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Substitution Reactions for Ligands of Platinum(II) Complexes. Solvation and Chloride Ion Exchange for Solutions of *trans*-Di- μ -chloro-dichlorobis(ethylene)diplatinum(II) in Ethanol¹

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A solution of the dimeric $[\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2]$ in ethanol has been shown to contain predominantly the monomeric species *trans*- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$. Spectrophotometric studies have yielded for the reaction: $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^- + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH}) + \text{Cl}^-$, $K = 5 \times 10^{-6} M$ at 25°. The isotopic exchange of the chlorides *cis* to C_2H_4 occurs according to a rate expression: $R_{\text{ex}} = k_d[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]$, where $k_d = 7.7 \times 10^{-2} M^{-1} \text{sec}^{-1}$ for 25°, and $\Delta H^\ddagger = 25 \text{ kcal/mol}$ and $\Delta S^\ddagger = 19 \text{ cal/deg mol}$. A possible mechanism for this process is discussed.

Introduction

In an earlier study with aqueous solutions of Zeise's salt, $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, Lokken and Martin² found that although the chloride *trans* to the ethylene ligand (designated as the *trans*-chloride in this paper) exchanged with free Cl^- very rapidly, the other two equivalent "*cis*-chloride" ligands exchanged according to the rate law

$$R_{\text{ex}} = k_c[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] + k_c'[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})] + k_d[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})] \quad (1)$$

The processes characterized by k_c and k_c' presumably were the aquations of the corresponding species which are usually observed for the chloro ligands of platinum(II) complexes. However, the third term clearly indicated a transition state involving a dimer species, and it was proposed that the mechanism involved a rapid exchange between the free chloride and the ligands in the known dimeric molecule, *trans*-di- μ -chloro-dichlorobis(ethylene)diplatinum(II). For economy of space this compound will be designated in this paper simply by the formula $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$.

A recent exchange study between PtBr_4^{2-} and Br^- has also indicated a partial contribution by a process involving a dimer transition state.³ However, it was concluded that the exchange occurred more rapidly than the formation of the doubly bridged dimeric complex $\text{Pt}_2\text{Br}_6^{2-}$, and a mechanism was required in which only a single bromide bridge formed. An additional occurrence of a dimer transition state was indicated by the observation that $\text{Pt}(\text{dien})\text{Br}^+$, where dien represents diethylenetriamine, and PtBr_4^{2-} mutually catalyze the exchange of bromide ligands of the other complex with free bromide.⁴

The dimer, $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$, can be crystallized from an ethanol solution formed by the addition of Zeise's salt after the KCl , which precipitates initially, has been separated by filtration. Since it was anticipated that a considerable concentration of the dimer species would

exist in the ethanol solutions, the present study was undertaken to characterize the exchange rates of the chloride ligands with free chloride for such solutions.

Experimental Section

Materials.— $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ and $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$ were synthesized from iridium-free K_2PtCl_6 by the method of Chatt and Searle.⁶ The $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$ was stored in a desiccator in the dark. *Anal.* Calcd for $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$: Pt, 66.3; Cl, 24.1. Found: Pt, 66.0; Cl, 23.5.

Absolute ethanol was obtained from the Commercial Solvents Corp. The typical water content was 0.1% by weight.

Chlorine-36 was obtained as 2.04 *N* HCl , specific activity 0.037 ($\pm 10\%$) mCi/ml from the Oak Ridge National Laboratory.

Tetraphenylarsonium chloride was obtained from the Aldrich Chemical Co. and converted to the acetate by anion exchange.

Other chemicals were generally reagent grade.

Equipment.—Ultraviolet absorption spectra were recorded with a Cary 14 recording spectrophotometer with a hydrogen lamp.

The chlorine-36 β emitter was counted with an end-window Gieger-Mueller tube, Nuclear Chicago Model D-34, window thickness 1.4 mg/cm^2 .

The vapor-phase osmometer used for molecular weight determinations in ethanol was a Hewlett-Packard Model 301 A. It was standardized with benzil at 25°, and the molecular weight determinations were made with freshly prepared solutions of $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$ in ethanol.

Procedures.—The ultraviolet spectrum of a solution of $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$ in ethanol, the dashed curve in Figure 1, was dramatically changed by the addition of 1 part in 500 of concentrated aqueous HCl , the solid curve. Solutions of only $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$ obeyed Beer's law at $\lambda > 260 \text{ m}\mu$, and small deviations below 260 $\text{m}\mu$ could be attributed to excessive absorption by the solvent. The greatest difference between the two spectra in Figure 1 appeared at about 260 $\text{m}\mu$, and the absorbances of several solutions of $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$ with various amounts of HCl at 25 and 35° have been recorded in Table I.

Isotopic exchange between ligand chloride and free chloride was studied in ethanol solutions prepared from $\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4$ and HCl which had been added as concentrated aqueous solution. It appeared that the H_2O added by this technique was no larger than the H_2O content of the available absolute ethanol. The exchange solutions were stored in actinic red erlenmeyer flasks in a water bath at the reaction temperature for 1–2 weeks prior to starting the exchange. The exchange was initiated by adding a small, known amount of HCl tagged with ^{36}Cl . Aliquots were withdrawn from the flasks and added to a measured

(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

(3) J. E. Tegginis, D. R. Gano, M. A. Tucker, and D. S. Martin, Jr., *ibid.*, **6**, 69 (1967).

(4) J. E. Tegginis and D. S. Martin, Jr., *ibid.*, **6**, 1003 (1967).

(5) C. I. Sanders and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **83**, 807 (1961).

(6) J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957).

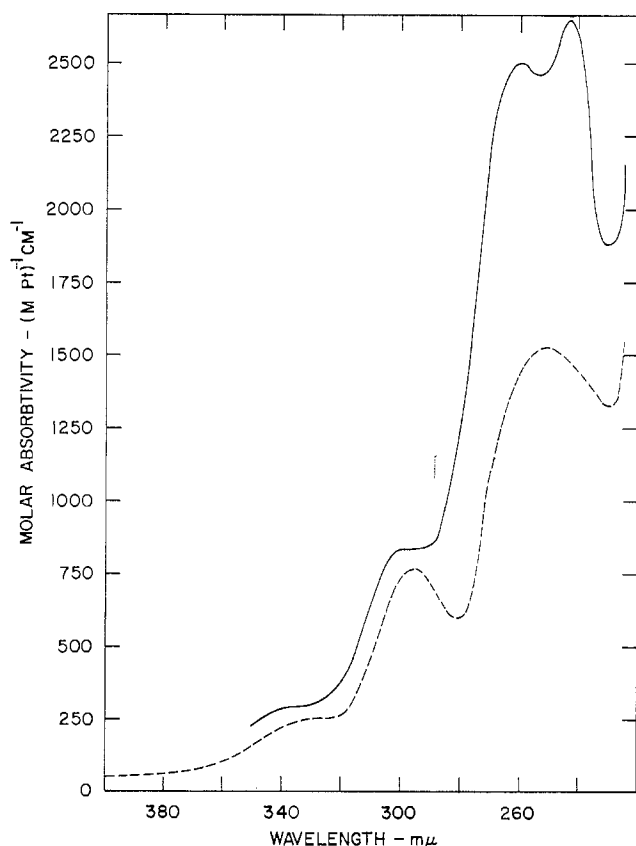


Figure 1.—Absorption spectrum of ethanol solutions of *trans*-Pt(C₂H₄)Cl₂(C₂H₅OH) (---) and Pt(C₂H₄)Cl₃⁻ (—) at 25° in a 1.00-cm cell. For *trans*-Pt(C₂H₄)Cl₂(C₂H₅OH) solution (4 × 10⁻⁴ M Pt), Pt₂(C₂H₄)₂Cl₄ was dissolved in ethanol. For Pt(C₂H₄)Cl₃⁻ solution (4 × 10⁻⁴ M Pt), Pt₂(C₂H₄)Cl₄ was dissolved in ethanol containing 0.1% by volume of concentrated aqueous HCl.

TABLE I
EVALUATION OF SOLVATION EQUILIBRIUM QUOTIENT
FOR Pt(C₂H₄)Cl₃⁻ IN ETHANOL^a

Tot. concn of Pt, mM	Added Cl ⁻ , mM	Absorbance at 260 mμ (1-cm cell)	[Pt(C ₂ H ₄)Cl ₃ ⁻], mM	10 ⁵ K, M
25°				
0.400	0.200	0.742	0.156	6.8
0.400	0.400	0.876	0.279	5.2
0.400	0.300	0.842	0.248	3.2
0.400	0.300	0.832	0.239	4.2
0.400	0.400	0.881	0.283	4.8
0.400	0.500	0.910	0.310	5.6
				Av 5.0 ± 1.0
35°				
0.300	0.092	0.510	0.075	5.1
0.300	0.183	0.579	0.138	5.3
0.300	0.275	0.614	0.169	8.2
0.400	0.092	0.658	0.080	4.8
0.500	0.183	0.890	0.162	4.5
0.500	0.275	0.950	0.216	7.8
				Av 6.0 ± 1.7

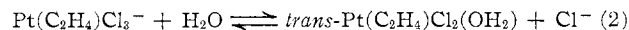
^a ε(260 mμ) for Pt(C₂H₄)Cl₃⁻ = 2522 M_{Pt}⁻¹ cm⁻¹; ε(260 mμ) for Pt(C₂H₄)Cl₂(C₂H₅OH) = 1427 M_{Pt}⁻¹ cm⁻¹.

volume of at least equal magnitude of a standardized aqueous KCl solution, ca. 0.5 M. After a 1-min interval, a tetraphenylarsonium acetate solution was added which precipitated (As(C₆H₅)₄)₂[Pt(C₂H₄)Cl₃]. The *trans*-chloride ligand in this had

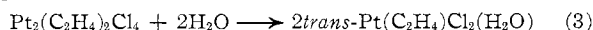
attained exchange equilibrium with free chloride which at this point had been highly diluted by the added KCl. The precipitates were collected on a weighed filter paper which was supported on a sintered-glass filter. They were washed with a dilute solution of tetraphenylarsonium acetate and air dried for 6 hr. The filter papers bearing the precipitates were weighed and then counted. Filter paper tares were carried through the washing and drying process to provide corrections for humidity changes. This procedure provided a specific activity for the precipitates which could be expressed as cpm/g-atom of Cl.

Results and Discussion

Hydration of Pt₂(C₂H₄)Cl₄.—When Zeise's salt is dissolved in H₂O, the solvation equilibrium is established

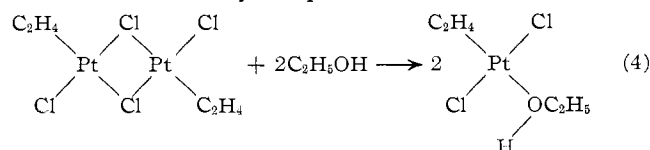


The spectrum obtained by adding 0.1 M HCl to these aqueous solutions is primarily due to the Pt(C₂H₄)Cl₃⁻, and for this species an extinction coefficient of 3360 M_{Pt}⁻¹ cm⁻¹ was evaluated at 240 mμ. The solution of Pt₂(C₂H₄)₂Cl₄ in H₂O, for which solvation appears to be complete, *i.e.*



provided a value of 1505 M_{Pt}⁻¹ cm⁻¹ for the molar absorptivity of this species. All molar absorptivities in this paper are expressed in terms of platinum atoms or monomer units so that this difference in the spectrum provides for an accurate evaluation of the equilibrium quotient for reaction 2. The values found for this quotient in H₂O and dilute HCl solutions were 2.6 ± 0.2 × 10⁻³ M at 25° and 3.0 ± 0.3 × 10⁻³ M at 35° which were in good agreement with the result of 2.5 × 10⁻³ M at 25° reported from potentiometric titrations of chloride ion by Allen and Theophanides.⁷

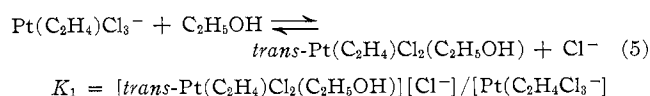
Solvation of Pt₂(C₂H₄)Cl₄ in Ethanol.—Solutions of Pt₂(C₂H₄)₂Cl₄ in ethanol agreed well with Beer's law in the range 10⁻⁵ to 10⁻² M Pt down to wavelengths where severe absorption by the solvent occurred. This fact indicated the predominant existence of either a monomeric or a dimeric species with inappreciable concentration of the other. A similar agreement was observed in H₂O, where the monomeric species *trans*-Pt(C₂H₄)Cl₂(H₂O) is believed to predominate, and for 80% by weight solutions of ethanol. These observations strongly suggested that the species in ethanol were monomeric, and this conclusion was confirmed by the molecular weight determination with the osmometer. Three determinations in the range of 7.5–12.5 mM Pt₂(C₂H₄)₂Cl₄ gave a molecular weight of 312 ± 7. It appeared therefore that at least 90% of the platinum was present as the monomeric species. It has therefore been concluded that the following reaction is essentially complete



The changes in the ultraviolet absorption spectrum of the ethanol solutions as HCl was added, shown in

(7) A. D. Allen and T. Theophanides, *Can. J. Chem.*, **43**, 290 (1965).

Figure 1, were attributed to the reversible replacement of solvent ligand by chloride. There was apparently rapidly established the equilibrium



The molar absorptivity for *trans*-Pt(C₂H₄)Cl₂(C₂H₅OH), ϵ_2 , was calculated from the absorbance at 260 m μ of the dashed curve in Figure 1, and a preliminary estimate of the molar absorptivity for Pt(C₂H₄)Cl₃⁻, ϵ_1 , was obtained from the solid curve. With the assumption that only the two platinum species in reaction 5 were present in appreciable concentrations, the equilibrium concentration for each species was calculated from the data in Table I by means of the following expressions. If *A* is the absorbance and *l* is the cell length

$$A/l = [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-]_{\epsilon_1} + [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]_{\epsilon_2} \quad (6)$$

$$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] + [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})] = [\text{Pt}_{\text{tot}}] \quad (7)$$

$$[\text{Cl}^-] = [\text{Cl}]_0 - [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] \quad (8)$$

where [Pt_{tot}] is the total platinum concentration and [Cl₀] is the concentration of added chloride. The indicated value for the equilibrium quotient, *K*₁, of $(5.0 \pm 1.0) \times 10^{-5} M$ is much smaller than the corresponding quotient for hydration in H₂O in accordance with the weaker solvation of the alcohol. It is to be noted that ionic strength was not constant for these determinations; however, because of the charge symmetry of reaction 5, a large ionic strength dependence is not expected. A ΔH° of nearly zero for the replacement of chloride ligand by solvent appears rather normal.

Chloride-Ligand Exchange.—Since in ethanol solutions monomer species existed predominantly, the isotopic exchange experiments with ³⁶Cl involved essentially a two-component system. The chloride ligands *cis* to ethylene in both Pt(C₂H₄)Cl₃⁻ and *trans*-Pt(C₂H₄)Cl₂(C₂H₅OH) comprised the one component, and the chloride *trans* to ethylene in Pt(C₂H₄)Cl₃⁻ and free chloride comprised the second component. The concentrations [Pt(C₂H₄)Cl₃⁻], [*trans*-Pt(C₂H₄)Cl₂(C₂H₅OH)], and [Cl⁻] were calculated from the amount of Pt₂(C₂H₄)₂Cl₄, the concentration of added chloride [Cl]₀, and the solvation equilibrium quotient *K*₁. This treatment assumes there is an inappreciable *cis* solvation, similar to the situation for the aqueous system.

The symbols utilized for the treatment of data are listed below

- I* Concentration of total ³⁶Cl activity in solution (cpm/l.)
- u* Concentration of activity in the *cis* chlorides (cpm/l.)
- S_u* Specific activity of ³⁶Cl in the *cis* position = $u/2[\text{Pt}_{\text{tot}}]$ (cpm/g-atom of Cl)
- S_s* Specific activity of the *trans* chloride and the free Cl⁻ ion = $(I - u)/[\text{Cl}^-]_0$ (cpm/g-atom of Cl)
- S_p* Specific activity of chloride in the [As(C₆H₅)₃]₃[Pt(C₂H₄)Cl₃] precipitate (cpm/g-atom of Cl)
- S₀* *S_p* at the time exchange was started
- S_D* *S_p* as $t \rightarrow \infty$ (after many half-times of exchange)
- c* Ratio of total free chloride ion added just before the precipitation step to the total free chloride introduced before the start of exchange

S_s' Specific activity of the *trans* chloride and free Cl⁻ during the precipitation step = $(I - u)/[\text{Cl}^-]_0(1 + c)$ (cpm/g-atom of Cl)

F Apparent fraction of exchange = S_p/S_D

The values of *S_p* were obtained from the weights and counting rates of the precipitates. The value of *S_D* for experiments with short half-lives was determined from replicate sampling of reaction solutions after at least 5 half-times.

Reactions with half-times greater than 100 hr were generally sampled for 2–3 half-times. Since the specific activity of the precipitate should be given by the logarithmic function

$$\ln(S_D - S_p)/(S_D - S_0) = -(\ln 2)t/\tau_{1/2} \quad (9)$$

an initial estimate of $\tau_{1/2}$ was chosen, and *S_D* was calculated by means of this equation from the last measured *S_p*. A reiterative procedure, utilizing the IBM 350/50 computer of the Iowa State University Computer Center, provided a revised least-squares estimate for $\tau_{1/2}$ from which a new value of *S_D* was calculated. The reiteration appeared to converge and was continued until changes in $\tau_{1/2}$ were <1 hr. For the one experiment for which $\tau_{1/2} \approx 1100$ hr, the sampling was continued for only 1 half-time, and the value of *S_D* was chosen to minimize the sum of the absolute deviations from a straight-line plot of $\log [(S_D - S_p)/S_D]$.

The rate of introduction of radioactive ³⁶Cl in the *cis* chloride can be inferred from the measured value of *S_p* at various times and *S_D*. In terms of a constant exchange rate, *R_{ex}*, the ³⁶Cl is introduced into the *cis* positions in accordance with the expression

$$\frac{du}{dt} = R_{\text{ex}}(S_s - S_u) \quad (10)$$

At the start of the experiment *S_u* = 0, and *S_s* = $I/[\text{Cl}^-]_0$. The solution of this differential equation yields

$$u = u_\infty(1 - e^{-\alpha t}) \quad (11)$$

where

$$u_\infty = 2[\text{Pt}_{\text{tot}}]I/(2[\text{Pt}_{\text{tot}}] + [\text{Cl}^-]_0) \quad (12)$$

$$\alpha = R_{\text{ex}}(2[\text{Pt}_{\text{tot}}] + [\text{Cl}^-]_0)/2[\text{Pt}_{\text{tot}}][\text{Cl}^-]_0 \quad (13)$$

Since

$$S_p = (2S_u + S_s')/3 \quad (14)$$

it follows that

$$S_p = \frac{u}{3[\text{Pt}_{\text{tot}}]} + \frac{I - u}{3[\text{Cl}^-]_0(1 + c)} \quad (15)$$

or

$$S_p = \frac{1}{3[\text{Cl}^-]_0(1 + c)} \times \left[I + \frac{u_\infty \{ [\text{Cl}^-]_0(1 + c) - [\text{Pt}_{\text{tot}}] \} (1 - e^{-\alpha t})}{[\text{Pt}_{\text{tot}}]} \right] \quad (16)$$

With the appropriate substitutions in eq 16 there is obtained

$$S_0 = I/3[\text{Cl}^-]_0(1 + c) \quad (17)$$

and

$$S_D = \frac{I(3 + 2c)}{3(1 + c)\{2[\text{Pt}_{\text{tot}}] + [\text{Cl}^-]_0\}} \quad (18)$$

A plot of $\ln [(S_D - S_p)/S_D]$ vs. time provides a straight line with a slope of $-\alpha$ and an intercept of $\ln [(1 - S_0)/S_D]$. In general, the value of $[(1 - S_0)/S_D]$ was >0.9 , and agreement of the initial exchange point was within 2–3% of the calculated value of $[(1 - S_0)/S_D]$. The values of α were obtained from least-squares lines through the semilogarithmic plots of $\ln [(S_D - S_p)/S_D]$. The R_{ex} for each experiment was calculated from α by means of eq 13. The indicated exchange half-times and the corresponding exchange rates for all the experiments are given in Table II.

TABLE II
ISOTOPIC EXCHANGE OF THE
cis-CHLORIDE LIGANDS WITH FREE CHLORIDE

Total platinum, mM	Added chloride, mM	<i>trans</i> -Pt-(C ₂ H ₄)Cl ₂ -(C ₂ H ₅ OH), mM	[Pt(C ₂ H ₄)Cl ₂] ⁻ , mM	Half-time of exchange, hr	Exchange rate, R_{ex} , M sec ⁻¹
25°					
2.50	5.70	0.0385	2.46	79.3	6.48×10^{-9}
3.75	5.70	0.0940	3.66	30.9	1.22×10^{-8}
10.0	4.44	5.60	4.40	0.238	2.94×10^{-6}
10.0	11.6	0.303	9.70	7.45	1.90×10^{-7}
15.0	23.0	0.0932	14.9	24.7	1.01×10^{-7}
25.0	20.8	4.43	20.6	0.408	6.95×10^{-6}
25.0	45.9	0.0597	24.9	39.5	1.07×10^{-7}
35°					
2.50	5.70	0.0452	2.45	15.7	3.28×10^{-8}
2.50	12.2	0.0153	2.48	88.4	7.71×10^{-9}
2.50	45.8	0.00346	2.50	519	1.67×10^{-9}
2.50	91.6	0.00168	2.50	631	1.44×10^{-9}
2.50	183.2	0.00083	2.50	1108	8.22×10^{-10}
3.75	5.70	0.106	3.64	4.07	1.53×10^{-7}
3.75	18.3	0.0153	3.73	71.5	1.43×10^{-8}
3.75	73.3	0.00324	3.74	332	3.94×10^{-9}
10.0	4.44	5.61	4.39	0.0900	7.79×10^{-6}
10.0	4.44	5.61	4.39	0.087	8.05×10^{-6}
25.0	20.8	4.47	20.53	0.109	2.60×10^{-6}
25.0	20.8	4.47	20.53	0.132	2.57×10^{-6}

Variations in the observed exchange rate were extraordinarily great. The half-time for the exchange at 35°, as indicated in Table II, varied from 5 min to greater than 1100 hr, and the quantity R_{ex} extended over a range of nearly 10^5 . In Figure 2 have been plotted the values of R_{ex} against the product of concentrations $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]$, which could be calculated from $[\text{Pt}_{\text{tot}}]$, $[\text{Cl}^-]_0$, and K_1 . The slopes of least-squares straight-line fits to the points in the figure were within two standard deviations of 1.0. Therefore, the rate is described very satisfactorily by the single-term second-order kinetics expression

$$R_{ex} = k_d[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})] \quad (19)$$

Rate constants, k_d , determined from least-squares straight lines with a slope of exactly 1.0 are included in Table III together with the indicated activation parameters. The data of Lokken and Martin² for the aqueous system are included in this table for comparison.

It appears therefore that the reversible solvation

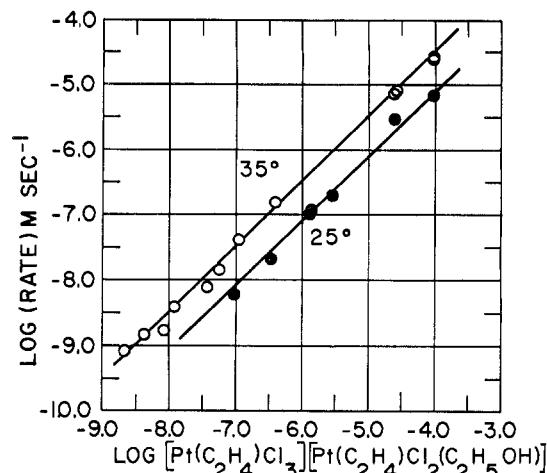


Figure 2.—Logarithmic plot of the exchange rate vs. the product of concentrations $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{Cl}_3^-][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]$.

TABLE III
RATE CONSTANTS AND ACTIVATION PARAMETERS
FOR THE EXCHANGE OF THE *cis*-CHLORIDE LIGANDS
IN H₂O AND ETHANOL

	Rate constants $\times 10^6$		ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/deg mol
	At 25°	At 35°		
In H ₂ O ($\mu = 0.318 M$) ²				
k_c , sec ⁻¹	0.29	0.97	21	-13
k_c' , sec ⁻¹	2.8	9.2	22	-5
k_d , sec ⁻¹ , M ⁻¹	860	2580	19	-2
In Ethanol				
k_c , sec ⁻¹	...	$<1.6 \times 10^{-7}$		
k_c' , sec ⁻¹		
k_d , sec ⁻¹ , M ⁻¹	7700 ± 640	$30,000 \pm 2000$	24	+17

process plays no detectable direct role in the exchange of the *cis* chlorides in ethanol. An upper limit can be placed on the first-order rate constant for such a solvation. If it is conservatively assumed that such solvation provides 50% of the slowest exchange reaction at 35°, the indicated rate constant would be $1.6 \times 10^{-7} \text{ sec}^{-1}$, which can be compared with the value of $9.7 \times 10^{-6} \text{ sec}^{-1}$ found for the aqueous system. The rate of solvation for the ethanol solution is therefore significantly lower than in H₂O. On the other hand, the value of $0.30 M^{-1} \text{ sec}^{-1}$ for k_d in ethanol is much higher than the corresponding value of $0.025 M^{-1} \text{ sec}^{-1}$ for H₂O. The activation enthalpy for ethanol of 24 kcal/mol appears to be significantly greater than the 19 kcal/mol for H₂O, and therefore the higher rate results from an extraordinarily high activation entropy of +17 cal/deg mol in contrast to -2 cal/deg mol for H₂O.

The magnitude of this activation entropy is unexpectedly high in comparison to the value of -16 cal/deg mol found for the rate constant for the dimer process in the catalysis of the exchange of $\text{Pt}(\text{dien})\text{Br}^+$ by PtBr_4^{2-} , where the transition state also possesses a charge of -1.⁴ It is concluded therefore that the mechanism for exchange is considerably different in the two systems. For $\text{Pt}(\text{dien})\text{Br}^+$ it was proposed that a PtBr_4^{2-} species displaces the bromide ligand with the

formation of a singly bridged dimeric intermediate. A somewhat different mechanism, which is possible for the present system, is shown in Figure 3, where $R = C_2H_4$ and $S = \text{solvent}$. In Figure 3a a *cis*-Cl ligand of a $Pt(C_2H_4)Cl_3$ ion attacks a $Pt(C_2H_4)Cl_2S$ molecule along the axial position. Since a group *trans* to C_2H_4 is usually displaced more readily, the solvent in this position is lost as a single chloride bridge is formed, shown in Figure 3b. A second bridge might form by the donation of an electron pair from Cl^0 to the axial coordination position of the attacking complex, as indicated in Figure 3c. The concerted process (Figure 3d), where the Cl^0 is replaced by solvent on the left platinum, moves Cl^0 into a position *trans* to ethylene on the right platinum, and only a single bridge remains. Exchange is effected as a tagged $^*Cl^-$ replaces the solvent as shown in Figure 3f, and the untagged Cl^0 , now *trans* to C_2H_4 , equilibrates with free chloride. The step from Figure 3d to 3e can be considered in competition with one for which the ethylene on the right moves down to occupy the position opposite Cl^0 , and the chloride originally opposite to it is lost to the solution. This alternative process will form the doubly bridged dimer species which is recrystallized from the solutions when ethanol evaporates. The formation of the symmetric dimer by this process and its dissociation, under the requirements of microscopic reversibility, does not lead to exchange of the *cis* chlorides. Hence, the formation of this species, *per se*, will not account for the exchange. Dissociation of this dimer by the reverse of the formation process described here is essentially the mechanism proposed by Pearson and Muir⁸ for cleavage of the doubly bridged dimeric complexes of platinum(II), by nucleophilic attack. The configuration in Figure 3b corresponds to their intermediate species. The relatively high entropy of activation may result in the loss of solvent at step 3b. The higher entropy of ethanol with respect to H_2O would also account for the difference in the ΔS^\ddagger between these two solvents.

The rate constant for exchange *via* a dimer transition state in this system is much smaller than the ones encountered in the bromide system. Apparently, a bromide ligand can donate electrons into a bridging bond much more readily than can a chloride. Such behavior is consistent with the greater nucleophilicity parameter of bromide in comparison with chloride that is found generally with substitution reactions for platinum(II) complexes.⁹ It is only with the especially high *trans* labilizing properties of the ethylene that it

(8) R. G. Pearson and M. M. Muir, *J. Am. Chem. Soc.*, **88**, 2163 (1966).

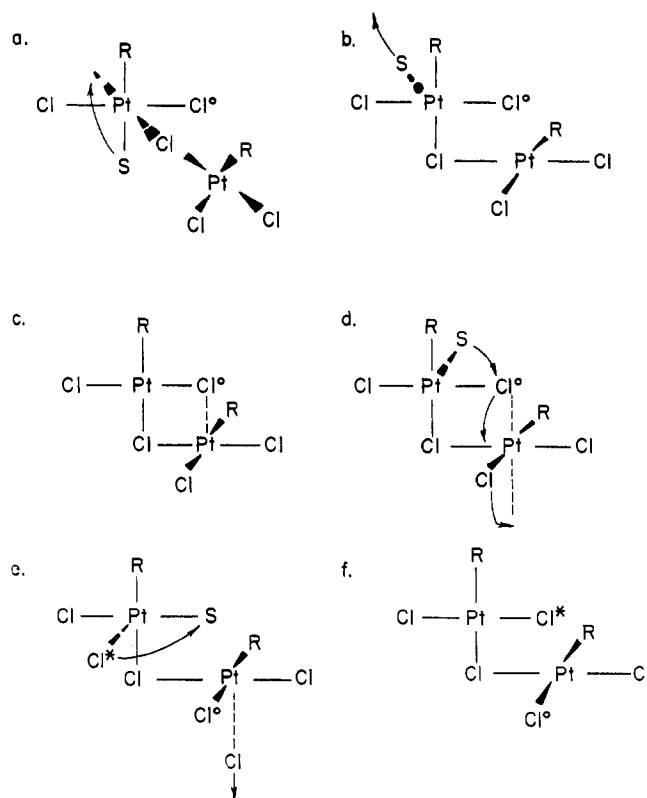


Figure 3.—A suggested mechanism for the exchange of the *cis* chlorides *via* a dimer transition state.

has been possible to observe the contribution of a dimer mechanism at all. The two alternative mechanisms do have the common feature that the exchange occurs as a consequence of the initial steps in the formation of the doubly bridged dimer, but in other respects they are quite different.

A considerable accumulation of kinetics behavior for the ligand-substitution reactions of platinum(II) fits coherently into an associative mechanism involving attack by the entering nucleophile. However, the present work adds to an increasing body of evidence that a number of these reactions involve more complex mechanisms. The deviations from simple rate laws have appeared generally in isotopic exchange studies where it is conveniently feasible to evaluate rates at lower concentrations of the entering nucleophile and to escape from the pseudo-first-order region. It does appear that valuable information may be lost unless the kinetics for these platinum(II) systems are evaluated over as wide a concentration range as is possible.

(9) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *ibid.*, **87**, 241 (1965).