequently the process is not just one of proton release, and thus formulation of the transient as one of the aforementioned species is not appropriate. The results support a process involving water elimination to form a four-coordinate entity containing an en-H group, $^-NHCH_2CH_2NH_2$ ($k_5 = (2.4 \pm 0.3) \times 10^5\ s^{-1}$)[5]

$$Pt(en)_2(OH)^{2+} \rightarrow Pt(en)(en\text{-}H)^{2+} + H_2O \qquad (5)$$

(The designation of the transient with peaks at 340 and 480 nm as $Pt(en)(en\text{-}H)^{2+}$ is also in agreement with its occurrence in the reaction of e_{aq}^- and $Pt(en)_2(OH)_2^{2+}$ as presented below.) The effect of hydroxide ion on the rate of this process may reflect a base-catalyzed sequence (eq 6 and 7), which is in

$$Pt(en)_2(OH)^{2+} + OH^- \rightarrow Pt(en)(en\text{-}H)(OH)^+ + H_2O \qquad (6)$$

$$Pt(en)(en\text{-}H)(OH)^+ \rightarrow Pt(en)(en\text{-}H)^{2+} + OH^- \qquad (7)$$

parallel with reaction 5, with the second step being faster than the first step ($k_6 = (3.1 \pm 0.5) \times 10^{10}\ M^{-1}\ s^{-1}$).[5]

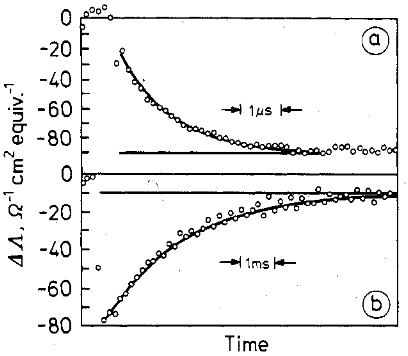

Figure 3. Equivalent conductivity changes with time, associated with the products of the reaction of OH and $Pt(en)_2^{2+}$: (a) first stage, pH 4.35, 404 μM $Pt(en)_2^{2+}$; (b) second stage, pH 4.4, 97 μM $Pt(en)_2^{2+}$.

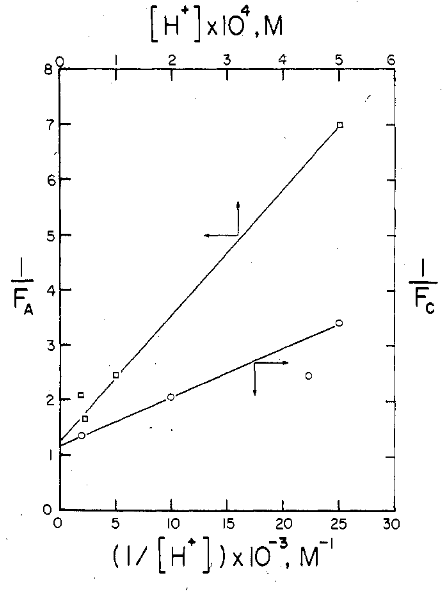

Figure 4. Fractional change in absorption at 340 nm (F_A) and in conductivity (F_C) as a function of proton concentration. Plot of $1/F_A$ vs. $[H^+]$: intercept 1.3; slope 1.1×10^4 M. Plot of $1/F_C$ vs. $1/[H^+]$: intercept 1.2; slope $8.6 \times 10^{-5}\ M^{-1}$.

In acidic media (pH <4.5), the changes in both the absorption and conductivity following the formation of $Pt(en)_2(OH)^{2+}$ could be resolved into two stages. These stages became more clearly separated in time as the pH was decreased. The first stage was characterized by a faster rate of growth in the absorption of $Pt(en)(en\text{-}H)^{2+}$ at 340 and 480 nm although the end level of the absorption changes became progressively smaller with decreasing pH. This was accompanied at 260 nm by a decrease in absorption. Our previous study has shown that this latter feature represents the development of an absorption band at shorter wavelength, suggestive of the formation of an additional transient with a possible peak below 250 nm.[5] During this same time interval, there was a decrease in conductivity as shown in Figure 3a. The rate and the extent of this increased with decreasing pH. The changes in the absorption and conductivity signals obeyed first-order kinetics, and the values of k_{obsd} (s^{-1}) were the same within experimental error. The results of varying the pH indicated that $k_{obsd} = k' + k''[H^+]$ with $k' = (3.0 \pm 0.4) \times 10^5\ s^{-1}$ and $k'' = (5.4 \pm 1.3) \times 10^9\ M^{-1}\ s^{-1}$. The value of k' is in good agreement with that of k_5 for the formation of $Pt(en)(en\text{-}H)^{2+}$ via eq 5. As eq 5 does not reflect an alteration in conductivity, the foregoing results suggest that the formation of $Pt(en)(en\text{-}H)^{2+}$ is in competition with a process involving protonation of $Pt(en)_2(OH)^{2+}$

$$Pt(en)_2(OH)^{2+} + H^+ \rightarrow Pt(en)_2(H_2O)^{3+} \qquad (8)$$

with k_8 being identified as k'' and with the absorption below 300 nm now attributable to $Pt(en)_2(H_2O)^{3+}$.

A check on the consistency of this competition mechanism is provided through an examination of the fractional changes in the absorption at 340 nm (F_A) and in the conductivity (F_C). The values of F_A and F_C are expected to be indicative of the extent to which $Pt(en)(en\text{-}H)^{2+}$ and $Pt(en)_2(H_2O)^{3+}$ are formed respectively at various proton concentrations. They are given by

$$1/F_A = 1 + k_8[H^+]/k_5 = \epsilon_{max}(340\ nm)/\epsilon_{obsd}(340\ nm) \qquad (9)$$

$$1/F_C = 1 + k_5/k_8[H^+] = \Delta\Lambda_{max}/\Delta\Lambda_{obsd} \qquad (10)$$

where $\epsilon_{max}(340\ nm) = 2900\ M^{-1}\ cm^{-1}$ (Table II) and $\Delta\Lambda_{max}$ is the maximum anticipated value (ca. $-300\ \Omega^{-1}\ cm^2\ equiv^{-1}$)

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[36] Moore, W. J. "Physical Chemistry", 3rd ed.; Prentice-Hall: Englewood Cliffs, N.J., 1962; p 337.

[37] Johnson, R. C.; Basolo, F.; Pearson, R. G. *J. Inorg. Nucl. Chem.* **1962**, *24*, 59.

for eq 8. Plots of these functions are given in Figure 4. The intercepts are close to the expected value of 1, and the ratios of k_8/k_5 obtained from the slopes are 1.1×10^4 M^{-1} (absorption) and 1.2×10^4 M^{-1} (conductivity). Owing to the need to estimate $\Delta\Lambda_{max}$ and to the effects of cumulative errors, considerable uncertainty is anticipated for these values. Nevertheless reasonable agreement exists, and the ratios of k_8/k_5 are comparable to that of $(1.8 \pm 1.0) \times 10^4$ M^{-1} calculated from the rate constant data. A further feature arising from this analysis is that possible acid catalysis associated with eq 5 does not appear to be a significant factor.[38]

The second stage was characterized by a further growth of $Pt(en)(en\text{-}H)^{2+}$ as evidenced by an increase in the absorption bands at 340 and 480 nm but without modification in their shapes or relative magnitudes. This was accompanied by a further decrease in absorption at 260 nm. Results of our earlier study indicated that the observed first-order rate constant describing these changes was inversely proportional to the concentration of proton over the pH range 2.8–4.3.[5] While our present work was limited to pH 3.3 and 4.4, two further features of importance have emerged. As shown in Figure 3b, the conductivity during this stage now increased to a final value very near zero with the implication that this was associated with proton release. The observed first-order rate constant for the conductivity change had the same value at a given pH as that for the optical change, indicating that these were coupled phenomena. These observations are compatible with a scheme involving the reverse step of eq 8

$$Pt(en)_2(H_2O)^{3+} \rightarrow Pt(en)_2(OH)^{2+} + H^+ \qquad (11)$$

($k_{11} = (6.6 \pm 1.8) \times 10^2$ s^{-1})[5] followed by the faster process of eq 5 to generate $Pt(en)(en\text{-}H)^{2+}$. A notable aspect in the overall development of $Pt(en)(en\text{-}H)^{2+}$ was that its level of formation was less than that at natural or basic pH. The extent of this was more pronounced as the pH was lowered (see Figure 6 of ref 5). While at pH 3.3 this effect can be attributed in part to the long-term decay of $Pt(en)(en\text{-}H)^{2+}$ (vide infra) not being well separated in time from its formation, such would not be the case at pH 4.4. This observation implies that a further decay mode for $Pt(en)_2(H_2O)^{3+}$ exists

$$Pt(en)_2(H_2O)^{3+} \rightarrow \text{product(s)} + H^+ \qquad (12)$$

and is in competition with the reaction of eq 11. As the final conductivity level was essentially zero, this route presumably also released protons.[39]

The decay of $Pt(en)(en\text{-}H)^{2+}$ obeyed second-order kinetics

$$Pt(en)(en\text{-}H)^{2+} + Pt(en)(en\text{-}H)^{2+} \rightarrow \text{product(s)} \qquad (13)$$

with a rate constant of $2k_{13} = (1.6 \pm 0.5) \times 10^6$ M^{-1} s^{-1} over the pH ranges of 4.4–10.5 for absorption measurements and of 8.9–10.5 for conductivity changes. This value is in good agreement with that reported ($2k_{13} = (1.5 \pm 0.4) \times 10^6$ M^{-1} s^{-1}, pH 2.9–8.5)[5] on the basis of optical measurements. While products were not observed optically, the conductivity in *basic* media (pH 8.9–10.5) went from zero to ca. -100 Ω^{-1} cm^2 $equiv^{-1}$ and then remained stable for times exceeding 1 s. The final level is approximately that expected if the disappearance of each $Pt(en)(en\text{-}H)^{2+}$ is associated with the uptake of 0.5 equiv of OH^- (or release of half the amount of protons). In contrast, there was no net conductivity change accompanying eq 13 in *acidic* solutions (pH 3.3, 4.4). The results in the acidic media would suggest that the reaction may be one of disproportionation to yield platinum(II) and platinum(IV) products such as $Pt(en)_2^{2+}$ and $Pt(en)_2(OH)_2^{2+}$. Their occurrence as the *initial* products in basic solution however would not be consistent with the observed decrease in conductivity. One possible explanation is that eq 13 involves the formation of a hydroxide-bridged dimer which is relatively stable in base but is rapidly decomposed in acid to give the above species. Such dimerization is reminiscent of the mechanism for Pt(II)-catalyzed substitution reactions of Pt(IV) complexes.[4]

In an attempt to characterize the electrochemical properties of the foregoing species, pulse radiolysis experiments employing polarographic detection were undertaken at pH 3.7–8.8. The working electrode was a hanging mercury drop referenced to a Ag/AgCl electrode with 0.2 M $NaClO_4$ serving as the supporting electrolyte. When the applied voltage was altered from +0.4 to −1.1 V, there was a general increase in the cathodic current. The shapes of the polarograms were found to be sensitive to pH; however, their slopes were such as to preclude any discernment of half-wave potentials. As a qualitative conclusion, it would appear that these species can function as moderately strong oxidizing agents.

Effect of Added Chloride Ion. In acidic media, the presence of free chloride ion in the reaction of OH and $Pt(en)_2^{2+}$ has previously been shown to lead to the development of a further transient with a peak at 260 nm.[5] Our experiments involving simultaneous measurements of both conductivity and optical changes were performed at pH 3.3, $[Pt(en)_2^{2+}] = 100$ μM, and $[KCl] = 10, 20$ μM. The limited range of free chloride concentrations was required to ensure that the formation of Cl and Cl_2^- from the reaction of OH and Cl^- would not be a complicating factor: the facile reaction of $Pt(en)_2^{2+}$ with Cl_2^- (and presumably Cl) also generates intermediates absorbing intensely in the 250–300-nm region.[16,40] Under these conditions, the conductivity changes at times less than 100 μs were very similar to those described above for the formation of $Pt(en)_2(H_2O)^{3+}$ (eq 8) and $Pt(en)(en\text{-}H)^{2+}$ (first stage, eq 5); however on time scales between 100 μs and ca. 1 s, marked alterations occurred. The initial decrease in conductivity (Figure 3a) was now followed by a further decrease of about -70 Ω^{-1} cm^2 $equiv^{-1}$. Concomitant with this was the growth in the absorption band with a peak at 260 nm. Both the conductivity and optical changes obeyed first-order kinetics, and the observed rate constants were the same within experimental error. They increased with chloride concentration as did the maximum absorption level at 260 nm. The relative modifications in these quantities were $k_{obsd}(20\ \mu M\ Cl^-)/k_{obsd}(10\ \mu M\ Cl^-) = 2.6 \pm 0.6$ and $A_{max}(20\ \mu M\ Cl^-)/A_{max}(10\ \mu M\ Cl^-) = 1.13 \pm 0.04$. In addition, the second stage in the formation of $Pt(en)(en\text{-}H)^{2+}$ was not observed in the presence of free Cl^-. As the second stage is derived from the disappearance of $Pt(en)_2(H_2O)^{3+}$ (eq 11 and 5), this suggests that the transient at 260 nm is formed through a competitive step involving Cl^-

$$Pt(en)_2(H_2O)^{3+} + Cl^- \rightarrow Pt(en)_2(Cl)^{2+} + H_2O \qquad (14)$$

For this reaction, a maximum decrease of about -110 Ω^{-1} cm^2 $equiv^{-1}$ would be expected, somewhat more than the observed value.[36,37] The relative changes in k_{obsd} and in A_{max} would imply that not only is this a competitive situation but it is also one involving the reverse reaction

$$Pt(en)_2(Cl)^{2+} + H_2O \rightarrow Pt(en)_2(H_2O)^{3+} + Cl^- \qquad (15)$$

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(38) The values of F_A obtained here and in a previous study[5] at the highest proton concentrations used indicate that the rate constant for possible acid catalysis in eq 5 would be about a factor of 10 less than k_8.

(39) While eq 12 has been presented as being a first-order disappearance of $Pt(en)_2(H_2O)^{3+}$, it may in fact be a second-order process in view of the long-term behavior of $Pt(en)(en\text{-}H)^{2+}$. If such is the case, this might represent a disproportionation act to yield $Pt(en)_2^{2+}$, $Pt(en)_2(OH)_2^{2+}$, and H^+ in amounts relative to $Pt(en)_2(H_2O)^{3+}$ of 0.5, 0.5, and 1. This in conjunction with eq 11 would then account for the final conductivity value being near zero.

(40) Jayson, G. G.; Parsons, B. J.; Swallow, A. J. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1597.

Owing to these complexities, accurate evaluations of k_{14} and k_{15} were not feasible; however, two approaches have been tried to estimate these values. A value of $k_{14} = 5 \times 10^8$ M^{-1} s^{-1} was calculated by assuming that the situation represented an approach to equilibrium. We believe this to be an upper limit to k_{14} as k_{15} would now be close to zero. Such would imply that the forward reaction (eq 14) had gone to completion whereas the ratio of A_{max} indicates that this is not so. This value of k_{15} would not be in keeping with results reported on the flash photolysis of *trans*-$Pt(en)_2(Cl)_2^{2+}$ where k_{15} was considered to be greater than k_{11} (=(6.6 ± 1.8) × 10^2 s^{-1}).[5] With the assumption that k_{15} was approximately 10^3 s^{-1}, k_{14} was estimated to be 3 × 10^8 M^{-1} s^{-1}. These values seem reasonable as the calculated ratio of A_{max} was now in agreement with the experimental ratio of 1.13. Within this context and with allowance for the fact that only 90% of $Pt(en)_2(OH)^{2+}$ formed at pH 3.3 will lead to $Pt(en)_2(H_2O)^{3+}$ (eq 5 and 8), the molar absorption coefficient at 260 nm for $Pt(en)_2(Cl)^{2+}$ was calculated to be 8000 M^{-1} cm^{-1} (Table II).

A comparison of this value and the wavelength maximum with those for the initial transient arising in the flash photolysis of $Pt(en)_2(Cl)_2^{2+}$ and from its reaction with H atoms is given in Table II. The reasonable agreement between these values provides one line of support for the occurrence of a common intermediate, $Pt(en)_2(Cl)^{2+}$, in these three cases. In acidic media, the reactions leading to its formation have been proposed to be[5,16]

$$H + Pt(en)_2(Cl)_2^{2+} \rightarrow Pt(en)_2(Cl)^{2+} + H^+ + Cl^- \qquad (16)$$

$$Pt(en)_2(Cl)_2^{2+} \xrightarrow{h\nu} \rightarrow Pt(en)_2(Cl)^{2+} + Cl \qquad (17)$$

The decay in the optical signal at 260 nm in each of the three cases obeyed second-order kinetics, suggesting that

$$Pt(en)_2(Cl)^{2+} + Pt(en)_2(Cl)^{2+} \rightarrow \text{products} \qquad (18)$$

Our conductivity results have provided further insight into this process. The optical decay correlated with an increase in conductivity, with both phenomena exhibiting the same second-order rate constant. In contrast to the situation encountered in the absence of added Cl$^-$ (Figure 3b), the final conductivity level was not zero: at 10 μM Cl$^-$, $\Delta\Lambda_\infty \simeq -120$ Ω^{-1} cm^2 equiv^{-1}, and for 20 μM Cl$^-$, $\Delta\Lambda_\infty \simeq -200$ Ω^{-1} cm^2 equiv^{-1} with these values being constant for times exceeding 0.1 s. These nonzero values indicate that Cl$^-$ may be incorporated into the final products, in agreement with an earlier proposal.[5] The fact that they differed would suggest that processes in addition to eq 18 may have been present, such as a possible cross reaction between $Pt(en)_2(H_2O)^{3+}$ and $Pt(en)_2(Cl)^{2+}$. Nevertheless, the second-order rate constants, measured under similar conditions (ca. 10 μM Cl$^-$) and with the assumption of ϵ_{260} = 8000 M^{-1} cm^{-1}, are in accord: $2k_{18}$ = (3.5 ± 1.0) × 10^7 M^{-1} s^{-1} (this work), (4.1 ± 1.6) × 10^7 M^{-1} s^{-1} (flash photolysis),[5] (4.9 ± 0.6) × 10^7 M^{-1} s^{-1} (H atoms).[16] Further evidence for a common intermediate comes from flash photolysis results for *trans*-$Pt(en)_2(Cl)_2^{2+}$ *at natural and basic pH*, where the transient at 260 nm decayed to a product having the same spectral properties (Table II) and kinetic behavior as that of $Pt(en)(en\text{-}H)^{2+}$.[5] At these pHs, the process associated with eq 8 would not prevent the formation of $Pt(en)(en\text{-}H)^{2+}$ but would do so *under acidic* conditions. Thus the present study in conjunction with the flash photolysis and H atom results supports the proposed mechanism and designation of the common intermediate as $Pt(en)_2(Cl)^{2+}$.

Reactions Associated with e_{aq}^- and $Pt(en)_2(OH)_2^{2+}$. Two major observations arose from experiments performed on solutions containing 95–508 μM $Pt(en)_2(OH)_2^{2+}$ (0.2–1.0 M *t*-BuOH, pH 3.8–9.8, or 0.1–1.0 M 2-propanol, pH 6–9.1) and saturated with argon or helium gas. In acidic media (pH 4.55, 5.0), there was an immediate increase in conductivity at the end of the irradiation pulse ($\Delta\Lambda_{max} \simeq 450$ Ω^{-1} cm^2 equiv^{-1}), followed by its rapid decay (within 2 μs) to zero.[41] On the same time scales, the optical changes were characterized by the development of absorption bands with peaks at 340 and 480 nm. Addition of N_2O eliminated the occurrence of these bands, indicating that they resulted from a reaction involving e_{aq}^-. A comparison of their spectral properties with those of the transient derived from the reaction of OH and $Pt(en)_2^{2+}$ and designated as $Pt(en)(en\text{-}H)^{2+}$ (Figure 2 and Table II) clearly indicates that the same species was being observed. As will be shown, these features provide further support for the formulation of this transient as $Pt(en)(en\text{-}H)^{2+}$.

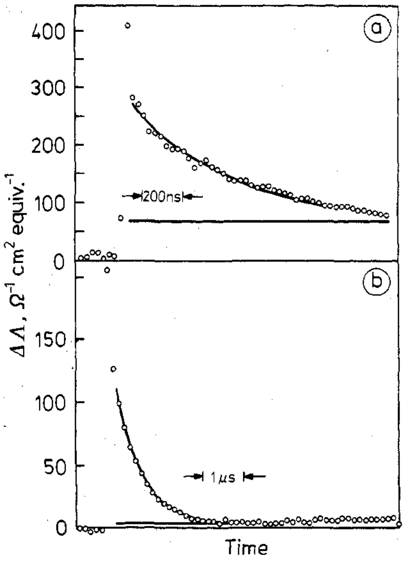

Figure 5. Equivalent conductivity changes with time, associated with the reaction of e_{aq}^- and $Pt(en)_2(OH)_2^{2+}$. Conditions: 301 μM $Pt(en)_2(OH)_2^{2+}$, 0.2 M *tert*-butyl alcohol, pH 5.0.

Considering in detail the conductivity aspects first, the level of the prompt increase is about that expected for the formation of e_{aq}^- and H$^+$ owing to the irradiation pulse. The subsequent decay of this signal could be resolved into two components with the first of these covering from about 450 to 250 Ω^{-1} cm^2 equiv^{-1} (the initial point of Figure 5a is indicative of this stage). Under conditions where the concentration of the platinum(IV) complex was greatly in excess of that for e_{aq}^-, the observed first-order rate constant for this process had the same value as that for the electron decay at 578 nm (Table I). This correspondence identifies this stage as being associated with the reaction

$$e_{aq}^- + Pt(en)_2(OH)_2^{2+} \rightarrow Pt(en)_2(OH)_2^{+} \qquad (19)$$

where $Pt(en)_2(OH)_2^+$ is anticipated to be the initial product.[34] As shown in Figure 5, the slower second stage resulted in the attainment of a zero conductivity level, reflecting the consumption of proton. The kinetics of this was described by a first-order rate law; however, the associated half-life ($t_{1/2}$) decreased with decreasing pH, $t_{1/2}$ being 0.40 ± 0.05 μs (pH 5.0) and 0.22 ± 0.02 μs (pH 4.55). These values are approximately those expected for the reaction of H$^+$ and OH$^-$ ($k = 1.4 \times 10^{11}$ M^{-1} s^{-1}):[42] $t_{1/2}$ would be 0.26 μs (pH 5.0) and 0.18 μs (pH 4.55). This comparison suggests that the consumption of proton (and thus the decrease in conductivity) has its origin in the rapid formation of OH$^-$ followed by its

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(41) Attempts to study the short-term conductivity changes at lower pHs were not successful owing to difficulties encountered with instrumentation response.

(42) Eigen, M. *Angew. Chem.* **1963**, *75*, 489.

neutralization. At pH 5.0 and 4.55, an alternative explanation invoking the direct interaction of H^+ and $Pt(en)_2(OH)_2^+$ does not appear to be satisfactory because the protonation steps for $Co(NH_3)_5(OH)^{2+}$ and $Pt(en)_2(en\text{-}H)^{3+}$ are considerably slower ($k = 5 \times 10^9$ and $1.9 \times 10^9\ M^{-1}\ s^{-1}$, respectively)[42] than that prevailing here ($k \simeq 10^{11}\ M^{-1}\ s^{-1}$).

These features demonstrate that $Pt(en)_2(OH)_2^+$ underwent further change. A reaction scheme which is consistent with the conductivity results and the occurrence of the transient with peaks at 340 and 480 nm is

$$Pt(en)_2(OH)_2^+ \rightarrow Pt(en)(en\text{-}H)^{2+} + OH^- + H_2O \qquad (20)$$

Our earlier conclusion was that $Pt(en)(en\text{-}H)^{2+}$ was formed by eq 5 rather than an oxo species, $Pt(en)_2(O)^+$, or an amido entity, $Pt(en)(en\text{-}H)(OH)^+$. If either of these were to be produced from $Pt(en)_2(OH)_2^+$ through water elimination, there would be no conductivity change subsequent to the electron decay, an expectation which is in disagreement with the experimental results. An implication of the proposed sequence (eq 19 and 20) is that $Pt(en)(en\text{-}H)^{2+}$ is a secondary product. This is supported by the observation that the absorption bands (340 and 480 nm) developed in several stages even though the ratios of $\epsilon_{340}/\epsilon_{480}$ and the half-widths of the bands remained constant throughout. At a time corresponding to the passage of 3 half-lives for the electron reaction (eq 19, $t \lesssim 200$ ns), the absorbances were approximately 70% of their maximum values. The remaining 30% increase took place within about 5 μs; however, the time for this varied with pH, being somewhat shorter at the more acidic or more basic values. While this shows the involvement of processes in addition to eq 20, we have not been able to define their kinetics owing in part to the relative small changes encountered. Concurrent and slight decreases in absorption below 300 nm may be a further indication of such reactions.

The situation was further complicated by the fact that the decay of $Pt(en)(en\text{-}H)^{2+}$ was very rapid: the rate of disappearance of the 340 and 480 nm peaks was about 500 times that anticipated for eq 13. For *t*-BuOH solutions, the decay rate was independent of pH (4.5, 8.5), source and concentration (fivefold) of alcohol, and concentration of the platinum(IV) complex (threefold). A minimum conclusion would be that the transient was not reacting with the starting materials or possible impurities. The situation did however depend upon the specific alcohol present, with 2-propanol solutions exhibiting a slightly higher reactivity than those containing *t*-BuOH. This suggested the possible reaction of the alcohol radical (R·) with $Pt(en)(en\text{-}H)^{2+}$ in addition to processes between like species, i.e., eq 13 and

$$Pt(en)(en\text{-}H)^{2+} + R\cdot \rightarrow \text{product(s)} \qquad (21)$$

$$R\cdot + R\cdot \rightarrow \text{product(s)} \qquad (22)$$

To test the consistency of this scheme, computer-based analysis was performed with use of data obtained at different doses and for both acidic and basic conditions and the known values of $2k_{13}$ and $2k_{22}$.[29] Good agreement between the computed and experimental findings was achieved for k_{21} being $4.0 \times 10^9\ M^{-1}\ s^{-1}$ (*tert*-butyl alcohol) and $6.5 \times 10^9\ M^{-1}\ s^{-1}$ (2-propanol). Precedence exists in the literature for the interaction of these and other alcohol radicals with metal ions, with rate constants in the range 10^7–$10^{10}\ M^{-1}\ s^{-1}$.[22c,d,43-45] These studies would indicate that eq 21 could signify either electron-transfer processes or formation of species with Pt–C bonds. As we did not observe any significant conductivity changes during the course of these reactions or any final products absorbing above 250 nm, no definite decision between these possibilities can be made.

As a qualitative finding, the presence of $Fe(CN)_6^{3-}$ (20 μM) caused the first half-life for the absorption decay at 480 nm to be 2–3 times shorter than that in the absence of ferricyanide ion (under our conditions, the electron reaction with $Fe(CN)_6^{3-}$ was negligible).[27] In addition, there was some bleaching of the absorption at 420 nm where $Fe(CN)_6^{3-}$ has a peak maximum. These two observations imply a reaction between $Pt(en)(en\text{-}H)^{2+}$ and this iron(III) complex. This and the known reactivity of the platinum transient toward $Fe(CN)_6^{4-}$ (leading to the generation of $Fe(CN)_6^{3-}$)[5] point to the capability of $Pt(en)(en\text{-}H)^{2+}$ to function as both an oxidizing and a reducing agent.

Other Facets. Adams and coworkers studied the reaction of OH and $PtCl_4^{2-}$ where two platinum(III) products were observed.[2] The initial transient had a peak at 450 nm and converted by first-order kinetics to a second species with a maximum at 410 nm. The former was not however detected in 10^{-2} N KOH or 10^{-2} N H_2SO_4. The major observations in this work were subsequently confirmed by others.[8] Broskiewicz and Grodkowski extended these efforts to conditions involving the presence of moderately high concentrations of NaCl (1.0 M), HCl (0.1 M), and KBr (0.1 M).[6] Two significant results were that additional transients absorbing near 300 nm were formed and that, in the presence of HCl or KBr, the products with 410- and 450-nm peaks were no longer observable. In the reaction of e_{aq}^- and $PtCl_6^{2-}$, a species having a peak at 410 nm was identified although the conditions were such that it must be recognized as being a secondary species rather than the primary product of this reaction.[2] A minimum conclusion from these studies would be that the transients are sensitive to pH and the presence of free halide ions, implicating the occurrence of acid–base and labile substitution processes. Our results while differing in details clearly demonstrate the presence and importance of these types of processes.

An intriguing suggestion put forward to account for the interconversion of the species absorbing at 450 nm to that at 410 nm was that they were five-coordinate products of an OH addition reaction ($Pt(Cl)_4(OH)^{2-}$), differing in structure, with the former being square pyramidal and the latter of a trigonal-bipyramidal form.[2] This contention finds support from EPR investigations on the products formed in the irradiation at 77 K of single crystals and polycrystalline samples of $K_2[Pt(Cl)_4]$ and a variety of other platinum(II) and -(IV) complexes.[3,10] These and other efforts have further served to indicate that these entities are low-spin d^7 systems.[14] Attempts to perform pulse radiolysis–EPR measurements on aqueous solutions of $Pt(en)_2^{2+}$ at room temperature failed to detect any such transients.[5] Wright and Laurence in their flash photolysis study of $PtCl_6^{2-}$, where the transient with a 410-nm peak was also encountered, proposed that this species may be of a square-planar form with two highly labile apical positions, i.e., a distorted octahedral system.[19]

Our present and earlier results on Pt(III) intermediates (containing the ligands NH_3, glycine, ethylenediamine, and related amines) are consistent with the possibility that the transients have different structures.[5,16,17] These entities can be classified into two groups, one of these characterized by an absorption band of considerable intensity ($\epsilon \simeq 4000$–$15000\ M^{-1}\ cm^{-1}$) with a maximum below 300 nm and the other represented by two absorption bands of lesser intensity ($\epsilon \leq 4000\ M^{-1}\ cm^{-1}$) with peaks near 350 nm and in the 450–600-nm region. A major outcome of the present study has been the correlation of these groups with particular kinetic

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(43) Cohen, M.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(44) Fujita, S.; Horii, H.; Mori, T.; Taniguichi, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3067.

(45) Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 697.

compositions for the transients. The former group contains those of the type $Pt(en)_2(X)^{n+}$ where X is Cl, OH, or H_2O. While their compositions would indicate a minimum coordination number of 5, we would propose that they may be of a six-coordinate type, with the sixth position occupied by water. The basis for this proposal resides in results obtained on the flash photolysis of $Pt(en)_2(Cl)_2^{2+}$ in the presence of millimolar amounts of free Cl^-.[5] Irradiation with wavelengths above 280 nm, for which photolysis of Cl^- is unlikely, produced a new and intensely absorbing transient (peak ca. 295 nm) suggestive of a possible reaction between $Pt(en)_2(Cl)^{2+}$ and Cl^-. Similar strongly absorbing products are also formed on electron reduction of $Pt(en)_2(Cl)_2^{2+}$ and on Cl_2^- oxidation of $Pt(en)_2^{2+}$ (0.5 M HCl).[16]

The second category is represented by $Pt(en)(en\text{-}H)^{2+}$, which has now been prepared by three different chemical routes. Consideration of these routes would imply a coordination number of 4, with the possible limiting forms of square-planar or tetrahedral geometries. Species having spectral and kinetic properties similar to those of $Pt(en)(en\text{-}H)^{2+}$ occur on reaction of OH with the glycine complexes *cis*-$Pt(gly)_2$ and *trans*-$Pt(gly)_2$.[17] The products associated with the cis compound are *not* the same as those of the trans complex. This difference precludes a tetrahedral form for the platinum glycine entities and presumably also for $Pt(en)(en\text{-}H)^{2+}$. Thus the systems may exhibit square-planar microsymmetry. Of note in this regard is the spectral similarity of these materials to those of the monoanionic complexes of Ni, Pd, and Pt containing dithiolene and related ligand systems.[11] The bis complexes possess spin-doublet ground states and square-planar geometry. These systems, while formally M(III), can be designated (depending upon the ligand) as a M(II) center stabilizing a ligand radical cation. In a similar vein, Whitburn and Laurence[46] have recently reported results on the reactions of nickel(II) macrocyclic complex ions with OH and dihalogen radical anions. They proposed that the transients which exhibit absorption peaks near 550 nm and which are derived from nickel(III) species are describable as nickel(II) complexes containing a nitrogen-based ligand radical. The amine nitrogen radical site is considered to have lost a proton in its formation. In the present context, an alternative description of $Pt(en)(en\text{-}H)^{2+}$ as a platinum(III) species containing an amido group would be that it is a platinum(II) entity with a nitrogen-based ligand radical where a proton has been lost from the radical site. Presumably charge delocalization between the platinum and nitrogen could lead to enhanced stability, and this may account for the apparent greater stability of $Pt(en)(en\text{-}H)^{2+}$ relative to the $Pt(en)_2(X)^{n+}$ forms. It is notable that this does not result in permanent degradation of the ligand. In this sense, the binding of ethylenediamine (and glycine) to a platinum(II) center has afforded some degree of radiolytic protection for the ligand toward OH, in contrast to its behavior as a free ligand.

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Registry No. *trans*-$[Pt(en)_2(OH)_2](ClO_4)_2$, 74643-96-2; $[Pt(en)_2](ClO_4)_2$, 28136-92-7; OH, 3352-57-6; H, 12385-13-6; $Pt(en)_2(OH)^{2+}$, 74592-11-3; $Pt(en)(en\text{-}H)^{2+}$, 74592-12-4; $Pt(en)_2(H_2O)^{3+}$, 74592-13-5; $Pt(en)_2(Cl)^{2+}$, 74592-14-6.

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(46) Whitburn, K. D.; Laurence, G. S. *J. Chem. Soc., Dalton Trans.* **1979**, *139.*

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Photoracemization of Δ- and Λ-Tris(ethylenediamine)chromium(III)

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The quantum yield (ϕ_R) for the photoracemization of $Cr(en)_3^{3+}$ at ambient temperature was determined. For the process $\Delta\text{-}Cr(en)_3^{3+} \rightleftharpoons \Lambda\text{-}Cr(en)_3^{3+}$ ϕ_R was found to be 0.015, independent of hydrogen ion concentration when varied from 0.08 to 1.0 M. Because extensive photolysis was necessary to obtain sufficient rearrangement for quantitative measurement, several methods of separation of $Cr(en)_3^{3+}$ from major photoproducts were utilized, and a method for determining quantum yield in the presence of a large quantity of other photoproducts was designed. Mechanisms consistent with experimental data are discussed with emphasis on one suggested by an orbital correlation diagram.

Introduction

Most investigations of the photochemistry of chromium(III)–amine complexes have dealt with photosubstitution[1,2] of a ligand by solvent, usually water. If the reaction coordinate for photoreaction is taken as one of the normal coordinates of the octahedral structure, models[3-6] of this process have considered almost exclusively the $E_g(S_2)$ symmetry vibration within the lowest excited quartet, a motion that causes elongation along the z axis or in the xy plane; such motion leads to species generally thought to be like d^4 or d^9 complexes and hence very fast to substitute.

Two possible fates of a molecule activated for substitution and containing chelated groups can be delineated: (1) The bond ruptured can be replaced by solvent in which case net photosubstitution occurs. This process is exemplified by many

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(1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, 1970.

(2) E. Zinato in "Concepts of Inorganic Chemistry", A. W. Adamson and P. D. Fleischauer, Eds., Wiley, New York, 1975, pp 143–201.

(3) J. I. Zink, *J. Am. Chem. Soc.*, **94**, 8039 (1972).

(4) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).

(5) C. Bifano and R. G. Linck, *Inorg. Chem.*, **13**, 609 (1974).

(6) L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **99**, 2208 (1977).