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

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The rate of replacement of bromide ligands in $PtBr_4^{2-}$ by diethylenetriamine in aqueous solution has been found to be pH dependent. At 25° the kinetic data obtained throughout the pH range 3–10 are consistent with the rate law $R = \{k_1[\text{dien}] + k_2[\text{dienH}^+] + k_3[\text{dienH}_2{}^{2+}]\}[PtBr_4{}^{2-}]$. The values for k_1, k_2, and k_3 are 3.3×10^{-2}, 2.5×10^{-2}, and $5.0 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$, respectively. There is no evidence for replacement of bromide ligands by $\text{dienH}_3{}^{3+}$. A mechanism has been proposed which relates the reactivities of the various amine species, as indicated by the corresponding constants in the rate expression, with their structures in aqueous solution.

Introduction

Extensive studies have been made of the kinetics of monodentate ligand replacement reactions of platinum(II) complexes. Consequently, the general characteristics of these systems are well understood. Many common complexing agents, however, form two or more bonds to the metal center. The mechanisms by which such polydentate groups displace singly bound ligands have not been investigated in detail. Complexes in which the tridentate ligand diethylenetriamine (dien) occupies three of the square-planar platinum(II) coordination sites have been utilized in kinetic studies by several workers.[1,2] However, dien has been used in these investigations to block three of the available coordination positions in order to facilitate the study of substitution at the remaining position. The dien complexes for these studies are prepared by simple substitution as indicated in eq 1. These reactions are

$$PtX_4{}^{2-} + \text{dien} \longrightarrow Pt(\text{dien})X^+ + 3X^- \qquad (1)$$

markedly pH dependent, a fact that is not clearly indicated by the chemical literature. For example, the method used by Martin and his group[3] for the preparation of $Pt(\text{dien})Br^+Br^-$ utilizes the reaction between $PtBr_4{}^{2-}$ and dien at a pH value of approximately 6. Under these conditions the reaction is essentially complete in 30 min at 25°, whereas the usually quoted preparation,[4] which proceeds in a more acidic medium, requires several hours at 100°. These data suggest that the rate of substitution is related to the concentrations of the various protonated forms of dien (which is tribasic) present at different pH values. The $PtBr_4{}^{2-}$–dien substitution, therefore, provides a convenient system with which to initiate kinetic studies of substitution of platinum(II) by potentially tridentate ligands.

Experimental Section

Materials.—Rubidium tetrabromoplatinate(II) was prepared and analyzed as described previously.[5] Technical grade dien was vacuum distilled prior to use. The water for kinetic experiments was redistilled from alkaline permanganate solution. All other materials employed were of analytical reagent grade.

Procedures. A. Determination of Dissociation Constants for the Conjugate Acids of dien.—Although the pK values for dien in aqueous solution have been reported by Prue and Schwarzenbach,[6] these data were not available for the exact conditions of the kinetic experiments described in this paper. Because the values are essential for the interpretation of this work, they were determined by direct potentiometric titration. This method consisted of adding 0.5, 1.5, and 2.5 equiv of hydrobromic acid to separate dien solutions. In each instance the pH value of the solution was measured utilizing a Beckman Research pH meter. The initial amounts of dien and HBr were such that the ionic strengths at the measured pH values were 0.32. In basic solution the free hydrogen ion concentration is extremely low compared to the total concentration of dien. Under these circumstances it can be assumed that added hydrogen ion is completely consumed by protonation of the amine. Consequently, the pH values measured after the separate addition of 0.5 and 1.5 equiv of acid to solutions of the base correspond to pK_3 and pK_2, respectively. After the addition of 2.5 equiv of acid, however, a significant concentration of free hydrogen ion is present in solution. Under these circumstances, to measure pK_1, it is necessary to use

$$\text{pH} = \text{p}K_1 + \log \frac{[\text{dienH}_2{}^{2+}]}{[\text{dienH}_3{}^{3+}]} \qquad (2)$$

where

$$[\text{dienH}_2{}^{2+}] = 3[\text{total dien}] - [\text{added HBr}] + [\text{measured H}^+]$$
$$[\text{dienH}_3{}^{3+}] = [\text{total dien}] - [\text{dienH}_2{}^{2+}]$$

These results are summarized in Table I. Values obtained by an extrapolation of the data of Prue and Schwarzenbach[6] are included for comparison.

B. Determination of Rate Constants by the Spectrophotometric Method.—Weighed amounts of finely powdered $Rb_2PtBr_4 \cdot H_2O$ were dissolved in an aqueous dien solution prequilibrated at 25°. Solutions were stored in opaque flasks. The pH value and ionic strength of the resultant solution was controlled by the addition of sodium bromide and hydrobromic acid to the original amine solution. A portion of the reaction mixture was then transferred to a quartz cell maintained at 25.00 ± 0.05° by a water jacket in a Perkin-Elmer Model 450 spectrophotometer. Previously reported work[7] has shown that the product[5] of the reaction ($Pt(\text{dien})Br^+$) does not absorb radiation in the visible region of the spectrum. Consequently, the progress of the reaction could be followed from the decrease in optical density of reaction solutions at either 415 or 520 mμ, which values correspond to absorption maxima[5] for $PtBr_4{}^{2-}$. Although the reac-

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[1] F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

[2] (a) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962); (b) J. E. Teggins and D. S. Martin, Jr., *ibid.*, **6**, 1003 (1967).

[3] D. S. Martin, Jr., and E. L. Bahn, *ibid.*, **6**, 1653 (1967).

[4] F. G. Mann, *J. Chem. Soc.*, 466 (1934).

[5] J. E. Teggins, D. R. Gano, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chem.*, **6**, 69 (1967).

[6] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 947 (1950).

[7] H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

TABLE I

p*K* VALUES FOR dien AT 25° AND IONIC STRENGTH 0.32[a]

	Exptl value	Ref 6 value (in 0.3 *M* KCl)
pK_3	10.01	9.96
pK_2	8.89	9.17
pK_1	4.23	4.47

[a] As defined by $\text{dienH}_3^{3+} \rightleftharpoons \text{dienH}_2^{2+} + H^+$ (K_1).

tions were followed at 415 mμ (because optical densities at this wavelength are of suitable magnitudes for measurements in 1-cm quartz cells), estimated half-lives at the two wavelengths were in agreement within experimental error. It was possible to record optical density values within 1.5 min after initiation of the reaction. The pH values of the original dien solutions and the completed reaction mixtures were measured with a Beckman Research pH meter. Under the reaction conditions the concentrations of the various protonated dien species, which were present in excess concentrations compared to $PtBr_4^{2-}$, did not change appreciably during the course of the reaction. Consequently, the hydrogen ion concentration during the reaction was assumed to be the arithmetic mean of the initial and final values. No significant difference in measured rate constants was observed when a reaction was followed by measuring the absorption of separate samples withdrawn from a reaction mixture in an opaque flask after suitable periods of time as opposed to employing one reaction mixture in a spectrophotometer cell for a series of measurements. Since photocatalysis by the spectrophotometer beam was not measurable, the latter, more economical method was used to obtain the reported data.

$PtBr_4^{2-}$ is known to aquate according to eq 3. Both Martin[5] and Grinberg[8] have estimated the corresponding equilibrium

$$PtBr_4^{2-} + H_2O \rightleftharpoons PtBr_3(H_2O)^- + Br^- \qquad (3)$$

constant to be approximately 3×10^{-3} *M* at 25°. Because excess free bromide was always present in the reaction mixtures reported in Table II, the concentrations of aquated complex species were very low. These data do not exclude, however, the possibility that aquated species were involved in the rate-determining step. Therefore, it was decided to execute a series of experiments in which the concentration of the aquo complex was varied appreciably. The results of this work are shown in Table III.

C. Determination of Rate Constants by the Potentiometric Method.—The method is based upon the fact that the free amine is protonated in reaction media, whereas dien ligands are unprotonated. Consequently, the progress of reactions is accompanied by the liberation of protons as indicated in eq 4. The degree of

$$PtBr_4^{2-} + \text{dien}\cdot xH^+ \longrightarrow Pt(\text{dien})Br^+ + 3Br^- + xH^+ \qquad (4)$$

protonation (as indicated by x) was calculated from the p*K* values of the amine, which are given in Table I.

A 50-ml reaction mixture was prepared by the same procedure that was employed in the spectrophotometric determinations. This solution was placed in a double-walled reaction vessel which was maintained at 25.0 ± 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 pH value of the solution was held approximately constant by addition of 0.1 *M* sodium hydroxide solution from a microburet. In practice these values varied within ±0.05 pH unit as recorded by a Beckman Research pH meter utilizing standard calomel and hydrogen electrodes. The amount of liberated hydrogen ion equivalent to complete substitution of $PtBr_4^{2-}$ by dien was calculated from the equilibrium data in Table I. It was possible, therefore, to calculate the volume of sodium hydroxide solution required to neutralize the hydrogen ion liberated when half of the $PtBr_4^{2-}$ had been substituted. These half-lives are given in Table IV.

TABLE II

DETERMINATION OF SPECIFIC RATE CONSTANTS BY THE SPECTROPHOTOMETRIC METHOD AT 25.0° AND μ = 0.318

Molar concn[a] × 10^3			$10^3k_1'$, M^{-1} sec^{-1}	
$PtBr_4^{2-}$	dien	pH	Obsd	Calcd
5	30	10.13	28	29
5	30	9.28	21	21
5	30	9.13	17	19
5	30	9.02	18	18
5	30	8.99	17	17
5	30	5.83	5.0	4.8
5	30	5.65	5.1	4.7
5	30	5.18	4.3	4.3
5	30	4.39	3.5	3.0
5	30	3.77	1.3[b]	1.3
5	30	3.00	0.3[b]	0.3
1	30	9.13	18	19
1	100	9.00	16	17
5	10	8.87	15[b]	15
3	50	8.86	15	15
5	100	8.97	16	17
10	30	8.99	16	17
1	30	5.63	5.2	4.7
1	30	5.93	5.0	5.0
2	30	5.65	4.8	4.7
5	96	5.84	5.0	4.8
5	60	5.95	5.2	5.0

[a] Accurate to within 0.5%. [b] Calculated from initial reaction rate.

TABLE III

DEPENDENCE OF REACTION RATE UPON $[PtBr_3(H_2O)^-]$ AT 25°, μ = 0.62,[a] 0.1 *M* dien, AND pH 5.44[a]

Molar equilib concn				
$PtBr_4^{2-}$ ($\times 10^{-3}$)	$PtBr_3(H_2O)^-$ ($\times 10^{-5}$)	Br^- ($\times 10^{-2}$)	$T_{1/2}$	$10^3k_1'$, M^{-1} sec^{-1}
4.95	5.00	30.0	1200	5.78
4.85	15.0	10.0	1218	5.68
3.95	105	1.11	1188	5.88

[a] Adjusted by addition of HNO_3 and KNO_3.

TABLE IV

POTENTIOMETRIC DETERMINATION OF RATE CONSTANTS AT 25°, 10^{-2} *M* $PtBr_4^{2-}$, AND μ = 0.318

				$10^3k_1'$, M^{-1} sec^{-1}	
pH	[dien], *M*	x^a	$T_{1/2}$, sec	Obsd	Calcd
9.1	0.096	1.18	300[b]	23	21
8.6	0.090	1.69	714	11	11
7.4	0.087	1.97	1428	5.5	5.7
5.1	0.084	2.12	1884	4.3	4.3
4.6	0.080	2.30	2646	3.3	3.5
4.0	0.076	2.68	4916	1.8	1.8

[a] Degree of protonation of dien as indicated in eq 3. [b] Relatively inaccurate because of short half-life.

Results and Calculations

In experiments where the dien is present in excess concentration, a pseudo-first-order treatment of the rate data was satisfactory. Under these conditions the observed first-order rate constant (k_1) could be calculated from the slope of the usual plot of the integrated rate expression. The specific rate constant for the substitution reaction (as defined by eq 5) was then calculated from eq 6.

$$\text{rate} = k_1'[\text{dien}][PtBr_4^{2-}] \qquad (5)$$

$$k_1 = k_1'[\text{dien}] \qquad (6)$$

In this manner values for k_1' were obtained for various reactant concentrations in the pH range 4–10.

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[8] A. A. Grinberg and G. A. Shagisultanova, *Izv. Akad. Nauk SSSR*, **6**, 981 (1955).

The rate constants for the two experiments performed in more acidic media were estimated from initial reaction rates. These data are given in Tables II and IV.

The values for observed first-order rate constants obtained at an ionic strength of 0.32 by the spectrophotometric method are consistent with the rate law

$$k_1 = 3.3 \times 10^{-2}[\text{dien}] + 2.5 \times 10^{-2}[\text{dienH}^+] + 5.0 \times 10^{-3}[\text{dienH}_2{}^{2+}] \quad (7)$$

where all constants have units of M^{-1} sec^{-1}. Because of the uncertainty involved in calculating the concentrations of the various amine species and the experimental errors associated with the kinetic data, it was decided that the use of more significant figures for the constants in eq 7 would have no experimental significance. Nevertheless, eq 7 is in good agreement with the observed rate constants.

Equation 7 was obtained by adjusting the constants to give the best possible agreement with the experimental data. Because the dien species are at equilibrium, other experimentally indistinguishable forms of the equation are possible.[9] For example, eq 8 would

$$k_1 = k_a[\text{dien}] + k_b[\text{dien}][\text{H}^+] + k_c[\text{dien}][\text{H}^+]^2 \quad (8)$$

be one of several possibilities. In the opinion of the authors it seems probable that each of the incompletely protonated amine molecules can react with the complex. If this subjective assumption is accepted, the relative reactivities of these molecules are conveniently indicated by the numerical values of the rate constants in eq 7.

The potentiometric determinations of rate constants were employed as a convenient independent method of checking the equilibrium data in Table I and the rate constants determined by spectrophotometric methods. As can be seen from Table IV, the predicted and observed data are again in good agreement.

An examination of the kinetic data in Table II shows that the observed second-order rate constants are independent of the dien and $\text{PtBr}_4{}^{2-}$ concentrations in the pH ranges 8.9–9.1 and 5.6–6.0. Thus the assumption that the reaction is first order with respect to both of these species under these conditions is justified. It is also apparent from Table III that under typical conditions the half-lives of otherwise comparable reaction mixtures were insensitive to the concentrations of the aquo complex present. The pH dependence of the substitution reaction is most easily explained by ascribing different rates of reaction to the various protonated and unprotonated dien species. The reactivities of these amine molecules are indicated by the numerical values of the rate constants in eq 7. Relative to the dien molecule these reactivities are: dien, 1.00; dienH^+ 0.75; $\text{dienH}_2{}^{2+}$, 0.15; and $\text{dienH}_3{}^{3+}$, 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 $\text{NH}_3{}^+$ group would not be expected to behave as a Lewis base. It seems probable that the three reactive dien species form an initial single nitrogen–platinum bond by displacing one bromide ligand.[10] Under these circumstances the charge upon the incoming group might not be expected to be an important factor in determining the reaction rate because any positive charge on the amine is localized in positions remote from the platinum center. The relative reactivities of dien and dienH^+ can be explained conveniently upon this basis. The dien group, which has three nitrogen atoms capable of participating in rate-determining steps, reacts slightly faster than dienH^+, which has two such sites. In the resultant monodentate intermediates the degree of protonation of the amine ligands would vary with the pH value of the solution. Although the pK values under these circumstances, which would differ from the corresponding values for free dien, are unknown, unprotonated nitrogen atoms would always be present. The intramolecular displacement of further bromide ions by these nitrogen atoms could easily be more rapid than the proposed intermolecular rate-determining reaction. This implies that once the dien ion forms one bond to the metal, the formation of additional bonds takes place more rapidly than ligand dissociation. Electrostatic repulsion would make the diprotonated form of the amine containing the maximum charge separation the more stable. Consequently, $\text{dienH}_2{}^{2+}$ would not contain a terminal nucleophilic group, whereas dien and dienH^+ must each contain at least one such group. Such an effect could contribute to the fact that the reactivity of $\text{dienH}_2{}^{2+}$ is less than would be predicted on pure statistical grounds compared to dienH^+ or dien.

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(9) The following papers consider different forms of a related rate law: (a) J. E. Teggins and R. M. Milburn, *Inorg. Chem.*, **4**, 795 (1965); (b) R. M. Milburn and H. Taube, *J. Am. Chem. Soc.*, **81**, 3515 (1959).

(10) The spectroscopic changes occurring during kinetic runs merely indicate the conversion of $\text{PtBr}_4{}^{2-}$ to Pt(dien)Br^+ according to a rate expression which is first order with respect to the concentration of the complex ion. The proposed monodentate intermediate would be difficult to detect because it would be present in relatively low concentrations at any time. It is not unrealistic, however, to suggest an initial reaction involving the formation of a single platinum–nitrogen bond because a concerted mechanism involving the simultaneous displacement of three bromide ligands in a $\text{PtBr}_4{}^{2-}$ ion would be improbable on a statistical basis. The author intends to study the related $\text{Pt(NH}_3)_3\text{Br}^-$–dien reaction, for which a monodentate substitution product might be detectable.