Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36830

Substitution by Tridentate Groups in Platinum(II) Complexes. II. The Diethylenetriamine–Tetrachloroplatinate(II) Reaction

By Edward D. Smith, John A. McCann, and John E. Teggins

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The rate of replacement of chloride ligands in $PtCl_4^{2-}$ by diethylenetriamine in aqueous solution has been found to be pH dependent. At 25° the kinetic data obtained throughout the pH range 4–10 are consistent with the rate law $R = \{k_1[\text{dien}] + k_2[\text{dienH}^+] + k_3[\text{dienH}_2^{2+}]\}[PtCl_4^{2-}]$. The values for k_1, k_2, and k_3 are 5.0×10^{-3}, 4.0×10^{-3}, and 7.1×10^{-4} M^{-1} sec^{-1}, respectively. There is no evidence for replacement of chloride ligands by dienH_3^{3+}. The algebraic form of the obtained rate law is identical with that reported for the reaction of $PtBr_4^{2-}$ with diethylenetriamine. These data have been interpreted in terms of a mechanism in which the rate-determining step involves the formation of the initial platinum–nitrogen bond between the amine and the complex ion.

Introduction

Extensive kinetic studies have been performed for monodentate ligand displacement reactions of platinum(II) complexes. Many common complexes, however, contain ligands which form more than one bond to platinum. Very little information has been reported concerning the mechanisms by which such polydentate groups displace singly bound ligands. This research group has observed that each of the possible protonated and unprotonated forms of the tribasic amine diethylenetriamine (dien) appear to react directly at different rates with $PtBr_4^{2-}$ to produce $Pt(\text{dien})Br^+$.[1] More recently, Rund and Palocsay[2] have proposed that 1,10-phenanthroline, which is a relatively rigid molecule, can react with $PtCl_4^{2-}$ *via* the aquo complex $PtCl_3(H_2O)^+$. Consequently, this investigation of the $PtCl_4^{2-}$–dien reaction serves to elucidate the influence of the displaced monodentate ligand upon the observed kinetics of substitution by dien.

Experimental Section

Materials.—Platinum foil was dissolved in aqua regia and precipitated as potassium hexachloroplatinate(IV) by the addition of potassium chloride and carbonate. Potassium tetrachloroplatinate(II) was prepared by the oxalate reduction of the resultant K_2PtCl_6.[3] The product was recrystallized three times from 1% aqueous solutions of potassium chloride. Platinum was determined gravimetrically after hydrazine reduction. The cation content was determined by an ion-exchange replacement of K^+ by H^+ and titration. *Anal.* Calcd for K_2PtCl_4: Pt, 47.0; K, 18.8. Found: Pt, 46.2; K, 18.8. Technical grade dien was vacuum distilled prior to use. The water for kinetic experiments was redistilled from alkaline permanganate solution. All other employed materials were of reagent grade.

Procedures. A. Determination of Dissociation Constants for the Conjugate Acids of dien.—These values were obtained by direct potentiometric titration as described in a previous publication.[1] The values obtained at 25° and ionic strength 0.32 were: pK_1, 4.23; pK_2, 8.89; pK_3, 10.01.

B. Determination of Rate Constants by the Spectrophotometric Method.—Weighed amounts of finely powdered K_2PtCl_4 were dissolved in an aqueous solution of dien which had been preequilibrated at 25°. The pH values and ionic strengths of the final solutions were controlled by the incorporation of sodium chloride and hydrochloric acid in the original amine solution. In the fundamental experiments reported in Table I both the free chloride and dien concentrations were considerably in excess of the complex concentration. A portion of the reaction mixture was transferred to a quartz cell maintained at 25° by a water jacket in a Perkin-Elmer Model 450 spectrophotometer. The complex product of the reaction ($Pt(\text{dien})Cl^+$) is colorless with an absorption maximum at 270 mμ.[4] The progress of the reaction could be followed, therefore, from the decrease in optical densities of reaction solutions at 395 mμ which corresponds to an absorption maximum for $PtCl_4^{2-}$. It was possible to record optical density values within 100 sec after initiation of reactions. The pH values of original dien solutions and completed reaction mixtures were measured using a Beckman Research pH meter. The reaction pH was assumed to be that estimated for solutions in which the substitution was 25% complete. Because reaction solutions were buffered by relatively large concentrations of dien salts, this value was close to the pH of the original dien solution.

$PtCl_4^{2-}$ is known to aquate according to eq 1 to produce the weakly acidic $PtCl_3(H_2O)^-$. The quoted equilibrium constants were reported by Martin.[5] Equations 1 and 2 combined with the

$$PtCl_4^{2-} + H_2O \rightleftharpoons PtCl_3(H_2O)^- + Cl^- \quad (K = 0.018\ M) \quad (1)$$

$$PtCl_3(H_2O)^- \rightleftharpoons PtCl_3(OH)^{2-} + H^+ \quad (K = 10^{-7}\ M) \quad (2)$$

dissociation constant for water allow the equilibrium constant for eq 3 to be estimated. Because excess chloride ion was always

$$PtCl_4^{2-} + OH^- \rightleftharpoons PtCl_3(OH)^{2-} + Cl^- \quad (K \approx 10^5\ M) \quad (3)$$

present in the reaction mixtures reported in Table I, the concentration of $PtCl_3(H_2O)^-$ was always much smaller than that of $PtCl_4^{2-}$ in the more acidic media. In the more basic solutions significant concentrations of $PtCl_3(OH)^{2-}$ would be present in equilibrium mixtures. Freshly prepared solutions of $PtCl_4^{2-}$ were employed for dien substitution reactions, and, fortunately, the substitution rates for $PtCl_4^{2-}$ by amine in basic solutions were faster than the aquation rate reported by Martin[5] for this complex ion. Since hydroxide ion reacts slowly with platinum complexes, hydroxo complexes are usually obtained by prior reaction with water followed by rapid proton transfer from the resultant aquo complex to a hydroxide ion present in solution.[6] This results in the rate of formation of the aquo complex being effectively equal to the rate of formation of the hydroxo complex. Thus $PtCl_3(OH)^{2-}$ concentrations present during the initial 20% of substitution reactions were relatively small. It was still possible, however, that very reactive $PtCl_3(H_2O)^-$ or $PtCl_3(OH)^{2-}$ could make an important contribution to the over-all reaction.[7] In order to investigate these possibilities a series of experiments was

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TABLE I

DETERMINATION OF SPECIFIC RATE CONSTANTS BY THE SPECTROPHOTOMETRIC METHOD AT 25° AND $\mu = 0.32$

Molar concn $\times 10^3$			10^4k_2, M^{-1} sec^{-1}	
$PtCl_4^{2-}$	dien	pH	Obsd	Calcd[b]
2.5	60	9.61	36	38.5
2.5	30	9.60	40	38.4
2.5	100	9.54	36	37.7
5.0	100	9.50	39	36.7
10	100	9.50	37	36.7
2.5	30	9.02	28	27.3
2.5	60	9.02	27	27.3
2.5	100	9.01	25	27.1
5	100	8.97	24	26.3
5	60	8.95	27	25.8
10	60	8.91	25	24.9
5	30	8.90	27	24.7
10	30	8.89	25	24.5
10	60	8.85	22	23.6
10	100	8.83	23	23.2
50	100	7.98	11	11.2
25	60	5.60	7.3	6.81
10	30	5.48	6.7	6.74
2.5	30	5.48	6.3	6.74
5	60	5.43	7.1	6.67
10	60	5.42	6.7	6.66
10	98	5.40	6.5	6.64
10	30	4.37[a]	3.9	4.12
5	60	4.25[a]	3.8	3.62
10	60	4.23[a]	3.9	3.55
2.5	60	4.14[a]	3.1	3.17
2.5	30	4.08[a]	3.0	2.95

[a] Calculated from initial rate for first 20% of reaction. [b] From eq 6 and 7.

performed with preequilibrated solutions containing varying amounts of $PtCl_3(H_2O)^-$ or $PtCl_3(OH)^{2-}$. The results of this work are shown in Tables II and III.

TABLE II

DEPENDENCE OF EXCHANGE RATE UPON $PtCl_3(H_2O)^-$ [a] AT 25°, $\mu = 0.35$,[b] pH 4.95, AND 0.1 M dien

Molar equil concn $\times 10^3$			$10^3T_{1/2}$, sec	10^4k_2, M^{-1} sec^{-1}
$PtCl_4^{2-}$	$PtCl_3(H_2O)^-$	Cl^-		
0.92	4.08	4.08	12.4	5.6
2.33	2.67	15.7	12.5	5.5
4.70	0.30	300	11.6	6.0

[a] Solutions were preequilibrated before addition of dien. [b] Adjusted by addition of HNO_3 and KNO_3.

TABLE III

DEPENDENCE OF EXCHANGE RATE UPON $PtCl_3(OH)^{2-}$ [a] AT 25°, $\mu = 0.5$,[b] pH 8.7, AND 0.06 M dien

Molar equil concn[c] $\times 10^3$			$10^3T_{1/2}$, sec	10^4k_2, M^{-1} sec^{-1}
$PtCl_4^{2-}$	$PtCl_3(OH)^{2-}$	Cl^-		
0.1	4.9	4.9	6.1	18.8
1.5	3.5	304	5.7	20.2
2.1	2.9	503	5.8	19.8

[a] Solutions preequilibrated before addition of dien. [b] Adjusted with $NaNO_3$ and HNO_3. [c] Approximate values because the accurate value for K_3 was not available.

C. Determination of Rate Constants by the Potentiometric Method.—The method is based upon the fact that uncomplexed dien is protonated in aqueous solutions, whereas amine ligands are unprotonated. This results in the liberation of hydrogen ion as indicated in the equation

$$PtCl_4^{2-} + \text{dien}\cdot xH^+ \longrightarrow Pt(\text{dien})Cl^+ + 3Cl^- + xH^+ \quad (4)$$

The degree of protonation (x) can be calculated from equilibrium data in ref 1.

A 25-ml reaction mixture was prepared by the same procedure that was employed in spectrophotometric determinations. This solution was placed in a double-walled reaction vessel maintained at 25 ± 0.1° by water circulation. The contents of the vessel were mixed by means of an air-driven magnetic stirrer. After initiation of the reaction the solution became more acidic because of the consequent liberation of hydrogen ion. When the pH value had decreased by 0.03 unit, sufficient 0.1 M sodium hydroxide solution was added to increase this value by 0.06 unit. Repetition of this procedure maintained the average pH during the course of the reaction close to the initial value. Because sodium hydroxide solutions were very concentrated compared to complex solutions, dilution of the reactant solution by the addition of base was negligible. The amounts of liberated hydrogen ion equivalent to complete substitution of $PtCl_4^{2-}$ by dien were calculated using the equilibrium data in ref 1. It was possible, therefore, to calculate the volume of sodium hydroxide solution required to neutralize the hydrogen ion liberated when half of the $PtCl_4^{2-}$ in a given reaction mixture had been substituted. The half-lives calculated from these data are given in Table IV.

TABLE IV

POTENTIOMETRIC DETERMINATION OF RATE CONSTANTS AT 25°, 10^{-2} M $PtCl_4^{2-}$, 0.06 M dien, AND $\mu = 0.32$

pH	x[a]	$10^3T_{1/2}$, sec	10^4k_2, M^{-1} sec^{-1} Obsd	10^4k_2, M^{-1} sec^{-1} Calcd[c]
8.98	1.39	4.3	27	26.5
7.98	1.89	8.6	13	11.2
7.00	2.00	14.5	7.9	7.40
4.95	2.16	20.6	5.6	5.96
3.90	2.68	55[b]	2.1	2.27

[a] Degree of protonation as indicated by eq 4. [b] Estimated from initial rate. [c] From eq 7 and 6.

Results and Calculations

In the majority of experiments dien was present in excess concentration compared to the complex ion. Under these circumstances a pseudo-first-order treatment of the rate data was satisfactory. The observed first-order rate constants (K_1) were calculated from the slopes of the usual plots of the integrated rate expression. The specific rate constant for the substitution reaction (as defined by eq 5) was then calculated from eq 6. The actual values employed for dien concentrations were those corresponding to 25% reaction.

$$\text{rate} = k_2(\text{dien})(PtCl_4^{2-}) \quad (5)$$

$$k_1 = k_2(\text{dien}) \quad (6)$$

The values for observed first-order rate constants obtained by both the spectrophotometric and the potentiometric methods at an ionic strength of 0.32 and 25° are consistent with the rate law

$$k_1 = 5.0 \times 10^{-3}[\text{dien}] + 4.0 \times 10^{-3}[\text{dienH}^+] + 7.1 \times 10^{-4}[\text{dienH}_2^{2+}] \quad (7)$$

All constants in eq 7 have units of M^{-1} sec^{-1}.

Excess chloride ion was always present in the reaction mixtures reported in Table I. Consequently, the concentrations of $PtCl_3(H_2O)^-$, as calculated from eq 1, were much lower than the corresponding $PtCl_4^{2-}$ concentrations. An examination of the data in Table II for preequilibrated reaction mixtures containing low free chloride ion concentrations indicates that the aquo complex was not sufficiently reactive to make a significant contribution to the rate constants reported in Table I. The data in Table III imply that $PtCl_3(OH)^{2-}$ and $PtCl_4^{2-}$ have very similar reactivities with respect to dien at pH ~9. Freshly prepared solutions of $PtCl_4^{2-}$ were employed for the experiments reported in Table I. The half-lives for the substitution of $PtCl_4^{2-}$ by the amine in basic solutions were shorter than the aquation half-life reported by Martin.[5] Thus the concentrations of the hydroxo complex present during the initial 20% of the substitution reaction were too low to influence significantly the calculated values for rate constants.

The potentiometric determinations of rate constants were used as a convenient independent method for checking the rate constants obtained by the spectrophotometric method. As can be seen from Table IV, good agreement exists between the two methods. These data also indicate that the employed equilibrium data for the protonation of dien were reasonably accurate.

An examination of the kinetic data in Table I shows that the observed second-order rate constants, as defined by eq 6, are independent of the reactant concentrations at a given pH value. Thus the assumption that the reaction is first order with respect to both of the species is justified. It is also apparent from Tables II and III that the small concentrations of $PtCl_3(OH)^{2-}$ and $PtCl_3(H_2O)^-$ present in reaction mixtures containing excess chloride ion would have little influence upon the observed kinetics. The pH dependence of the substitution reactions is most easily explained by ascribing different rates of reaction to the various dien species. The relative reactivities of these amine molecules are given by the numerical values of the rate constants in eq 7. Relative to the dien molecule these reactivities are: dien, 1.00; $dienH^+$, 0.80; $dienH_2^{2+}$, 0.14; $dienH_3^{3+}$, 0.00. These relative values are almost identical with the previously reported[1] corresponding ratios for the $PtBr_4^{2-}$–dien reaction (dien, 1.00; $dienH^+$, 0.75; $dienH_2^{2+}$, 0.15; $dienH_3^{3+}$, 0.00). The low reactivity of the completely protonated amine ion suggests that a dien group must contain at least one unprotonated nitrogen atom if it is to act as a nucleophilic substituent toward the metal ion. This conclusion is not surprising because an RNH_3^+ group would not be expected to behave as a Lewis base.

It seems probable that the rate-determining steps for each of the substitution reactions of $PtBr_4^{2-}$ or $PtCl_4^{2-}$ by amine involve the formation of an initial single platinum–nitrogen bond. Under these circumstances the reaction would require the displacement of one halide ligand by an unprotonated nitrogen center regardless of the degree of protonation of the total amine molecule. Because the positive charge, if any, of the incoming group would be localized in positions remote from the platinum center during the rate-determining reaction, the influence of this charge would be minimized. Therefore, the number of nucleophilic nitrogen sites per dien molecule would influence its reactivity. The unprotonated dien molecule, which has three such sites, reacts slightly faster than the monoprotonated ion which has two nucleophilic nitrogen atoms. Electrostatic repulsion would make the diprotonated form of the amine containing the maximum charge separation the more stable. Consequently, $dienH_2^{2+}$ would not contain a terminal nucleophilic group, whereas dien and $dienH^+$ must contain at least one such group. Such an effect could contribute to the fact that the rate of substitution of $PtCl_4^{2-}$ by $dienH_2^{2+}$ is less than would be predicted on statistical grounds compared to $dienH^+$ or dien. It is to be noted that purely electrostatic effects could not account for the observed relative reactivities because the positively charged amine ions react more slowly than dien with the negatively charged complex ion. Each of the dien species is six to seven times more reactive with respect to $PtBr_2^{2-}$ than $PtCl_4^{2-}$. This phenomenon could be consistent with the assumption that the rate-determining reaction involves the formation of one Pt–N bond. The situation is equivalent to monodentate displacement by substituted ammonia. If the substituent is not in the vicinity of the nucleophilic nitrogen atom, its influence upon the energy of the activated complex would be due to inductive changes in electron density at the active site rather than steric interaction between the substituent and the complex ion. Now suppose that the rate-determining step involves the formation of two or more bonds from an amine molecule to platinum. Because bromo ligands are much larger than chloro ligands, very different interactions between the incoming dien and the initial halide ligands would result. Therefore, the relative values for the series of constants in the rate expression (eq 7) should be different for $PtCl_4^{2-}$ and $PtBr_4^{2-}$ reactions. Because the reaction product contains a tridentate ligand, any reaction mechanism would have to include steps in which dien forms more than one bond to platinum. Since these events would occur after the rate-determining reaction in the proposed mechanism, however, they would not influence the observed kinetics.

After completion of the substitution reactions reported in this paper the optical densities of solutions at 395 mμ, which is the location of an absorption maximum for $PtCl_4^{2-}$, had decreased to approximately 3% of their initial values. In addition a new peak appeared at 270 mμ. The latter value has been reported by Gray[4] as a principal absorption maximum for $Pt(dien)Cl^+$. These data are consistent with the replacement of three chloride ligands in a $PtCl_4^{2-}$ ion by one dien molecule as indicated in eq 4. Watt and Cude[8] have reported that the product of the reaction of relatively high concentrations of $PtCl_4^{2-}$ with dien·3HCl in necessarily acidic solution is a precipitate of $Pt_2Cl_4(dienH)_2{}^{2+}PtCl_4^{2-}$. The most probable explanation for the formation of the product observed by Watt and Cude is that under more highly acidic conditions intermediates containing less than three nitrogen bonds to a platinum ion could be stabilized by protonation of the unattached portion of the ligand. Intermolecular reaction between such spe-

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cies could result in the indicated dimeric cation. Because the systems reported in this paper were studied at 25°, it is not surprising that the reaction products were different from those obtained by Watt and Cude, who refluxed more concentrated and more acidic solutions for several hours at 100°.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAN DIEGO STATE COLLEGE, SAN DIEGO, CALIFORNIA 92115,
AND BATTELLE MEMORIAL INSTITUTE, PACIFIC NORTHWEST LABORATORY, RICHLAND, WASHINGTON 99352

Bis(2-ethylhexyl)phosphoric Acid Exchange in Dilute Solutions of Copper(II) Complexes by Nuclear Magnetic Resonance Spectroscopy

BY F. L. LAFFERTY,[1a] R. C. JENSEN,[1a] AND J. C. SHEPPARD[1b]

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The temperature dependence for the exchange of bis(2-ethylhexyl)phosphoric acid with the copper(II) complex of this acid has been studied in trichloroethylene using nmr line-broadening techniques. The chemical-exchange rate constant is 8.8×10^6 sec^{-1} at 298°K (assuming two sites for relaxation of the acid hydrogen). The scalar coupling constant is 1.8×10^6 Hz. The spin–lattice relaxation time for the unpaired electron of the copper(II) complex is 4.9×10^{-7} sec.

Introduction

The ligand exchange of copper(II) complex ion systems has been studied by nuclear magnetic resonance (nmr) spectroscopy,[2-13] electron spin resonance (esr) spectroscopy,[8-10,13] ultrasonic relaxation,[14] polarography,[15,16] and isotopic dilution,[17-19] employing various ligands (H_2O,[2,3,6,8,9,13,14,19] NH_3,[5,7,17,18] F^-,[12] CH_3OH,[4] ethylenediamine,[2,7,9,10] alkyl-substituted ethylenediamines,[11] 2,2-dipyridine,[13] ethylenediaminetetraacetic acid,[15,16] and glycines[7]). In most cases only approximate values of limits for the rate constant could be given. The more reliable rate constants have been obtained from nmr and esr line widths. Most of the copper systems using nmr and esr were carried out in a temperature region where the line widths were dependent upon several relaxation mechanisms. In this study nmr techniques have been used to observe the chemical exchange of bis(2-ethylhexyl)phosphoric acid, HD2EHP, with the copper(II) complex ion of this acid without interference from other relaxation mechanisms.

When a ligand is coordinated to a paramagnetic metal complex ion, the spin–spin relaxation time, T_2, of hydrogen atoms near the metal center is decreased by the magnetic interaction between the hydrogen nuclei and the unpaired electrons. This decrease in T_2 measurably broadens the hydrogen line widths of the uncomplexed ligand. The line width at half its maximum amplitude, $\Delta\nu$, in hertz is related to T_2 by $1/T_2 = \pi\Delta\nu$. Two processes of relaxation contribute to T_2. The process which is independent of the presence of the paramagnetic ion will be designated T_{2L}, and the process which is dependent on the presence of the paramagnetic ion will be designated T_{2P}. If T_{2L} and T_{2P} are independent of each other, then for dilute solutions $1/T_2 = (1T_{2L}) + (1/T_{2P})$ and T_{2P} can be determined. For the limiting case of a dilute, single paramagnetic species causing only a small shift in the resonance frequency, it can be shown[6] that $T_{2P}P_M = T_{2M} + \tau_M$, where T_{2M} is the spin–spin relaxation time of the ligand hydrogens in the coordination sphere of the paramagnetic complex ion and P_M is a probability factor relating τ_M, the chemical-exchange lifetime of the ligand hydrogens in the metal coordination sphere, to τ_L, the chemical exchange lifetime of the uncomplexed ligand hydrogens. P_M is approximately equal to $m[M]/l[L]$, where l is the number of hydrogens in an uncomplexed ligand contributing to the observed resonance line, m is the number of these hydrogens subject to relaxation in a paramagnetic coordination sphere, [M] is the molar concentration of the paramagnetic ion, and [L] is the molar concentration of the uncomplexed ligand. Normally m/l is set equal to n, and this notation will be followed.

Because T_{2M} and τ_M differ in their temperature dependencies, there may be temperature regions where one will dominate. For the copper–D2EHP system, a temperature region was found where the ligand-exchange rate dominated the other relaxation mechanisms.

Experimental Section

A Varian A-60 spectrometer was used to record the magnetic resonance of the acid hydrogen (δ ~12 ppm) of $(HD2EHP)_2$. Operating parameters such as radiofrequency field strength, filter band width, and sweep time were optimized so as not to

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