

Pauli–Peierls equation¹⁹

$$\kappa_{e^-} = \frac{4m^*\mu_0^2}{h^2} (3\pi^2n)^{1/2} \left(1 - \frac{m^2}{3m^{*2}}\right)$$

where m^* is the effective mass, μ_0 is the Bohr magneton, n is the electron density, m is the electron mass and h is the Planck constant. Without the subtractive term in the parentheses, the magnetic susceptibility is the Pauli susceptibility arising from the unpaired electrons at the top of the Fermi distribution. The subtractive term with $m = m^*$ is the Landau diamagnetism which amounts to one-third of the Pauli moment. Introduction of m^* after Peierls corrects for departure from a perfectly free electron gas.

Except for the value for $\text{Na}_{.78}\text{WO}_3$, the effective masses show a rise to a maximum at $\text{M}_{.30}\text{WO}_3$ and then a fall-off. (It might be noted here that we have restricted ourselves to cubic bronzes only, so problems of anisotropy have been avoided.) The existence of this maximum in m^* suggests that there is a perturbation of the band structure which diminishes as x in M_xWO_3 exceeds 0.3. The decay in m^* at large x is consistent with the increasing mobility of the electrons in the alkali-richer bronzes. The source of the initial rise in m^* is not clear. It may only be an apparent effect coming from the assumption that all the electrons are free. As discussed above, there might be localization of the electrons in the dilute bronzes which would reduce the number of free carriers. However, in $\text{Ag}_{0.01}\text{WO}_3$ ²⁰ where trapping would be more likely because of the higher ionization potential of silver, the conductivity data seem to imply complete freeing of the carriers at room temperature and above.

(19) See, for example, A. H. Wilson, "The Theory of Metals," 2nd Ed., Cambridge University Press, Cambridge, 1954, p. 155.

(20) M. J. Sienko and B. R. Mazumder, *J. Am. Chem. Soc.*, **82**, 3508 (1960).

Alternatively, the initial rise in m^* might be attributable to the fact that at low values of x in M_xWO_3 , the concentration of M^+ ions introduced may not seriously perturb a $5d_e$ band, if the latter indeed is the principal conducting band. As more M^+ is introduced into the lattice, the concentration of scattering centers increases, each M^+ appreciably lowering the energy of the eight tungsten neighbors that comprise the unit cell. States are thus effectively removed from the band, since banding can occur only with approximately equal energy states. On the other hand, when sufficiently high concentrations of M^+ have been added, a major portion of the tungsten atoms may be so perturbed and hence their states could mix to give band formation. The higher the concentration of M^+ , the more valid is the approximation of a regularly periodic potential.

In summary, the model that begins to develop for the tungsten bronzes is a $5d_e$ conduction band with local traps arising from tungsten atoms that have M^+ ions in their vicinity. There should be a finite excitation energy from these traps, but a fairly high mobility and low effective mass for any electrons that have been ejected from the traps. As the concentration of M^+ increases, the number of trapping centers increases, leading to reduced mobility and higher effective mass. Eventually the traps begin to overlap, the activation energy vanishes and metallic conduction sets in. From there on, increasing the concentration of M^+ reduces the aperiodicity in the band and leads to increasing mobility and decreasing effective mass. A major test of these ideas would come from experiments at lower temperatures.

Acknowledgments.—We acknowledge with thanks the stimulating discussions we have had with Professors Raymond Bowers and James Krumhansl of the Cornell Physics Department.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Nitrite Substitution in Chloroamineplatinum(IV) Complexes

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RECEIVED OCTOBER 31, 1960

A kinetic study was made of the nitrite substitution reaction in several chloroamineplatinum(IV) complexes. In the absence of platinum(II) the reaction was found to involve an induction period of from 1 to 2 hr. and variable dependence upon platinum(IV) concentration. With the addition of platinum(II) the induction period disappeared and the reaction was found to obey the rate law $R = k[\text{Pt(IV)}][\text{Pt(II)}][\text{NO}_2^-]$ and to be roughly the same as the rate of chloride exchange. All of these observations are explained on the basis of a slow reduction of platinum(IV) to platinum(II) by nitrite ion and then a second two electron oxidation-reduction reaction involving a bridged intermediate. *trans*-[Pt(tetrameen)₂Cl₂]²⁺ reacts with nitrite ion only to be reduced to [Pt(tetrameen)₂]²⁺ and no substitution occurs.

Much of the information concerning reaction mechanisms of hexacoordinated complexes has been gained from kinetic studies with the many complexes of cobalt(III).³ Preliminary investigations by Wilks⁴ of the reaction between *trans*-

[Pt(en)₂Cl₂]²⁺ and nitrite ion indicated that the reaction proceeded by the direct replacement of one chloride ion to yield [Pt(en)₂NO₂Cl]²⁺. Recently, Musket⁵ observed that the reaction was much more complex than it previously had been believed to be.⁶ For example, Musket found that the reaction has an induction period lasting from 1 to 3 hr. and that the reaction is catalyzed by the

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(2) Symbols of ligands are en = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and tetrameen = $\text{NH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{NH}_2$.

(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Ch. 3.

(4) P. H. Wilks, Masters Thesis, Northwestern University (1957).

(5) S. F. Musket, Masters Thesis, Northwestern University (1960).

(6) F. Basolo, A. F. Messing, P. H. Wilks, R. G. Pearson and R. G. Wilks, *J. Inorg. Nuclear Chem.*, **8**, 203 (1958).

TABLE I
RATE CONSTANTS FOR NITRITE SUBSTITUTION IN CHLOROAMMINEPALATINUM(IV) COMPLEXES^a AT 50° AND WITH NO ADDED
Pt(II)

[Pt(IV)], M	[NaNO ₂], M	[NaClO ₄], M	<i>trans</i> -[Pt(en) ₂ Cl ₂] ²⁺ [HClO ₄], M	<i>k'</i> (M ⁻¹ min. ⁻¹) ^o	Ind. per., min.	<i>k</i> ₁ (M ⁻² min. ⁻¹)
0.0012	0.232	0.832 × 10 ⁻²	165	1.42 × 10 ⁻⁴
.0023	.227	0.840 × 10 ⁻²	85	1.38 × 10 ⁻⁴
.0031	.200	0.026	...	1.64 × 10 ⁻²	90	1.68 × 10 ⁻⁴
.0049 ^b	.220	1.83 × 10 ⁻²	130	1.33 × 10 ⁻⁴
.0050	.150	.055	0.015	1.57 × 10 ⁻²	85	1.35 × 10 ⁻⁴
.0050 ^c	.200020	1.72 × 10 ⁻²	70	1.40 × 10 ⁻⁴
.0050 ^d	.200020	1.75 × 10 ⁻²	95	1.37 × 10 ⁻⁴
.0051 ^b	.200020	1.58 × 10 ⁻²	90	1.31 × 10 ⁻⁴
.0051	.200	.020	...	1.72 × 10 ⁻²	90	1.50 × 10 ⁻⁴
.0055	.200020	1.61 × 10 ⁻²	100	1.14 × 10 ⁻⁴
.0096	.200	.005	...	2.56 × 10 ⁻²	70	1.43 × 10 ⁻⁴
.0098	.200	.005	...	2.59 × 10 ⁻²	50	1.57 × 10 ⁻⁴
.0099 ^c	.180025	2.48 × 10 ⁻²	85	1.34 × 10 ⁻⁴
.0149	.190	2.82 × 10 ⁻²	60	1.21 × 10 ⁻⁴
.0190	.175	3.79 × 10 ⁻²	65	1.39 × 10 ⁻⁴
.0052 ^e	.200	.020	...	5.80 × 10 ⁻²	40
.0050 ^f	.200	.020	...	1.94 × 10 ⁻²	85
<i>cis</i> -Pt(NH ₃) ₄ Cl ₂ ²⁺						
.0025 ^b	.200	.027	...	1.58 × 10 ⁻⁴	1600	1.5 × 10 ⁻⁴
<i>trans</i> -[Pt(NH ₃) ₄ Cl ₂] ²⁺						
.0010 ^b	.200	.032	...	1.00 × 10 ⁻²	10	6.4 × 10 ⁻⁴
.0012 ^h	.200026	1.01 × 10 ⁻²	60	5.9 × 10 ⁻⁴
.0024 ^b	.200	.027	...	1.73 × 10 ⁻²	40	6.2 × 10 ⁻⁴
.0045 ^{b,c}	.200026	1.62 × 10 ⁻²	30	5.4 × 10 ⁻⁴
.0051 ^b	.200	.020	...	1.84 × 10 ⁻²	30	5.9 × 10 ⁻⁴

^a Used as the perchlorate salt unless otherwise noted, all runs made at $\mu = 0.235$. ^b Used as the nitrate salt. ^c Dissolved complex treated with KMnO₄ before reaction. ^d (NH₄)₂Ce(NO₃)₆ added to reaction mixture, [Ce(IV)]₀ = 2.5 × 10⁻⁴ M. ^e CuSO₄ added to reaction mixture, [Cu(II)] ≈ 10⁻³ M. ^f Fe₂(SO₄)₃ added to reaction mixture, [Fe(III)] ≈ 10⁻³ M. ^o Pseudo-first order constants divided by nitrite ion concentration.

addition of [Pt(en)₂]²⁺. The entire system has now been studied in some detail and the results of this investigation are reported here.

Experimental

Reagents and Equipment.—All of the platinum compounds used in this investigation are known compounds and they were prepared by methods described in the literature.^{7,8} These compounds were purified by recrystallization and characterized by means of analyses. All of the reagents used in this study were of the best grade available. A constant temperature bath capable of maintaining the temperature within ±0.1° at 50° for a long period of time was used. Spectrophotometric measurements were made on a Cary Model 11 recording spectrophotometer. A microammeter, silver electrodes and a microburet were used to make amperometric titrations of chloride ion.

Procedure.—Reaction mixtures were usually about 0.005 M in the platinum(IV) complex and about 0.1 to 0.2 M in nitrite ion. All runs were carried out in volumetric flasks coated with black Apiezon wax to prevent photocatalysis. All reactants were thermally equilibrated before mixing in order to assure that the induction period was not caused by temperature differences. The extent of reaction was followed by amperometric titrations of the chloride ion that was released. Titrations with this method are somewhat faster than with the Volhard method and are reproducible to about ±0.02 ml. The procedure followed in these titrations was to place small aliquots of the reaction mixture in about 100 ml. of ice cold acetone to which had been added 20 ml. of concentrated nitric acid per liter of acetone. Then a few drops of wool violet (1 g./l.) were added and the solution titrated with 0.01 M silver nitrate solution. The end-point was taken as the minimum of a plot of mamp. vs. ml. of titrant.

(7) "Gmelins Handbuch der Anorganische Chemie," Vol. 68, pp. 476-610, Verlag Chemie (1957).

(8) F. Basolo, M. L. Morris and R. G. Pearson, *Discussions Faraday Soc.*, 29, 80 (1960).

Results

Since the nitrite ion was present in large excess it was possible to treat the experimental data by plotting $\log(V_{\infty} - V)$ vs. time, where V is the volume of silver nitrate used at time t and V_{∞} is the amount at infinite time. After an induction period, these pseudo first order plots usually were fairly linear without too much scattering; an example is shown in Fig. 1. The second order rate constants, k' , that were calculated from the slopes are shown in Tables I and II.

Discussion

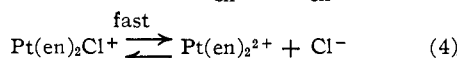
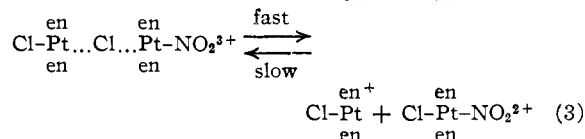
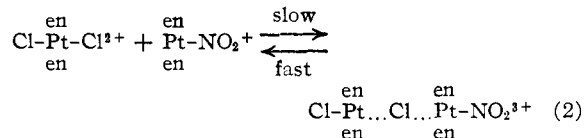
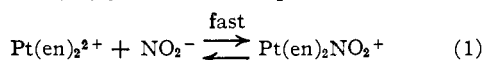
Inspection of the data from the *trans*-[Pt(en)₂Cl₂]²⁺ runs in Table I reveals several interesting features. The most important is that the observed second order rate constants are a function of the initial concentration of the platinum(IV) complex when there is no platinum(II) present. To check whether this was a consequence of small amounts of platinum(II) being present as impurities (the platinum(IV) salts were prepared by chlorination of the analogous platinum(II) complexes), several runs were made after treating the platinum(IV) complex with an oxidizing agent.⁹ In every case there was no change in the observed rate constants. Also of interest was the appearance of an induction period of from 1 to 2.5 hr. which had previously been observed by Musket.⁵ This too was unaffected by treatment with permanganate or ceric ion. Most of the runs were

(9) Upon adding nitrite ion the excess oxidizing agent is destroyed.

made in the absence of acid to avoid complications due to the decomposition of nitrous acid.

With the addition of small amounts of platinum(II) to the reaction mixture, the results changed dramatically. The pseudo first order plots were quite linear and showed no induction period. The rate increased with increasing platinum(II) concentration. As the concentration of the reagents were varied it became clear that the catalyzed reaction was first order in platinum(II), platinum(IV) and nitrite ion. Similar results were obtained with *cis*- and *trans*-[Pt(NH₃)₄Cl₂]²⁺ and *trans*-[Pt(en)₂Cl₂]²⁺, the latter ion being most extensively studied.

The catalysis by platinum(II) and the form of the rate law is identical with the behavior shown by a large number of other substitution reactions of chloro complexes of platinum(IV).^{8,10,11} The mechanism for the catalytic reaction then can be written in the same way as for the examples studied earlier. Using *trans*-[Pt(en)₂Cl₂]²⁺ catalyzed by [Pt(en)₂]²⁺ as an example, it would be



That two chlorides are not released and a dinitro complex formed, may be due to an unusual stability of the chloronitro complex compared to the dinitro. A more likely explanation is that a nitro bridged intermediate,¹² which is needed by this mechanism to form a dinitro product, has a much smaller tendency to form.

The product of reaction between *trans*-[Pt(en)₂Cl₂]²⁺ and nitrite ion in the absence of platinum(II) is also the chloronitro complex. This suggests that the same catalytic mechanism is operating since a simple substitution reaction would be expected to give a dinitro product eventually. In all runs, with or without platinum(II), even long standing failed to release more than one mole of chloride ion per mole of dichloro complex. In the case of samples not containing added platinum(II), a few per cent. excess chloride ion was found. This, however, was accounted for by the appearance of 5-10% of platinum(II) after times corresponding to infinity on the scale for which kinetic studies were made.¹³

(10) F. Basolo, P. H. Wilks, R. G. Pearson, R. G. Wilkins, *J. Inorg. Nuclear Chem.*, **6**, 161 (1958).

(11) F. Basolo and R. Johnson, *ibid.*, **13**, 36 (1960).

(12) We have called the bridged species shown in equations 2 and 3 an intermediate, for reasons discussed in ref. 8. It could equally well be an activated complex.

(13) Platinum(II) was determined by permanganate titration after destroying the nitrite ion with sulfamic acid. Platinum(II) in small

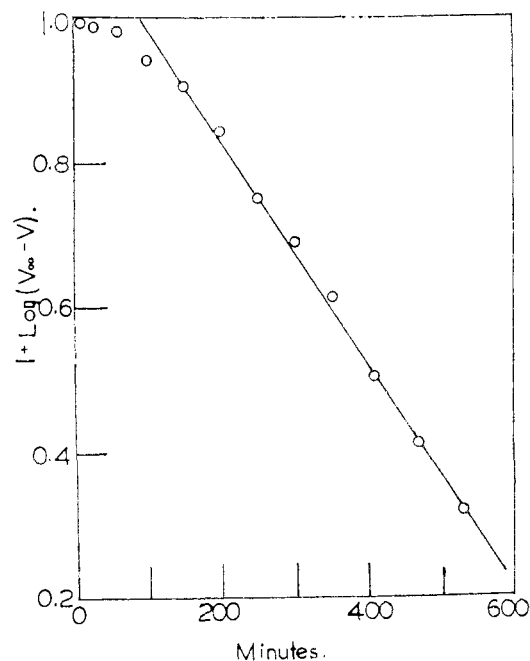
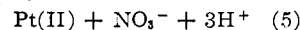


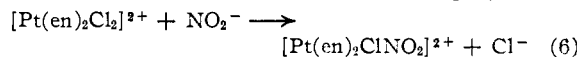
Fig. 1.—Pseudo-first order plot; [Pt(en)₂Cl₂]²⁺ = 0.005 M, [NO₂⁻] = 0.200 M.

The oxidation-reduction potential for the over-all Pt(IV) + HNO₂ + H₂O

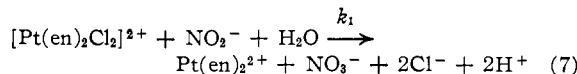


reaction is 0.4 to 0.8 volt for E^0 , the value depending on the groups coordinated to platinum.¹⁴ This indicates that nitrite ion readily can reduce platinum(IV) to platinum(II). It is also known⁴ that excess nitrous acid can oxidize platinum(II) complexes to a dinitro complex of platinum(IV). Tables I and II show that adding small amounts of acid (10% of the nitrite ion) has little effect on the rate when no platinum(II) is added or when only small amounts are added. However, if larger amounts of platinum(II) are added, nitrous acid does cause a large drop in rate, presumably by oxidizing the divalent platinum.

In view of all of the above observations, it seems logical to assume that the reaction between a chloro complex of platinum(IV) and nitrite ion to produce a nitro complex is a two stage process in



which the first step is reduction to platinum(II)



of some of the original complex. This platinum(II) then causes a catalyzed reaction of the platinum(IV) with nitrite ion according to equations 1 to 4, and with an over-all rate constant k_2 .

That this scheme can explain the observed results can be shown by deriving the rate law. By com-

amounts always was found during the kinetic runs as well, but the analyses were not reliable.

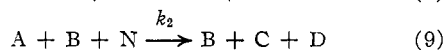
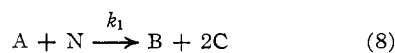
(14) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, New York, N. Y., 1952.

TABLE II
RATE CONSTANTS FOR NITRITE SUBSTITUTION IN CHLOROAMMINEPLATINUM(IV) COMPLEXES^a AT 50° AND WITH ADDED Pt(II)

[Pt(IV)], M	[Pt(II)], M	[NaNO ₂], M	[NaClO ₄], M	k' (M ⁻¹ min. ⁻¹)	k ₂ c (M ⁻² min. ⁻¹)
0.0048	0.1 × 10 ⁻⁴	0.200	0.020	2.12 × 10 ⁻²
.0046 ^d	0.1 × 10 ⁻⁴	.200	...	1.72 × 10 ⁻²
.0050	0.55 × 10 ⁻⁴	.200	.020	3.39 × 10 ⁻²	6.18 × 10 ²
.0050	1.00 × 10 ⁻⁴	.200	.020	6.03 × 10 ⁻²	6.03 × 10 ²
.0050 ^{d,e}	1.00 × 10 ⁻⁴	.200	...	2.27 × 10 ⁻²
.0050	2.00 × 10 ⁻⁴	.200	.020	12.0 × 10 ⁻²	6.00 × 10 ²
.0047	4.00 × 10 ⁻⁴	.180	.040	23.5 × 10 ⁻²	5.86 × 10 ²
.0047	5.00 × 10 ⁻⁴	.200	.020	30.4 × 10 ⁻²	6.08 × 10 ²
.0048	6.00 × 10 ⁻⁴	.150	.070	37.8 × 10 ⁻²	6.30 × 10 ²
.0094	1.00 × 10 ⁻⁴	.200	.005	6.10 × 10 ⁻²	6.10 × 10 ²
.0144	1.00 × 10 ⁻⁴	.190	...	6.05 × 10 ⁻²	6.05 × 10 ²
.0047	4.00 × 10 ⁻⁴	.100	.120	23.6 × 10 ⁻²	5.89 × 10 ²
[Pt(NH ₃) ₄ Cl] ³⁺ f					
.0025	2.5 × 10 ⁻⁴	.200	.020	No Cl ⁻ in 2 weeks	
.0025	2.5 × 10 ⁻³	.200	.012	t = 80°, no Cl ⁻ in 3 days, ~20% re-lease in 4 weeks	
cis-[Pt(NH ₃) ₄ Cl] ²⁺ f,g					
.0025	0.0020	.200	.020	2.43 × 10 ⁻⁴	1.22 × 10 ⁻¹
.0030	.0025	.200	.020	3.23 × 10 ⁻⁴	1.29 × 10 ⁻¹
trans-[Pt(NH ₃) ₄ Cl ₂] ²⁺ f,g					
.0025	2.0 × 10 ⁻⁴	.200	.027	3.93 × 10 ⁻²	1.96 × 10 ²
.003	2.0 × 10 ⁻⁴	.200	.026	3.82 × 10 ⁻²	1.91 × 10 ²
.003	2.0 × 10 ⁻⁴	.200	.026	3.92 × 10 ⁻²	1.96 × 10 ²
.003	4.0 × 10 ⁻⁴	.180	.046	7.83 × 10 ⁻²	1.96 × 10 ²
.003	5.0 × 10 ⁻⁴	.150	.076	10.32 × 10 ⁻²	2.06 × 10 ²
.003	6.0 × 10 ⁻⁴	.150	.076	11.00 × 10 ⁻²	1.83 × 10 ²

^a All platinum salts are perchlorates unless otherwise noted, all runs made at $\mu = 0.235$. ^b Pt(II) added as [Pt(en)₂](ClO₄)₂. ^c $k_2 = k'/[Pt(II)]$. ^d Perchloric acid added; [HClO₄] = 0.020 M. ^e Potassium permanganate added to dissolve complexes before reaction. ^f Pt(II) added as [Pt(NH₃)₄](ClO₄)₂. ^g Pt(IV) used as the nitrate salt.

binning equations 3, 4 and 5 and using abreviations one obtains the following schematic mechanism.



where A is [Pt(en)₂Cl₂]²⁺, B is [Pt(en)₂]²⁺, N is the nitrite and C is the chloride ion. Making note of the fact that the nitrite ion was present in large excess, it is possible to write differential equations using the relationships $k_1' = k_1N$ and $k_2' = k_2N$.

$$dA/dt = -k_1'A - k_2'AB \quad (10)$$

$$dB/dt = k_1'A \quad (11)$$

Dividing (10) by (11) and integrating (assuming no B at zero time) results in

$$A = A_0 - B - 1/2k_2'/k_1'B^2 \quad (12)$$

Substituting (12) into (11) and again integrating yields

$$\frac{1}{r} \ln \frac{(KB + 1 + r)(1 - r)}{(KB + 1 - r)(1 + r)} = k_1't \quad (13)$$

where

$$r = (2A_0k_2'/k_1' + 1)^{1/2} \text{ and } K = k_2'/k_1' \quad (14)$$

Expanding and rearranging (13) and making use of the fact that $r \gg 1$ and hence $r^2 = 2A_0k_2'/k_1'$ (since experimentally k_2' is much larger than k_1') gives

$$B = \frac{2A_0(e^{rk_1't} - 1)}{r(e^{rk_1't} + 1)} \quad (15)$$

From the stoichiometry, $A_0 = A + B + C$, it can be shown that

$$C = 1/2k_2'/k_1'B^2 \quad (16)$$

Substituting (16) and (14) into (15) and rearranging extensively finally results in

$$\log \frac{1 + (C/A_0)^{1/2}}{1 - (C/A_0)^{1/2}} = \frac{1}{2.303} r k_1' t \quad (17)$$

Equation 17 states that a plot of the left hand side vs. time should be a straight line with zero intercept. Such plots are indeed found; two examples are shown in Fig. 2. Deviations occur only at 80-90% completion. The slopes of these lines are given by $rk_1'/2.303$ which can be rearranged to give

$$k_1 = \frac{(2.303 \times \text{slope})^2}{2A_0k_2N^2} \quad (18)$$

The value of k_2 to be used in calculating k_1 can be taken from runs made in which the first slow step of the mechanism is by-passed by adding platinum(II). These values are found in Table II. The last column of Table I shows that over a wide range of concentrations of platinum(IV) complex, nitrite ion and acid the values of k_1 calculated from equation 18 are fairly constant. That this mechanism and the resulting equations can reproduce the experimental data over most of the reaction is shown by Fig. 3.

The only chloroammineplatinum(IV) complex investigated that did not appear to fit this mechanism was *trans*-[Pt(tetramine)₂Cl₂]²⁺. With this complex 1.5-2.0 chloride ions per ion of complex were released. Pseudo first order plots were linear with no induction period but there was more

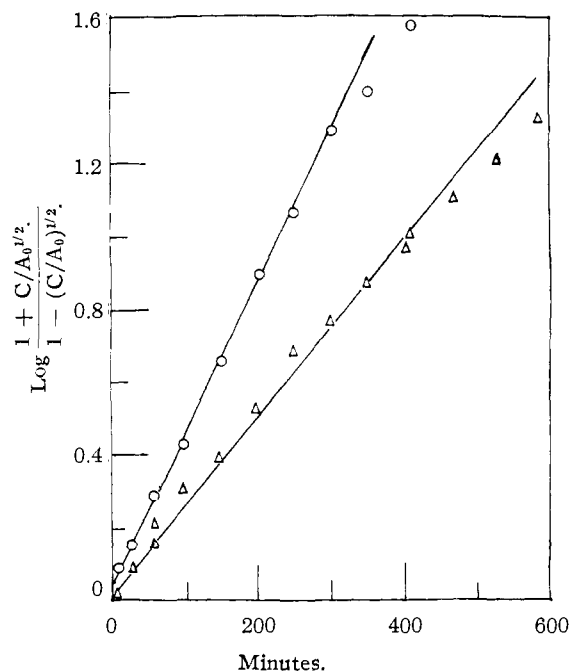


Fig. 2.—Plot of left-hand side of equation (15) vs. time; Δ , $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+} = 0.0050 M$, $[\text{NO}_2^-] = 0.200 M$; \circ , $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+} = 0.019 M$, $[\text{NO}_2^-] = 0.175 M$.

scatter to the data. Variation of the initial amount of platinum(IV) appeared to have little effect on the observed second order rate constants while the addition of platinum(II) in the form of $[\text{Pt}(\text{tetra-} \text{meen})_2]^{2+}$ or $[\text{Pt}(\text{en})_2]^{2+}$ had no catalytic effect. Runs with varying amounts of acid resulted in similar rate constants, although somewhat lower than runs made with no acid present. Most significant, however, were the results of titrations with permanganate. These titrations showed that most, if not all, of the release of chloride ion was due to the reduction of platinum(IV) to platinum(II). Thus it appears that there is essentially no substitution with this particular complex.

Such a result is completely consistent with the postulated mechanism. Because of the bulkiness of the C-methyl groups on the chelate rings, the $[\text{Pt}(\text{tetra-} \text{meen})_2]^{2+}$ cannot get close enough to form a bridged complex through the chloro group. Therefore the bridged mechanism is not available to this system and only reduction can take place. The mechanism for this particular process however is not clear from this investigation and needs further study. That substitution does not take place is also consistent with the observation that there is no chloride exchange with this complex.⁸

From the first order plots for $[\text{Pt}(\text{tetra-} \text{meen})_2\text{Cl}_2]^{2+}$ pseudo-first order rate constants were obtained, which on division by the nitrite ion concentration gave a value of k_1 equal to about $6 \times 10^{-3} M^{-1} \text{min}^{-1}$. If this can be identified with the rate of reduction as in equation 7, then it is of interest that this is some ten times faster than k_1 for $\text{trans-}[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$. Steric strain in the alkylated complex evidently gives rise to a tendency to go to a state of reduced coordination number.

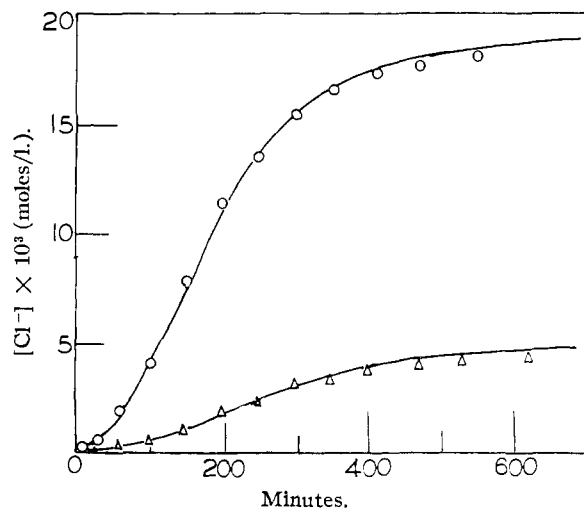


Fig. 3.—Calculated and experimental $[\text{Cl}^-]$ vs. time: —, calculated from equations 14 and 13; Δ , experimental points, $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+} = 0.005 M$, $[\text{NO}_2^-] = 0.200 M$; \circ , experimental points, $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+} = 0.019 M$, $[\text{NO}_2^-] = 0.175 M$.

Further comparison of the chloride exchange data reported by Basolo, Morris and Pearson⁸ and the present nitrite substitution results indicates a close similarity between the two reactions. Although there is a 25° difference in the temperatures of the measurements inspection of the results listed in Table III shows a striking correlation between the two sets of constants. Indeed, a log-log plot of these constants is linear with a slope of almost unity. The fact that the chloride exchange is somewhat faster may be due to the inclusion of the formation constant of the five-coordinate intermediate of reaction 3 in k_2 . However, it would be expected that this intermediate would be more stable for nitrite ion than for chloride ion since nitrite ion is a good nucleophilic reagent for platinum(II).¹⁵ A more likely explanation is that re-

TABLE III

RATE CONSTANTS FOR THE PLATINUM(II) CATALYZED REACTION

Platinum complex	Nucleophile	Temp. (°C.)	$k(M^{-2} \text{min}^{-1})^a$
$\text{trans-}[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$	NO_2^- ^b	50	6.07×10^2
$\text{trans-}[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$	Cl^*	25	9.1×10^2
$\text{cis-}[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$	NO_2^- ^c	50	1.26×10^{-1}
$\text{cis-}[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$	Cl^*	25	1.6×10^{-1}
$\text{trans-}[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$	NO_2^- ^d	50	1.95×10^2
$\text{trans-}[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$	Cl^*	25	2.0×10^2
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^{+3}$	NO_2^- ^e	50	Very slow ^e
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^{+3}$	Cl^*	25	3.9×10^{-2}
$\text{trans-}[\text{Pt}(\text{tetra-} \text{meen})_2\text{Cl}_2]^{2+}$	NO_2	50	No substitution
$\text{trans-}[\text{Pt}(\text{tetra-} \text{meen})_2\text{Cl}_2]^{2+}$	Cl^*	25	No exchange

^a Chloride exchange results are from ref. 8. ^b $k_1 = 1.39 \pm 0.09 \times 10^{-4} M^{-1} \text{min}^{-1}$. ^c $k_1 = 1.5 \times 10^{-4}$. ^d $k_1 = 6.0 \pm 0.3 \times 10^{-4}$. ^e No chloride released in two weeks, at 80° there was some after one week. ^f k_1 is approximately $60 \times 10^{-4} M^{-1} \text{min}^{-1}$.

(15) R. G. Pearson, H. B. Gray and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

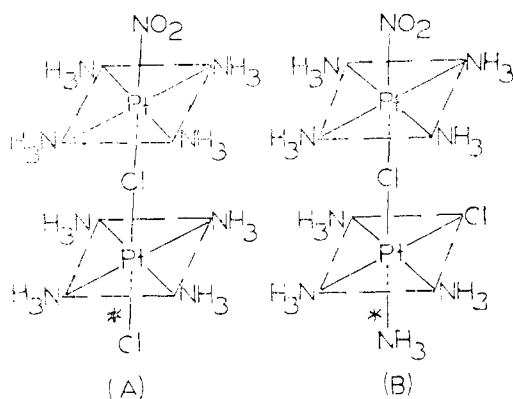


Fig. 4.—Bridged intermediates proposed to explain nitrite substitution in *trans*- (a) and *cis*-[Pt(NH₃)₄Cl₂]²⁺ (b).

action 2 is readily reversible. Thus the ratio of the reverse rate constant of (2) to the forward constant of (3) may be rather large. In the isotope exchange reaction this ratio is necessarily unity.

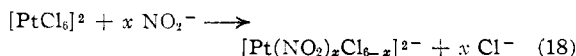
Reasoning from the chloride exchange results⁸ leads one to predict that the nitrite reaction with [Pt(NH₃)₅Cl]³⁺ would have a k_2 of about $3 \times 10^{-2} \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$, *i.e.*, about 1/20,000 as fast as the nitrite reaction with *trans*-[Pt(en)₂Cl₂]²⁺. However, on the basis of the postulated mechanism with bridge formation taking place through the chloro group, one would predict that *trans*-[Pt(NH₃)₄NO₂Cl]²⁺ would be formed and that ammonia would be released and not chloride ion. All that can be stated from our results is that the reaction is certainly very slow as predicted by the mechanism. An attempt to make a run on a preparative scale to isolate *trans*-[Pt(NH₃)₄NO₂Cl]⁺ failed because of extensive reduction (about 30%) and because both dichloro and chloronitro products seemed to be formed. The observation that [Pt(NH₃)₄Cl₂]²⁺ is formed during the reaction has been noted before by Basolo, Morris and Pearson⁸ and by Rubinstein¹⁶ who reported that, in the presence of chloride ion, catalytic amounts of [Pt(NH₃)₄]²⁺ will convert [Pt(NH₃)₅Cl]³⁺ in high yield to *trans*-[Pt(NH₃)₄Cl₂]²⁺. Because of this and the reduction by nitrite the reaction is certainly more complex than those of the other chloroamineplatinum(IV) complexes studied.

Examination of Table III shows that the rate of nitrite substitution (k_2) of *trans*-[Pt(NH₃)₄Cl₂]²⁺ is about 1,500 times faster than that for the *cis* isomer. This difference is roughly the same as that found in the chloride exchange measurements (see Table III). A probable reason for this may be seen by considering the bridged intermediates for these two complexes. For the *trans* isomer in Fig. 4A reduction of the platinum(IV) complex to platinum(II) by the bridged mechanism requires the rupture of the Pt-Cl bond opposite the chloro group, as represented by the asterisk. However in the *cis* isomer this process requires the cleavage of a Pt-N bond (asterisk in Fig. 4B), since ammonia is opposite the chloro bridge. Since

the Pt-N bond is stronger than the Pt-Cl bond, it follows that the rate with the *cis* isomer will be slower than with the *trans* isomer. This is completely in agreement with the observation that in such systems the *cis* isomer is more difficult to reduce than is the *trans* form.¹⁶

Although a chloronitroamineplatinum(IV) complex was not isolated and completely characterized during this study there is sufficient evidence in support of such products. In all of the runs, except with *trans*-[Pt(tetrameen)₂Cl₂]²⁺ which underwent reduction, only one chloride ion was ever observed to be released if the reactions were carried out in the dark. This had previously been reported by Wilks⁴ and Musket.⁵ Such an observation argues strongly for a chloronitro complex, since on the basis of the bridge mechanism it is impossible to form a dinitro complex as mentioned previously. From the preparative point of view salts of such complexes as *trans*-[Pt(en)(NH₃)₂ClNO₂]²⁺, *trans*-[Pt(NH₃)₃ClClNO₂]⁺, *trans*-[Pt(NH₃enCl)ClNO₂]⁺, *trans*-[Pt(NH₃enNO₂)ClNO₂]⁺ and *trans*-[Pt(a en b)ClNO₂]⁺ where a is methylamine or ethylamine and b is Cl or NO₂ have been isolated.⁵ In every case the chloronitro complex was prepared by treating nitrite ion with the corresponding *trans* dichloro complex, often at high temperatures and for long periods of time. These results can be completely accounted for on the basis of the bridge mechanism.

Recently Chernyaev, Nazarova and Miranova¹⁷ reported their results of a study of the reaction of nitrite ion with chloroplatinate(IV) ion



They were able to prepare chloronitro complexes with x from 1 to 5 but were not able to isolate the hexanitro compound. To explain their results they proposed that platinum(IV) was reduced to platinum(II) and direct substitution of from 1 to 4 chlorides by nitrite took place. These complexes then were oxidized to platinum(IV) with two chloride ions taking up *trans* positions in the complexes. They then proposed that nitrite ion replaces one of the chlorides in the Cl-Pt-Cl axis to give the final products. The authors emphasized that their experimental results showed that chlorine was not replaced directly by the nitro groups in chloroplatinate(IV). This conclusion is precisely the same as the one arrived at in this study, namely, that nitrite substitution in chloroamineplatinum(IV) complexes proceeds through a complex reduction-oxidation mechanism involving a bridge between the reduced and oxidized forms of platinum. Thus the proposed bridge mechanism can be used to explain completely why only one chloride ion is replaced in the last step of the chloroplatinate(IV)-nitrite ion reaction.

Acknowledgment.—We wish to acknowledge the support of the U. S. Atomic Energy Commission Contract At (11-1) 89-Project No. 2 and the National Science Foundation grant NSF-G5104.

(16) A. M. Rubinstein, *U.R.S.S. Compt. rend.*, **28**, 55/58 (1940); *Izvst. Plat.*, **20**, 53/53, 56 (1947).

(17) I. I. Chernyaev, L. A. Nazarova and A. S. Miranova, *Russ. J. Inorg. Chem.*, **4**, 340 (1959).