

detectable amount of the protonated species is present under the experimental conditions studied and a deviation from a simple, first-order dependence on $[H^+]$ is observed.

An acid-independent pathway, k_0 , has been observed for all complexes in both groups, with the exception of the hypophosphite complex. For the monosubstituted chromium(III) complexes containing nonbasic or weakly basic ligands, there is a good linear correlation between ΔS_0^\ddagger and the molar entropy of the free ligand.⁷ The ΔS_0^\ddagger values for the fluoro, azido, and cyano complexes all show a positive deviation from this linear relationship, and for this reason it has been suggested⁵⁻⁷ that the transition state for the acid-independent pathway for these complexes involves the transfer of a proton from a coordinated water molecule to the strongly basic ligand, forming a hydroxochromium(III) ion and a neutral acid molecule rather than an aquochromium(III) ion and an anionic leaving group. In addition, the value of k_0 for an internal proton-transfer mechanism should not depend greatly on the ionic strength of the medium because the leaving group would be a neutral molecule and there would be no change of charge in the transition state. In agreement with this expectation, the k_0 values shown in Table III for the monocyno complex in the three different media are all in good agreement.

For monosubstituted pentaquochromium(III) com-

plexes containing the less basic halogen or halogenoid ligands, *i.e.*, iodide, bromide, chloride, azide, or thiocyanate, the rate parameter k_0 for the acid-independent pathway decreases with increasing ligand field strength and a fairly good correlation exists between the ΔG_0^\ddagger and ΔH_0^\ddagger values for the aquation reactions and the frequency of the lowest energy d-d absorption band. (A similar correlation exists over a wide range of ligand field strengths for the monosubstituted pentaamminecobalt(III) complexes.²⁶) In contrast with the trends observed with the other monosubstituted chromium(III) complexes, the free energy of activation for the acid-independent aquation of the monocyno complex is surprisingly low, being slightly less than that of the monobromo complex.¹² We believe that the intramolecular transfer of a proton to the ligand, which becomes more probable with the increasing basicity of the ligand, can account for this relatively low activation energy and that this provides additional support for the proposal that the acid-independent pathway involves an intramolecular proton transfer.

Acknowledgment.—We are indebted to Dr. R. Krishnamurthy, whose research opened up this area of study, for many helpful discussions and suggestions, and to Mr. Donn Darsow, who prepared the potassium hexacyanochromate(III) used in this work.

(26) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, p 65.

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Salt Effects on Substitution Reactions of Platinum(II) Complexes

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Rate data for the reaction of $Pt(NO_2)_4^{2-}$ with SCN^- in the presence of various cations and at different ionic strength values⁵ (ranging from 0.1 to 0.01 *M*) are reported. Reaction occurs in at least three steps, the first one being the substitution of two NO_2^- groups by two thiocyanate ions. The results are discussed in terms of the specific salt effect. The nucleophilic attack is accelerated specifically by the various cations.

Introduction

It has long been recognized that rate constants for nucleophilic substitutions of four-coordinated planar platinum(II) complexes follow the two-term rate law: $rate = k_1[complex] + k_2[complex][L]$ ($L =$ entering group). Accordingly, the processes represented by the two terms are thought of as bimolecular attacks on the substrate by either the solvent (k_1 path) or the entering group (k_2 path). In either case, formation of a labile five-coordination intermediate (which may just as well be an activated complex) is postulated.^{1,2}

(1) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 2.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958, Chapter 4; see also U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

This work is concerned with the reaction between $Pt(NO_2)_4^{2-}$ and SCN^- in the presence of Li^+ , K^+ , $N(C_2H_5)_4^+$, and Ba^{2+} . These cations were present as thiocyanate, tetranitroplatinate(II), and perchlorate salts, added in order to keep the ionic strength constant at the desired value. We limited ourselves to the study of the first stage of the reaction involving substitution of two NO_2^- groups.

Experimental Section

Materials.—The complex $K_2[Pt(NO_2)_4]$ was prepared following the methods of the literature.³ The corresponding salts of Li^+ , Ba^{2+} , and $N(C_2H_5)_4^+$ were obtained by ion exchange from $K_2[Pt(NO_2)_4]$ on a Dowex 50-X8 resin. The solution of H_2-

(3) "Gmelins Handbuch der Anorganischen Chemie," Vol. 68, Verlag Chemie, G. m. b. H., Berlin, 1942, part C, p 166.

[Pt(NO₂)₄] formed by the ion-exchange procedure was treated immediately with a stoichiometric amount of the carbonate of the desired cation. Purity of all of the complexes was checked by elemental and spectral analyses. By the same route, the Li⁺, Ba²⁺, and N(C₂H₅)₄⁺ thiocyanates were prepared from the potassium salt. The perchlorates were obtained by neutralizing perchloric acid with the proper carbonates. All of the salts were purified by recrystallization from their aqueous solutions.

Reaction Products.—In Figure 1 there are reported changes in optical density with time showing the three stages of substitution.

The product of the first stage, Pt(SCN)₂(NO₂)₂²⁻, could be isolated by precipitation with Pt(NH₃)₄²⁺ from the reaction mixture. Precipitation was carried out when the first stage had occurred just beyond 90% and the second stage had occurred for less than 5% (roughly the a region in Figure 1), as monitored by kinetic data (see below). The precipitate was found by analysis to be [Pt(NH₃)₄][Pt(SCN)₂(NO₂)₂]. Attempts to obtain the corresponding potassium salt by direct reaction of stoichiometric amounts of reagents were unsuccessful, owing to the fact that the resulting yellow solution turned red-orange upon being concentrated (probably because of the presence of thiocyanate-bridged polymeric complexes). However, we succeeded in preparing K₂[Pt(SCN)₂(NO₂)₂] by cationic exchange on Dowex 50 W-X12 of [Pt(NH₃)₄][Pt(SCN)₂(NO₂)₂]. The potassium salt was isolated from the resin-exchange solution by stripping the water off *in vacuo* at room temperature.

The [Pt(NH₃)₄][Pt(SCN)₂(NO₂)₂], precipitated from K₂[Pt(SCN)₂(NO₂)₂] (or from its original resin-exchange solution), proved identical with the sample directly isolated from the reaction mixture. In fact, we found the same lattice plane spacings, as determined by the X-ray powder-pattern Debye method.

X-Ray analysis revealed that a mixture of [Pt(NH₃)₄][Pt(NO₂)₄] and [Pt(NH₃)₄][Pt(SCN)₂(NO₂)₂] was obtained when treating with [Pt(NH₃)₄]²⁺ the reaction solution at low SCN⁻ concentration after the first stage had proceeded for approximately 50%.

The K₂[Pt(SCN)₂(NO₂)₂] was examined by ir spectrophotometry, with the mull technique using Nujol and Tripen. Some of the peaks observed and the corresponding assignments are reported in Table I.⁴⁻⁶ Other peaks were observed at 2060, 580, 480, 440, 355, 310, 295, and 290 cm⁻¹.

TABLE I

VIBRATION FREQUENCIES (CM ⁻¹) OF K ₂ [Pt(SCN) ₂ (NO ₂) ₂]		
Freq, cm ⁻¹	Assignment	Ref
2120	SCN	4
2115		
1390		
1375	NO ₂ asym + sym str	5
1340		
840	NO ₂ out-of-phase + in-phase bend	5, 6
830		
705 vw	C-S str	4, 5
630 m	NO ₂ wag	6

Kinetics.—The reactions were followed spectrophotometrically at 300 mμ, at which wavelength the absorption of the starting complex differed most from that of the first stage product. Measurements were taken with a Beckman DU spectrophotometer equipped with a thermostated cell compartment. The temperature was 33.3 ± 0.05°.

In order to obtain satisfactory reproducibility of absorbance values in all of the kinetic runs, the initial amount of substrate

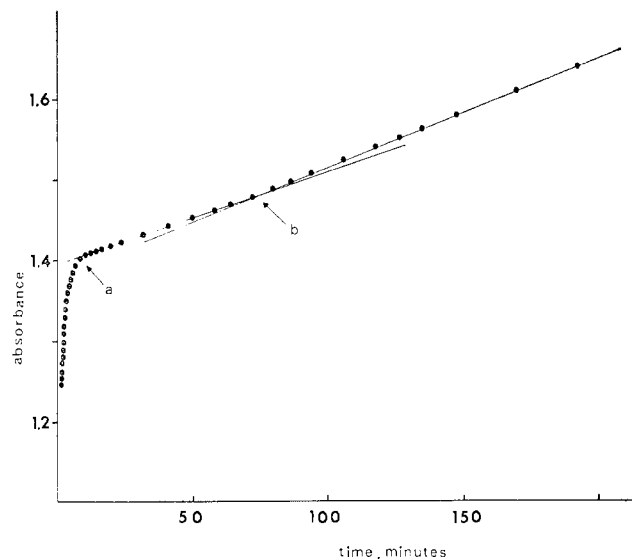


Figure 1.—Absorbance changes of a solution of $1.75 \times 10^{-3} M$ K₂[Pt(NO₂)₄] + 0.2 M KSCN at 300 mμ, against time; temperature 33.3 ± 0.05°.

was measured by weighing of $2 \times 10^{-2} M$ stock solution. The substrate and reagent solutions and a 10-ml pipet were separately thermostated; then the reaction mixture was prepared by quickly pipetting the nucleophile into the substrate solution. The zero reaction time was considered to be that corresponding to half of the reagent solution being added. The reaction mixture was then transferred into the 1-cm quartz cell and the absorbance measurements were taken after *ca.* 2 min.

Results

In each run the reference cell contained a blank solution of nucleophile and added salt at the same concentration as in the reaction mixture. The complex concentration ($1.75 \times 10^{-3} M$) was so chosen as to get a sizable change of absorbance in the course of the reaction. We could not measure values of the initial and final absorbance (A_0 and A_∞ , respectively) since at the outset of the first stage the substitution reaction was accompanied by a detectable aquation of the starting material.⁷ Moreover, near the end of the first stage, spectral changes began to be affected by the subsequent stage. The A_0 and A_∞ values were therefore calculated by an indirect method. The absorbance of the reaction mixture, prior to the third stage, is given by

$$A = \epsilon_A C_A + \epsilon_B C_B + \epsilon_C C_C \quad (1)$$

where ϵ is the molar extinction coefficient, C is the molar concentration, and the A, B, and C subscripts refer to the substrate and the products of the first and second stage in that given order. These concentrations can be expressed by means of the well-known equations for consecutive first-order reactions,⁸

(7) Such aquation was evidenced by the spectral changes observed in a $1.75 \times 10^{-3} M$ solution of K₂[Pt(NO₂)₄] in the presence of perchlorates. The absorbance changed with the time until a constant equilibrium situation was established, regardless of the perchlorate concentration. At any rate, such a spectral change was rather small so that we can assume that the extent of aquation is rather moderate.

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1953, p 166.

() C. Pecile, *Inorg. Chem.*, **5**, 210 (1966); I. Bertini and A. Sabatini, *ibid.*, **5**, 1025 (1966).

(5) J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 4073 (1959).

(6) M. Le Postollec, J. P. Mathieu, and H. Poulet, *J. Chim. Phys.*, **60**, 1319 (1963).

as a function of the rate constants of first and second stages, k_1' and k_2' . The entering group concentration was in excess throughout. Owing to the fact that under the experimental conditions k_2' turned out to be much smaller than k_1' , a sufficiently long time can be chosen as to make $e^{-k_1't} \approx 0$ and $e^{-k_2't} \approx 1 - k_2't$. Under these conditions, the absorbance becomes a linear function of time

$$A = A_{\text{extr}} + St \quad (2)$$

where

$$A_{\text{extr}} = a \left[\epsilon_B \frac{k_1'}{k_1' - k_2'} - \epsilon_C \frac{k_2'}{k_1' - k_2'} \right] \quad (3)$$

$$S = a(\epsilon_C - \epsilon_B) \frac{k_1'k_2'}{k_1' - k_2'} \quad (4)$$

and a = initial complex concentration.

For a short time we have

$$k_1' = \frac{1}{t} \ln \frac{A_{\text{extr}} - A_0}{A_{\text{extr}} + St - A} \quad (5)$$

whereby k_1' and A_0 may be obtained. It is not feasible to obtain from eq 3 the theoretical value of A_∞ for the case in which the second stage rate is negligible (*viz.*, $a\epsilon_B$), since ϵ_C and k_2' cannot be obtained directly and separately. However, if the customary equation $A = A_\infty - (A_\infty - A_0)e^{-k_1't}$ may be assumed to hold for up to 70% of reaction, by plotting A values *vs.* $e^{-k_1't}$, A_0 and A_∞ can be determined.

The linear plot of absorbance *vs.* time for the second stage is shown in Figure 2.

The same figure shows the fitting of eq 5, together with the reliability of the calculated A_0 and A_∞ values. These last values, estimated for several runs, vary within rather narrow ranges and their average values were used to calculate the concentration of the initial and final complexes, even for runs at much lower concentrations of the entering group. A similar procedure was employed for a much simpler case by Kreevoy, *et al.*⁹

In order to ascertain the presence of specific salt effects (and of nonelectrostatic ones, if any), we were forced to use as low ionic strengths as possible, thus avoiding the great excess of entering group usually employed in reactions of this type. Actually a complex:entering group molar ratio equal to 1 was used in some runs. In this case the kinetic equation is

$$-\frac{d(a-x)}{dt} = [k_1 + k_2(b+2x)](a-x) \quad (6)$$

where a and b are the initial concentrations of substrate complex and reagent, respectively. By integrating we obtain

$$\ln \frac{a-x}{(k_1/k_2) + b - 2x} = \ln \frac{a}{(k_1/k_2) + b} - [k_1 + k_2(b-2a)]t \quad (7)$$

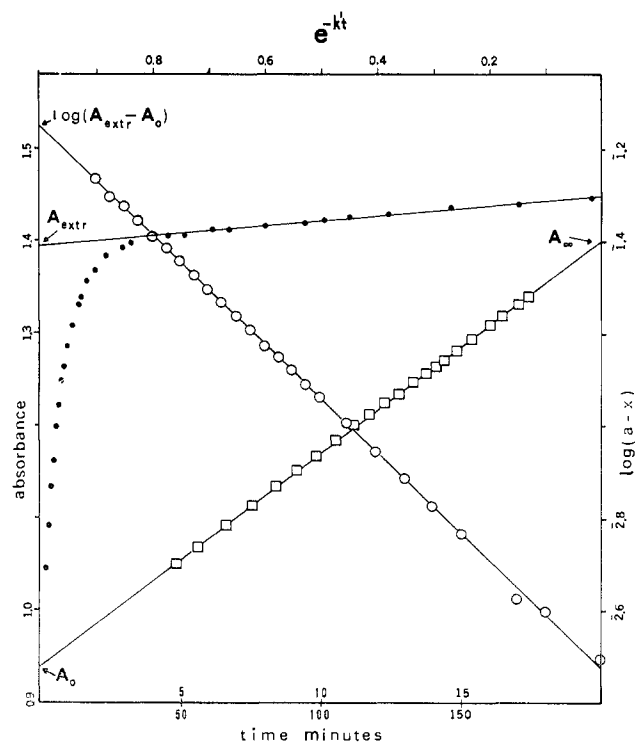


Figure 2.—Reaction rate of $K_2[Pt(NO_2)_4]$ ($1.75 \times 10^{-3} M$) and $KSCN$ ($0.05 M$) in the presence of $KClO_4$ at 33.3° . Dots: absorbance at $300 m\mu$ against time; time scale, 0–200 min; ordinate, scale to the left. Circles: $\log(A_{\text{extr}} + St - A)$ against time; time scale, 0–20 min; ordinate, scale to the right. Squares: absorbance against $e^{-k't}$; ordinate, scale to the left.

that is, $y = a - k't$.

A double least-squares treatment was used to calculate k_1 and k_2 from the optical densities of various mixtures, at the same ionic strength and at different nucleophile concentrations, measured as a function of time. The values of a and b being known, it was assumed that $a - x$ was proportional to $A_\infty - A$. We minimized the expression $\sum(y - a - k't)^2$, using a first approximation value for the ratio k_1/k_2 . First-approximation values of $k' = k_1 + k_2(b - 2a)$ were obtained for the different b 's, and we assumed that *relative errors* on the negative and positive direction were equally probable. Then we minimized the expression

$$\sum \left[1 - \frac{k_1}{k'} - \frac{k_2}{k'}(b - 2a) \right]^2$$

and we obtained values of k_1 and k_2 . The whole procedure was repeated until the values of k_1 and k_2 remained constant, and we controlled the final values of k_1 and k_2 to be independent of the initially chosen value for their ratio. Usually 10 iterations were sufficient. The computer IBM 7090 of CNUCE of the University of Pisa was used to carry out these calculations. Depending on the various concentrations of the entering group, kinetic runs were followed to an extent ranging from 30 to 70%, since at low values of such concentrations deviations from linearity became important. In such cases, an equilibrium was

(9) M. M. Kreevoy, P. J. Steinwand, and W. V. Kayser, *J. Am. Chem. Soc.*, **88**, 124 (1966).

TABLE II
 VALUES OF k' (SEC⁻¹) OBSERVED AND CALCULATED FOR THE EXAMINED REACTIONS

$\mu = 0.015$			$\mu = 0.025$			$\mu = 0.055$			$\mu = 0.105$		
10 ^b	Obsd	Calcd	10 ^b	Obsd	Calcd	10 ^b	Obsd	Calcd	10 ^b	Obsd	Calcd
(a) Lithium Salts											
25	0.97	0.97	25	0.88	0.91	25	0.94	0.92	25	0.72	0.72
35	1.20	1.24	50	1.84	1.73	50	1.92	1.98	50	1.91	1.90
50	1.72	1.63	100	3.67	3.38	100	3.98	4.09	100	4.14	4.25
75	2.27	2.30	200	6.15	6.68	250	11.49	10.43	200	8.75	8.96
100	2.93	2.96				500	20.25	21.00	500	23.52	23.08
									1000	47.82	64.61
(b) Potassium Salts											
25	0.77	0.77	25	0.70	0.70	25	0.69	0.69	17.5	0.24	0.24
50	1.42	1.43	50	1.46	1.50	50	1.75	1.71	25	0.61	0.62
75	2.10	2.09	100	3.17	3.09	100	3.57	3.75	50	1.92	1.87
100	2.76	2.76	200	6.23	6.28	200	8.00	7.83	100	4.40	4.38
						500	20.31	20.08	150	6.99	6.88
									200	9.06	9.39
									350	16.95	16.91
(c) Tetraethylammonium Salts											
25	0.80	0.80	25	0.61	0.61	25	0.61	0.61	25	0.40	0.40
50	1.66	1.66	50	1.62	1.57	50	1.63	1.65	50	1.49	1.48
75	2.55	2.52	100	3.41	3.47	100	3.80	3.73	100	3.65	3.64
100	3.35	3.38	200	7.25	7.29	200	7.99	7.90	200	7.71	7.97
						500	20.04	20.40	500	21.49	20.95
(d) Barium Salts ^a											
22.8	0.91	0.89	22.8	0.73	0.72	22.8	0.73	0.72	22.8	0.60	0.61
33.3	1.26	1.36	26.64	0.90	0.92	45.6	2.11	2.16	45.6	2.47	2.39
45.6	2.10	1.92	45.6	1.90	1.89	91.2	5.07	5.02	91.2	6.04	5.94
66.6	2.83	2.88	68.4	3.10	3.04	182.4	10.85	10.76	182.4	12.58	13.06
			91.2	4.14	4.20						

^a The ionic strength is higher by 0.002.

probably being established. In Table II we report the calculated and observed values of k' for the various conditions, and in Tables III and IV we report the values of k_1 and k_2 and their errors, calculated from the equations

$$\frac{E_{k_1}}{k_1} = \sqrt{\frac{\left(\sum \frac{d_i^2}{k'}\right) \sum (2a - b)^2}{(n-2)[n\sum b^2 - (\sum b)^2]}}$$

$$E_{k_2} = \sqrt{\frac{(\sum d_i^2)n}{(n-2)[n\sum b^2 - (\sum b)^2]}}$$

where n is the number of kinetic runs carried out with different values of b at each ionic strength and d_i is the difference between the k' values (calculated as above from absorbance data) and those obtained from the final values of k_1 and k_2 . For each ionic strength and each cation, a number of b values from 4 up to 7 have been used. The greatest number of b values was employed for the K^+ data on which the calculation of A_0 and A_∞ is based. Results concerning k_2 are reported in Figure 3 also, following Guggenheim and Prue's method,¹⁰ where $\log k_{2,0}'$ defined as

$$\log k_{2,0}' = \log k_2 - 2AZ_A Z_B \frac{\sqrt{\mu}}{1 + \sqrt{\mu}}$$

is plotted *vs.* the ionic strength, μ .

 TABLE III
 VALUES OF $10^4 k_1$ (SEC⁻¹) FOR THE REACTION
 $\text{Pt}(\text{NO}_2)_4^{2-} + 2\text{SCN}^- \rightarrow \text{Pt}(\text{NO}_2)_2(\text{SCN})_2^{2-} + 2\text{NO}_2^-$
 IN WATER AT 33.3°

Ionic strength	Li ⁺	K ⁺	(C ₂ H ₅) ₄ N ⁺	Ba ²⁺ ^a
0.105	1.19 ± 0.02	1.12 ± 0.01	0.83 ± 0.01	1.56 ± 0.03
0.055	1.35 ± 0.05	1.10 ± 0.02	1.02 ± 0.01	1.49 ± 0.02
0.025	1.24 ± 0.08	1.02 ± 0.02	0.99 ± 0.02	1.34 ± 0.01
0.015	1.24 ± 0.02	1.03 ± 0.004	1.14 ± 0.008	1.44 ± 0.07

^a The ionic strength is higher by 0.002.

 TABLE IV
 VALUES OF $10^6 k_2$ (M⁻¹ SEC⁻¹) FOR THE REACTION
 $\text{Pt}(\text{NO}_2)_4^{2-} + 2\text{SCN}^- \rightarrow \text{Pt}(\text{NO}_2)_2(\text{SCN})_2^{2-} + 2\text{NO}_2^-$
 IN WATER AT 33.3°

Ionic strength	Li ⁺	K ⁺	(C ₂ H ₅) ₄ N ⁺	Ba ²⁺ ^a
0.105	4.72 ± 0.08	5.03 ± 0.04	4.34 ± 0.08	7.79 ± 0.31
0.055	4.22 ± 0.19	4.07 ± 0.04	4.18 ± 0.04	6.29 ± 0.08
0.025	3.30 ± 0.31	3.19 ± 0.04	3.80 ± 0.04	5.10 ± 0.08
0.015	2.65 ± 0.11	2.65 ± 0.01	3.45 ± 0.04	4.57 ± 0.04

^a The ionic strength is higher by 0.002.

Discussion

The fact that the product of the first step is $\text{Pt}(\text{SCN})_2(\text{NO}_2)_2^{2-}$ is consistent with the mechanism

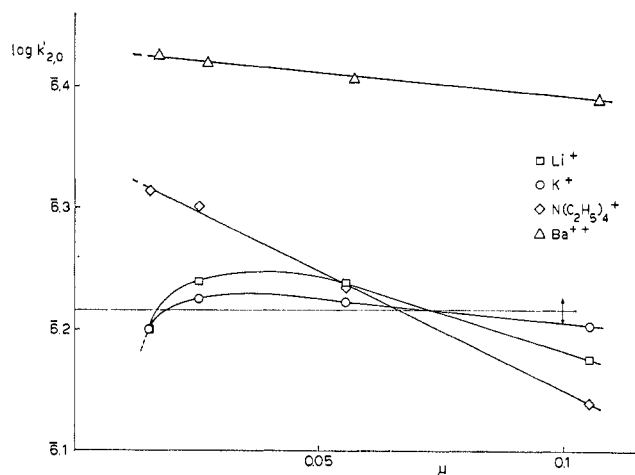
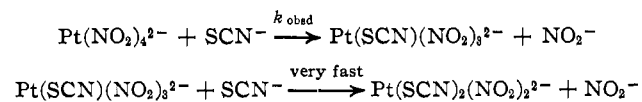


Figure 3.—Plot of $\log k_{2,0}'$ against the ionic strength, μ .

The ir spectrum suggests that the product is *cis*-thiocyanate, $\text{Pt}(\text{SCN})_2(\text{NO}_2)_2^{2-}$.⁴⁻⁶ It is remarkable, however, that the peak at 705 cm^{-1} is single and very weak.

Most of the nucleophilic substitution reactions of four-coordinated platinum(II) complexes are concerned with neutral complexes of the types *cis*- and *trans*- PtL_2X_2 .¹¹ Such reactions display practically no dependence on μ , whereas a dependence is found for the reactions of cationic platinum(II) complexes with negatively charged entering groups. For instance, Chan¹² and Martin¹³ independently found the occurrence of a salt effect in the reactions of $\text{Pt}(\text{dien})\text{X}^+$ (*dien* = diethylenetriamine; *X* = Cl or Br) with Cl^- , Br^- , and I^- as entering groups.

However, no data are reported in the literature concerning the influence of different cations on rates of reactions between anionic platinum(II) complexes and negative entering groups. Therefore, it is worthwhile to examine the salt effect on the basis of the classical Brønsted-Debye theory,¹⁰ as can be accomplished by considering the Guggenheim-Prue plot reported in Figure 3. It is evident, at first sight, that such an approach can account for only a minor portion of the salt effect, even at very low concentration. In fact, points corresponding to the various cations should place themselves on straight lines converging into a common intercept at infinite dilution. This is not generally the case, except rather approximately for K^+ and Li^+ . On the other hand, the arrangement of the experimental points on smooth curves clearly shows the accuracy of the measurements. The limited validity of the Brønsted-Debye theory has been confirmed for many reactions between anions,¹⁴⁻¹⁷

even at low ionic strengths, as for the reactions of the $\text{Fe}(\text{CN})_6^{3-}$ - $\text{Fe}(\text{CN})_6^{4-}$ isotopic exchange.¹⁸

The operation of salt effect on the k_1 term also confirms the failure of the classical theory⁸ to account for the experimental observations. Thus, it is convenient to examine the salt effects on k_1 and k_2 separately, at low ($\mu = 0.01$) and high ($\mu = 0.1$) concentrations. As for the k_2 term under the last mentioned conditions, the salt effect decreases in the order $\text{Ba}^{2+} > \text{K}^+ > \text{Li}^+ > \text{N}(\text{C}_2\text{H}_5)_4^+$. This behavior is common to reactions between anions displaying nonelectrostatic salt effects,^{19,20} in which case the influence of cations must be of outer-sphere type.^{20h} That is, the cation affects the reagents through its solvation sphere. That nonelectrostatic effects are operative is not surprising, despite the sizable dimensions of the reagents, owing to the close proximity of the reaction center to the site at which the attack by the entering groups occurs.^{20b} Moreover, the possibility exists of the cation interacting with the filled, non-bonding, originally $5d_{z^2}$ orbital of the platinum. In this way, formation of the five-coordinate activated complex is facilitated by an accelerated bond-making process. In fact, owing to the resulting decreased d-electron density on the central metal, repulsion between the entering nucleophile SCN^- and the filled $5d_{z^2}$ orbital will be reduced, whereas interaction with the empty, originally $6p_z$ metal orbital will be enhanced. Such a feature of the d^8 transition metal ions is known to favor an electrophilic attack proceeding *via* oxidative addition. This occurs through interaction between the electrophile and the central metal. Such mechanisms have recently been proposed for the isotopic exchange reactions of *trans*- $\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl}$ and D^+ ²¹ and for the cleavage by acids of the metal-carbon bond in platinum(II) complexes.²² In these reactions, however, the inner-sphere interaction of the small H^+ ion with the complex may be particularly favored.

The above interpretation of the salt influence on the k_2 term is confirmed by the salt effect on the k_1 term, at high concentrations. The entering H_2O (k_1 path) may be considered, in fact, as behaving roughly as an anion (through its high electronic density on the attacking oxygen-dipole end), so that the various cations can still affect the attack much in the same way as they do for the k_2 term. The sole exception is observed for Li^+ which is more effective than K^+ . This is not surprising since the role of the cation in the attack of the

(16) J. W. Gryder, *J. Chem. Phys.*, **37**, 718 (1962).

(17) B. Perlmutter-Hayman and G. Stein, *ibid.*, **40**, 848 (1964).

(18) R. J. Campion, C. F. Deck, P. King, Jr., and A. C. Wahl, *Inorg. Chem.*, **6**, 672 (1967).

(19) A. Indelli, V. Bartocci, E. Ferranti, and M. G. Lucarelli, *J. Chem. Phys.*, **44**, 2069 (1966); A. Indelli and P. L. Bonora, *J. Am. Chem. Soc.*, **88**, 924 (1966).

(20) (a) J. C. Sheppard and A. C. Wahl, *ibid.*, **79**, 1020 (1957); (b) A. Indelli and E. S. Amis, *ibid.*, **82**, 332 (1960); (c) M. Bobtelsky, B. Perlmutter-Hayman, and G. Stein, *Bull. Res. Council Israel*, **A**, **9**, 195 (1960); (d) C. W. Davies, *Progr. Reaction Kinetics*, **1**, 161 (1961); (e) M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *Inorg. Chem.*, **4**, 361 (1965); (f) P. G. Rasmussen and C. H. Brubaker, *ibid.*, **3**, 977 (1964); (g) B. Perlmutter-Hayman and Y. Weissmann, *J. Phys. Chem.*, **71**, 1409 (1967); (h) M. R. Kershaw and J. E. Prue, *Trans. Faraday Soc.*, **63**, 1198 (1967).

(21) C. D. Falk and J. Halpern, *J. Am. Chem. Soc.*, **87**, 3523 (1965).

(22) U. Belluco, M. Giustiniani, and M. Graziani, *ibid.*, **89**, 6494 (1967).

(11) U. Belluco, *Coord. Chem. Rev.*, **1**, 111 (1966).

(12) C. S. Chan, *J. Chem. Soc.*, **A**, 1000 (1966).

(13) D. S. Martin and E. L. Bahn, *Inorg. Chem.*, **6**, 1653 (1967).

(14) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 348, 1167 (1949).

(15) R. M. Healy and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **77**, 5258 (1955).

H₂O molecule is presumably of the inner-sphere type. The same effectiveness order Li⁺ > K⁺ has been observed in almost all of those reactions between anions in which the nucleophilic reagent is OH⁻.¹⁹

The salt effect at low μ values appears much more complicated and is far from understood. A comparison can be made with analogous situations, although in a less pronounced fashion, already observed for other ionic reactions. In particular, the more effective acceleration of the tetralkylammonium cation compared with that of K⁺ at low concentrations on both k_1 and k_2 ²³ resembles the accelerating influence of R₄N⁺ ions

(23) This, *inter alia*, proves that the effect is not apparent and does not stem from the method employed to calculate k_1 and k_2 .

in the reactions of BrCH₂COO⁻ with S₂O₃²⁻^{19,24} and of IO₄⁴⁻ with I⁻.²⁵ In all likelihood, the observed behavior of R₄N⁺ ions results from a delicate balance of accelerating and retarding factors.

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(24) A. Indelli, *J. Phys. Chem.*, **65**, 972 (1961).

(25) A. Indelli, F. Ferranti, and F. Secco, *ibid.*, **70**, 631 (1966).

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The Reaction between 1,10-Phenanthroline and Platinum(II) Compounds. I. The Reaction in Aqueous Solution

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1,10-Phenanthroline reacts slowly and quantitatively with K₂PtCl₄ to give Pt(phen)Cl₂. Like most substitution reactions of platinum(II), this one proceeds by a direct path and also by a path that involves intermediate incorporation of a molecule of solvent. The respective rate constants at 45° in water are $3.74 \times 10^{-3} M^{-1} \text{sec}^{-1}$ ($\Delta H^\ddagger = 11.8 \text{ kcal/mol}$, $\Delta S^\ddagger = -24 \text{ eu/mol}$) and $11.5 \times 10^{-3} M^{-1} \text{sec}^{-1}$ ($\Delta H^\ddagger = 17.3 \text{ kcal/mol}$, $\Delta S^\ddagger = -16 \text{ eu/mol}$) at an ionic strength of 10.3×10^{-2} . Both paths are first order in phenanthroline and first order in platinum(II) concentrations. The reaction rate is sensitive to ionic strength and to the basicity of the phenanthroline but insensitive to pH in the range of 2.7–4.9. The slowness of the reaction and the unusual second-order solvent path appear to be the result of the inflexibility of the phenanthroline. The ratio of the rate of its reaction with K₂PtCl₄ to the rates of the more flexible ligands bipyridyl and ethylenediamine is 1:3:100, which is not explicable in terms of changes in nucleophilicity. The reactions of phenanthroline with *cis*- and *trans*-Pt(NH₃)₂Cl₂ are much slower than with PtCl₄²⁻, and its reaction with Pt(C₂H₄)Cl₂ is very much faster. The results are discussed in terms of a mechanism that is strongly dependent on dissociation of the platinum(II) complex.

Introduction

When Pt^{II}X₄ reacts with a flexible bidentate ligand, the first X group is substituted by one end of the ligand in a slow, rate-determining step. The other end of the ligand then displaces a second X group in a faster step.^{1,2} Both steps have the same mechanism as the substitution by a unidentate ligand: the interchange of a single coordinated group by another. The greater speed of the second step is merely the result of a sort of statistical advantage (anchimeric assistance) it has over the first. This stepwise process is probably impossible for 1,10-phenanthroline. The inflexibility of the molecule and the closeness of its donor nitrogens would seem to preclude its coordination though a single nitrogen.³ Unidentate phenanthrolines have been postulated as intermediates to explain the acid dependence of some dissociation reactions.^{4–6} These de-

pendences are often peculiar,^{4–7} and an alternative interpretation has been given, not involving a unidentate intermediate.^{8–10} The consequences of the closeness of the phenanthroline nitrogens can be seen in the structure of Zn(phen)Cl₂.¹¹ The N–Zn–N angle is only 80°, although the bond length is normal, whereas that in Zn(NH₃)₂Cl₂¹² is 108°. It was anticipated that these properties of the phenanthroline might cause its substitution reactions with metals of slight lability to exhibit some peculiarities, such as abnormal slowness. The kinetics of phenanthroline–metal dissociations have been examined for a number of metal ions.^{4–10} A few association reactions have also been studied, all using fairly labile metal ions.^{13,14} The association mechanism that has emerged involves the formation of an outer-sphere aggregate of phenanthro-

- (1) P. Haake and P. A. Cronin, *Inorg. Chem.*, **2**, 879 (1963).
- (2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, New York, N. Y., 1967, pp 218–228, 406.
- (3) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 3807 (1954).
- (4) D. W. Margerum, R. I. Bystroff, and C. V. Banks, *ibid.*, **78**, 4211 (1956).
- (5) D. W. Margerum, *ibid.*, **79**, 2728 (1957).
- (6) R. S. Bell and N. Sutin, *Inorg. Chem.*, **1**, 359 (1962).

- (7) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 3596 (1948).
- (8) J. E. Dickens, F. Basolo, and H. M. Neumann, *ibid.*, **79**, 1286 (1957).
- (9) A. Jensen, F. Basolo, and H. M. Neumann, *ibid.*, **80**, 2354 (1958).
- (10) L. Seiden, F. Basolo, and H. M. Neumann, *ibid.*, **81**, 3809 (1959).
- (11) C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, **5**, 1185 (1966).
- (12) C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.*, **94**, 249 (1936).
- (13) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).
- (14) R. G. Pearson and P. Ellgen, *ibid.*, **6**, 1379 (1967).