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Anchimeric Assistance in the Reactions of Dichloro(ethylenediamine-N,N′-diacetic acid) platinum(II) and Its Conjugate Base

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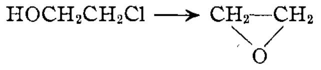
The rate of elimination of chloride ion from dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II) [$Pt(H_2EDDA)Cl_2$] is considerably increased when the free acid groups are neutralized. In acid solution the stable product is chloro(ethylenediamine-N,N′-acetic acid acetato)platinum(II) [Pt(HEDDA)Cl], whereas in solutions of higher pH the diacetato complex [Pt(EDDA)] is formed. The kinetics of the chloride ion elimination reactions have been investigated and the pH dependence of the reaction rate has been explained in terms of the reactions of the acid and base forms of the complex. The reactions of dichloro(N,N′-dimethylethylenediamine)platinum(II) [$Pt(Me_2en)Cl_2$] in acetate ion solution have been studied and the results compared with the results of the chloride substitution in the above complexes to show the importance of the neighboring group effect.

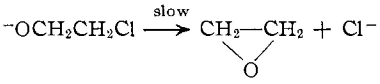
The phenomenon of neighboring group participation and anchimeric assistance is well known for organic reactions. For metal complexes, however, relatively few systems in which this behavior is possible have been investigated kinetically. Organic cyclization reactions of the type[1]



$$HOCH_2CH_2Cl \longrightarrow CH_2\text{—}CH_2 \text{ (bridged by O)} \quad (1)$$

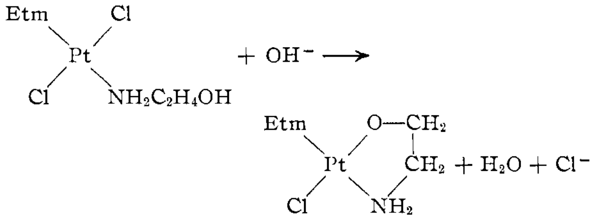
find inorganic analogs in chelate ring-closure reactions of metal complexes. The dependence of the rate of reaction 1 on the hydroxide ion is due to equilibrium 2 followed by the displacement of chloride ion by the alkoxide part of the molecule (3).

$$HOCH_2CH_2Cl + OH^- \overset{\text{fast}}{\rightleftharpoons} {}^-OCH_2CH_2Cl + H_2O \quad (2)$$



$${}^-OCH_2CH_2Cl \xrightarrow{\text{slow}} CH_2\text{—}CH_2 + Cl^- \quad (3)$$

Recent studies[2] of the reactions of *trans*-$Pt(Etm)_2Cl_2$ (where Etm = ethanolamine) provide an interesting example of this type behavior in the formation of chelate rings.



(4)

Again the OH^- dependent path is thought to involve a rapid acid–base equilibrium of the alcohol group followed by the rate-determining displacement of the chloride ion by the alkoxide group.

The rate of elimination of the coordinated water molecule from the quinquedentate EDTA complex of cobalt(III) to give the fully chelated complex shows a marked dependence on pH.[3] The increased rate of reaction was explained by the acid dissociation of the free carboxylic acid group. The carboxylate group was found to react about eight times faster than the undissociated acid. The present paper reports the results of a kinetic study of a similar platinum(II) complex, dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II).

Experimental Section

Materials.—Ethylenediamine N,N′-diacetic acid was obtained from K and K Laboratories, Inc., and N,N′-dimethylethylenediamine from the Aldrich Chemical Co. Inc. These were used without further purification.

Preparation of Complexes. Dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II).—This complex was prepared by the method described by Liu.[4] The infrared spectrum showed a single sharp $-COO^-$ band at 1730 cm^{-1} as reported. Titration of the complex on a Radiometer TTT1 titrator gave a titration curve which showed a single break and gave the equivalent weight of the compound as 221. This corresponds to the theoretical value. The pK_a value determined at 25° was 3.25. *Anal.* Calcd for $PtC_6H_8N_2O_4Cl_2$: Pt, 44.2. Found: Pt, 44.1.

Dichloro(N,N′-dimethylethylenediamine)platinum(II).—The method of preparation was the same as that used[5] for the preparation of the corresponding dichloro(ethylenediamine)platinum(II). *Anal.* Calcd for $PtC_4H_{12}N_2Cl_2$: Pt, 55.0; C, 13.53; N, 7.90; H, 3.33. Found: Pt, 55.0; C, 13.34; N, 7.87; H, 3.44.

Spectrophotometric Measurements.—Ultraviolet absorption spectra were measured with Cary Model 14 and Beckman DU spectrophotometers using quartz cells.

pH Measurements.—For simple pH measurements a Corning Model 7 pH meter with a glass electrode was used. This was standardized at pH 5 and 9 (Fisher Scientific standard buffer solutions). The Radiometer instrument used in the pH titrations was standardized in the same manner.

Potentiometric Titrations.—These were carried out with the Radiometer titrator with a silver–silver chloride electrode. Chloride ion solutions were titrated with standard silver nitrate solution.

Buffer Solutions.—For controlling the pH of reaction mixtures above pH 3.5, an acetate buffer was used. The normal buffer concentration was 0.04 *M*, but some reactions were carried out at the same pH values using a higher concentration (0.10 *M*) to establish that the buffer had no effect on the reaction rate. In the pH region 2–3.5, a chloroacetate buffer was employed.

Kinetic Studies.—In all cases the reactions were carried out at an ionic strength of unity. The supporting electrolyte used

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was sodium perchlorate. Solutions for kinetic experiments were prepared by adding a weighed amount of solid complex to a solution containing the buffer and the appropriate concentration of sodium perchlorate. The solutions were brought to the reaction temperature before the addition of complex. Because of the low solubility of dichloro(N,N'-dimethylethylenediamine)-platinum(II) in water, its reactions were carried out in a 1:1 by volume ethanol–water mixture. The small amount of complex which remained undissolved after several minutes shaking was removed on a filter before kinetic studies were started. The reaction mixtures of $Pt(H_2EDDA)Cl_2$ were maintained at the required temperature in the temperature-controlled cell compartments of the spectrophotometers: In all cases the complex concentration was 2×10^{-3} *M*. The very slow reactions of dichloro(N,N'-dimethylethylenediamine)platinum(II) were carried out in a thermostat bath, and samples were withdrawn at convenient time intervals for optical density measurements. All the reactions studied were first order and the rate constants were computed from the slope of a plot of $-\log (A_\infty - A_t)$ against t.

Results and Discussion

In a solution of 0.10 *M* perchloric acid, a 2×10^{-3} *M* solution of $Pt(H_2EDDA)Cl_2$ undergoes a slow change. The spectrum at zero time is shown in Figure 1 (A). After about 18 hr at room temperature the spectrum ceased to change and is shown as spectrum B. During the reaction stable isosbestic points were revealed at λ 340 and 308 mμ. Potentiometric titration of the final solution with standard silver nitrate indicated that the solution contained 1.0 mole of free chloride ion for each mole of complex.

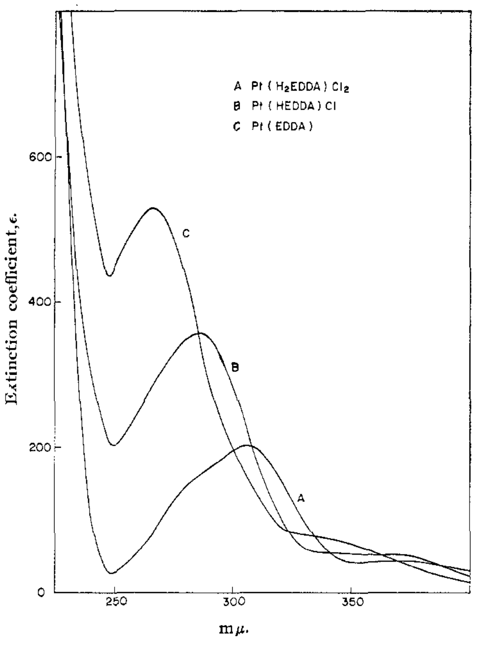
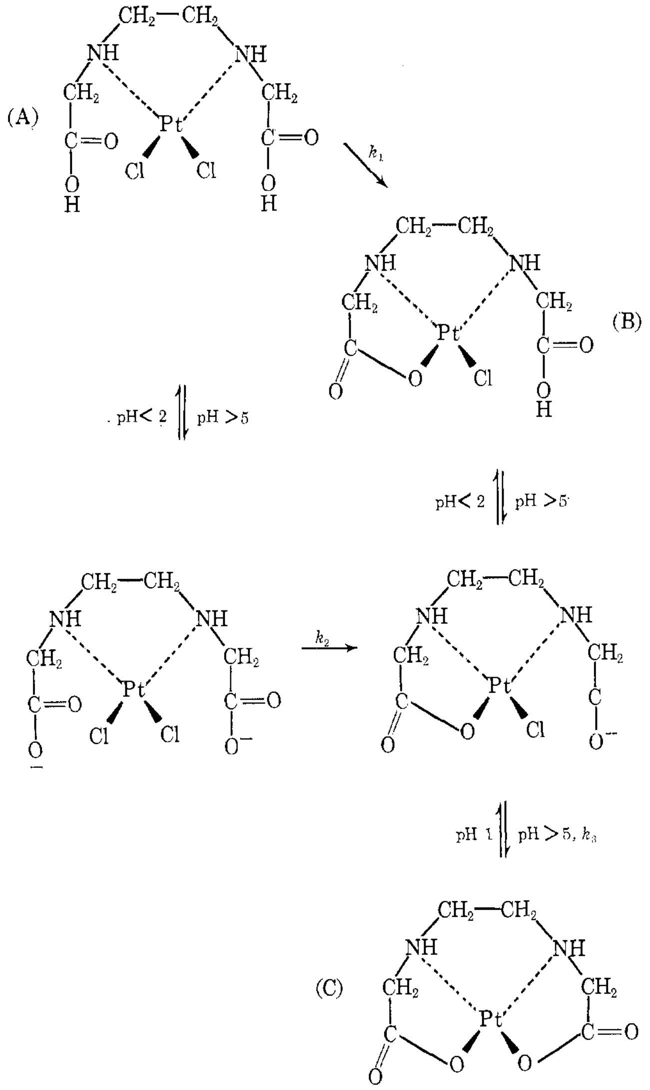


Figure 1.—Spectra in water at 25° of A, dichloro(ethylenediamine-N,N'-diacetic acid)platinum(II); B, chloro(ethylenediamine-N,N'-acetic acid acetato)platinum(II); C, (ethylenediamine-N,N'-diacetato)platinum(II).

The spectral changes of a solution of the dichloro complex at pH 5.4 were more complicated. The change was much more rapid and the previous isosbestic points were stable for only a short time. Eventually a new isosbestic appeared at λ 285 mμ and finally spectrum C was obtained. The change from spectrum A to spectrum C was complete in about 6 hr at room temperature. In this case titration of the final solution showed that 2.0 moles of free chloride ion per mole of complex was present in solution. When solution C was brought to pH 1 by addition of perchloric acid and allowed to react at 43°, the spectrum reverted to that of B. The reaction was complete in about 3 hr. When hydrochloric acid was added to both solutions B and C so that the final concentration of HCl was 1.0 *M*, then spectrum A was obtained almost immediately at room temperature.

We suggest that the observations described are explained by the reaction scheme shown in Scheme I.

Scheme I



In dilute perchloric acid the dichloro complex loses only one coordinated chloride ion to form monochloro-(ethylenediamine-N,N'-acetato acetic acid)platinum(II). In solutions of higher pH, the second chloride ion is substituted and the (ethylenediamine-N,N'-diacetato)platinum(II) complex is formed. The reactions can be reversed if the acidity is altered. In hydrochloric acid the original dichloro complex is reformed.

A preparation of (ethylenediamine-N,N'-diacetato)-

platinum(II) has been reported.[4] The method involves the removal of chloride ion by addition of the calculated amount of silver sulfate followed by neutralization of the carboxylic acid groups by a stoichiometric quantity of barium hydroxide. A solution obtained after treatment in this manner gave a spectrum similar to C. However, the complex was not isolated on evaporation of the solution and a white insoluble material was obtained. When a solution of the monochloro complex at pH 1 was treated with excess Ag^+, the spectrum of the diacetato complex (C) was obtained.

Although we were not able to isolate Pt(EDDA) as a solid, we feel that the solution chemistry provides conclusive evidence that this indeed is the final product of the reaction.

Kinetic Studies.—By monitoring the optical density change at λ 285 mμ, the isosbestic point for the spectra of Pt(HEDDA)Cl and Pt(EDDA), it was possible to study the substitution of the first chloride ion over the pH range 1–7. Even when further reaction takes place at the higher pH values, good linear semilogarithmic plots were obtained.

In Figure 2 (A) we show the values of k_{obsd} at 25.0° as a function of pH. This graph has a shape similar to a pH titration curve, and the point of inflection is at pH 3.25, which is the pK_a of the acid complex. Thus we can express the observed rate constant in terms of two first-order velocity constants for the reaction of the acid and base forms of the complex.

$$k_{obsd}[\text{complex}] = k_1[\text{Pt(H}_2\text{EDDA)Cl}_2] + k_2[\text{Pt(EDDA)Cl}_2{}^{2-}]$$

or

$$k_{obsd} = \frac{k_1[\text{H}^+]}{K_A + [\text{H}^+]} + \frac{k_2K_A}{K_A + [\text{H}^+]}$$

where

$$K_A = \frac{[\text{Pt(EDDA)Cl}_2{}^{2-}][\text{H}^+]^2}{[\text{Pt(H}_2\text{EDDA)Cl}_2]} = 10^{-3.25}$$

Thus k_1 and k_2 can be calculated from the values of k_{obsd} at pH 1.0 and >5.0, respectively. Once the pH dependence of the reaction rate had been established, duplicate experiments were carried out at two other temperatures at these extremes of pH. The Arrhenius activation energies and entropies calculated from these experiments are given in Table I together with the values of the rate constants and the estimated errors.

At pH values >2 the stable product is the quadridentate complex. By observing the change in absorbance at λ 260 mμ, where the difference in the extinction coefficients of Pt(EDDA) and Pt(HEDDA)Cl is large, it is possible to determine the rate of elimination of the second chloride ion. At this wavelength, the semilogarithmic rate plots were curved due to two consecutive reactions. The required rate constants were determined from the straight portion of the plot obtained toward the end of the reaction. The results obtained in this way were reproducible. The velocity constants observed at 43.2° plotted as a function of pH are shown in Figure 2 (B). The shape of this curve is similar to that obtained for the substitution of the first chloride ion. Since the rate goes to zero below pH 2, it is clear that only the base form of the monochloro complex reacts. The values of the rate constants (k_3) for this reaction and the activation parameters are listed in Table I.

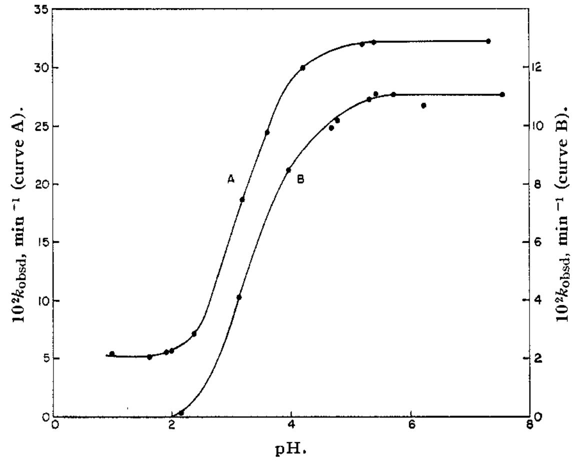


Figure 2.—Observed first-order rate constants as a function of pH for the reactions of A, $Pt(H_2EDDA)_2Cl_2$ (25.0°); B, Pt(HEDDA)Cl (43.2°).

TABLE I

RATE CONSTANTS FOR THE CHELATION OF PLATINUM(II) COMPLEXES

Complex	Temp, °C	k_1, sec^{-1}
$[Pt(H_2EDDA)Cl_2]$	25.0	$9.00 \pm .27 \times 10^{-5}$
	35.0	$2.64 \pm .08 \times 10^{-4}$
	41.6	$4.60 \pm .14 \times 10^{-4}$
		k_2
$[Pt(EDDA)Cl_2]^{2-}$	15.0	$1.77 \pm .05 \times 10^{-4}$
	25.0	$5.37 \pm .16 \times 10^{-4}$
	33.3	$1.26 \pm .04 \times 10^{-3}$
		k_3
$[Pt(EDDA)Cl]^-$	34.1	$6.05 \pm .18 \times 10^{-4}$
	37.8	$9.17 \pm .27 \times 10^{-4}$
	43.2	$1.85 \pm .06 \times 10^{-3}$

Activation Parameters

	E_a, kcal	$\Delta S^\ddagger$, eu
k_1	18.8 ± 0.7	-16 ± 2
k_2	18.9 ± 0.6	-12 ± 1.5
k_3	23.8 ± 1.0	$+2 \pm 3$

The effect of protonating the free carboxylate groups is most marked. For the replacement of the first coordinated chloride ion, there is a sixfold increase in rate as we go from the acid to base forms. For the substitution of the second chloride, the effect is even more pronounced in that the carboxylic acid group does not react at all. This is probably an equilibrium effect primarily.

The rate constants for the reaction in aqueous solution of dichloro(N,N′-dimethylethylenediamine)platinum(II) in both the presence and absence of acetate have been determined from absorbance measurements of λ 253 and 305 mμ, to provide a reference. The results of these investigations are shown in Table II. The rate of reaction is not altered by the addition of up to 1 M concentrations of acetate ion. Titration of the

TABLE II

RATE CONSTANTS FOR CHLORIDE LOSS FROM $Pt(Me_2en)Cl_2$ in 1:1 ETHANOL–H_2O AT 25°

[Acetate], *M*	pH	k_{obsd}, sec^{-1}
0	5.5	1.11×10^{-5}
0	$[OH^-] = 0.05$ *M*	1.00×10^{-5}
0.04	6.5	1.02×10^{-5}
1.00	6.76	1.03×10^{-5}

reaction mixtures at the end of the reaction with silver nitrate revealed that both chloride ions had been liberated. The product was the same in all four reactions, presumably the hydrolysis product.

Even with a poor ligand such as carboxylate ion the neighboring group effect is displayed. Although free acetate ion does not react with a similar complex, when chelation is possible then the incoming carboxylate ion assists the elimination of the coordinated chloride ion. The amount of assistance determines whether the monochloro or diacetato complex is formed. The increased rate of reaction of the carboxylate ion over the carboxylic acid group is due to the entropy term rather than a lowering of the activation energy. The activation energies for the substitution of the first chloride ion are the same in both cases. The larger entropy of activation for the carboxylate ion reaction is consistent with an internal SN2 displacement of the chloride ion. The activation energy for replacement of the second chloride ion is higher by about 5 kcal. This could explain the lack of reaction of the carboxylic acid group, since the entropy of activation would be expected to be much lower than for the reaction of the conjugate base. Also the ring-opening reaction would be expected to be acid catalyzed, and this would help to push the equilibrium completely over toward the monochloro complex.

The fact that the activation energy for the formation of the second chelate ring to give the diacetatoplatinum(II) complex is higher than that for the formation of the first ring seems to indicate that some steric strain is involved.

The pronounced dependence of the reaction of $Pt(H_2EDDA)Cl_2$ on pH can be contrasted with the reaction of the quinquedentate $[Co(HEDTA)Cl]^-$ to give Co(EDTA). The rate of the latter reaction is virtually independent of pH.[6,7] It was suggested that the carboxylate ion group could not assist the elimination of a negatively charged ligand due to electrostatic repulsion. The present work shows that the same reasoning cannot be applied to the complexes of platinum(II). The SN2 character of the reaction of platinum(II) complexes leads to marked anchimeric assistance effects, whereas the SN1 character of the cobalt(III) reactions does not allow such assistance.

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Crystal Field Analysis of the Spectra of Tetragonal Nickel(II) Pyridine Complexes

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The optical absorption spectra of mulls of $Ni(py)_4Br_2$ and $Ni(py)_4Cl_2$ have been determined at liquid nitrogen temperature The splitting of the absorption bands due to the strong axial field is discussed using crystal field theory. Assignments are made and agreements between experiment and theory are excellent. The difference between solution and solid data is discussed. The *Dq*'s of Cl^- and Br^- were calculated to be 680 and 600 cm^{-1}, respectively.

Introduction

In the course of investigating[2,3] some pyridine complexes of nickel(II), we noticed some interesting properties in the electronic absorption spectrum of the tetragonal complexes. There has been a great deal of interest in tetragonal metal complexes[4–8] with much of the work being centered on Co(III) and little attention being paid to Ni(II). The appearance of "extra" bands in $Ni(py)_4Cl_2$ was taken as evidence for tetragonal distortion,[9] but a complete interpretation of the spectra was not attempted.

The complexes chosen for this study are $Ni(py)_4X_2$ where $X^- = Cl^-$ and Br^-. These have been shown to be paramagnetic with the X groups occupying the *trans* positions.[10,11] Both of these complexes are ideally suited for analysis because the electronic spectrum

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