

## 95. *Interchange of Hydrogen Isotopes with Complex Salts. Part II. Kinetics of the Interchange with Platinous and Palladous Tetrammines.*

By J. S. ANDERSON, H. V. A. BRISCOE, L. H. COBB, and N. L. SPOOR.

Experiments on the interchange of hydrogen isotopes between water and complex ions have been extended to tetrammino-platinous and -palladous chlorides. The rate of interchange with amines of different metals decreases in the order  $\text{Co} > \text{Pt} > \text{Pd}$ , and runs parallel to the stability of the complex ions. Tetrammino-palladous chloride undergoes interchange by a complex mechanism; in addition to interchange by the acid dissociation mechanism discussed in Part I (preceding paper), it reacts in acid solution by reversible dissociation of ammonia from the complex. The bearing of the results upon the general theory of complex salts is discussed.

IN Part I we deduced from the kinetics of the interchange of hydrogen between stable cobaltamines and water that the ammine complex must undergo an acid dissociation of the type  $\text{M} \leftarrow \text{NH}_3 \rightleftharpoons \text{M} - \text{NH}_2^- + \text{H}^+$ . If this be so, other types of ammine, and amines of metals other than cobalt, should be worth investigation from the same viewpoint, since the kinetic velocity constants might be correlated, as we pointed out, with the stability of the amines. We now discuss the results obtained with tetrammino-platinous and -palladous complexes, which accord in general with the ideas developed in Part I. A comparison of the palladous and platinous compounds is of particular interest in view of the gradation in ammine-forming ability in the nickel-palladium-platinum triad of metals, and the interchange experiments, as will be seen, not only afford a correlation of the "acid strength" of the complex with its general stability, but shed light also on the mechanism of breakdown of the amines, and on the transition between the stable "luteo-complex" type and the dissociable ammoniates.

### EXPERIMENTAL.

The velocity of the exchange reactions was determined by an experimental method generally similar to that described in Part I. The "heavy" amines having been prepared, the interchange of hydrogen for deuterium was carried out in phosphate buffer solutions of suitable pH.

Tetramminoplatinous chloride was prepared by heating platinous chloride, free from platinic chloride, with aqueous ammonia at  $80^\circ$  for 12 hours. The solution was filtered from a little undissolved platinous chloride, and evaporated to obtain the dihydrate,  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ . This was further purified by crystallisation, made "heavy" in the manner previously described, and then dehydrated in a vacuum at  $100^\circ$ .

Tetramminopalladous chloride monohydrate,  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , was similarly obtained by the action of aqueous ammonia in excess on palladous chloride. The ammine was separated by concentration of the solution and by fractional precipitation with alcohol, and was finally recrystallised from dilute ammoniacal alcohol (Found: Pd, 40.4, 40.5. Calc.: Pd, 40.45%). The "heavy" salt was dehydrated in a vacuum over quicklime.

Potassium chloro-platinite and -palladite respectively were used as precipitants in the interchange experiments for the foregoing two salts; these precipitants, by virtue of their high solubility and rapid rate of dissolution, gave immediate quantitative precipitation of Magnus's green salt,  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ , and the corresponding pink  $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$  respectively, and thus arrested the interchange completely. The solution was then filtered, and the water was purified before density determination, in the manner already described.

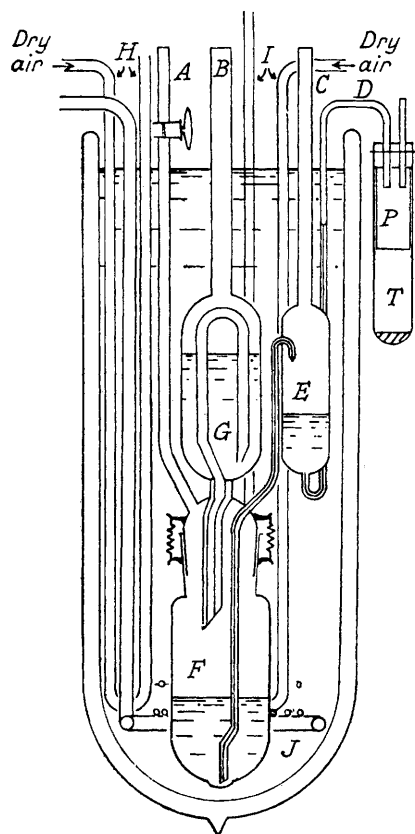
The work on tetramminoplatinous chloride comprised series of measurements on the relation of the rate of interchange to the total concentration of ammine (in which we were at that time chiefly interested) at  $20^\circ$  and constant hydrogen-ion activity; also on the rate of interchange in solutions of constant ammine concentration and constant pH at  $0^\circ$ ,  $7^\circ$ ,  $14^\circ$ , and  $20^\circ$ .

With tetramminopalladous chloride, for reasons discussed later, we made a detailed study of the influence of hydrogen-ion concentration on the rate of interchange, and extended these measurements into the regions of low hydrogen-ion activity, where the interchange reaction becomes very rapid. For this purpose, extensive series of measurements were made at  $0^\circ$ , and the technique was refined to permit of the study of reactions having a time of half-change of only 12 mins. at  $0^\circ$ . Owing to the high temperature coefficient of the reaction, it was imperative that any possibility of a change of temperature of the solution during sampling and precipitation should be avoided. The urgency of this consideration is apparent when it is borne in mind that the fastest reaction studied ( $t_{1/2} = 13$  mins. at  $0^\circ$ ) would have a time of half-change of only 30 secs. at  $20^\circ$ . The solutions were therefore made up, sampled, and precipitated in the apparatus shown in Fig. 1, which could be immersed completely in the Dewar vessel calorimeter.

The heavy tetramminopalladous chloride was weighed into the reaction vessel F, which was attached to the rest of the apparatus by a ground joint. The apparatus was placed in a deep, cylindrical Dewar vessel, the tubes A, and B or C were stoppered, and the whole was packed around with clean crushed ice and distilled water. The buffer solution (30 c.c.), already cooled nearly to  $0^\circ$ , was then pipetted through B into the siphon chamber G, whereupon A or B and C

were connected to the duplicate tube systems H and I, through which dry, carbon dioxide-free, pre-cooled air could be blown into the apparatus. Attainment of thermal equilibrium was ensured by allowing the apparatus to stand for an hour, and the reaction was then started by blowing into B with the tap A open: the buffer solution then siphoned over into F, the delivery taking about 4 secs. With B closed and A open, the solution was stirred by blowing air through it by way of C and E. In order to take a sample, the automatic pipette E was filled by blowing through A. The volume of this sampling pipette was 4 c.c., but since delivery into E took place at about 1 c.c. per sec., smaller samples could be judged by blowing for the requisite time. By blowing through A and C together, the sample was discharged through the light, narrow-bore tube D into the test-tube T containing the precipitant. In order to avoid errors due to splashes upon the upper part of the test tube that was not cooled in ice, a roll of filter-paper P was fitted inside the upper two-thirds of T. This could subsequently be removed and rejected. Delivery into T occupied about 4 secs.; the test-tube was then removed from the apparatus without removing it from the ice-bath; the filter-paper P was removed, and the test-tube stoppered and vigorously shaken. Precipitation was complete within about 6 secs. after the delivery of the sample, during the whole of which time the solution was kept at 0°. During the whole of the exchange reaction, the contents of the Dewar vessel were stirred occasionally with air from the bubbler tube J; and it was shown that the temperature was constant within about 0.02°.

FIG. 1.



### Results and Discussion.

(i) *Tetramminoplatinous Chloride.*—(a) *Dependence of velocity of interchange upon concentration of ammine.* Various weights of the 81% heavy salt were dissolved in 30 c.c. of phosphate buffer solution, originally made up to pH 5.91, at 20°. The results are summarised in Table I. As found with the cobaltammines,  $\log k$ , when plotted against the logarithm of the concentration of ammine, approximates to a straight line; from the slope of this,  $k$  is proportional to  $[\text{ammine}]^{-0.21}$ . As remarked in Part I, this anomalous dependence upon the concentration of the ammine at once finds its explanation when combined with our later measurements of the activity of hydrogen ions in phosphate buffer solutions, in the presence of tetramminoplatinous chloride. Over the same range of ammine concentrations, the effective  $[\text{H}^+]$  varies approximately as  $[\text{ammine}]^{0.21}$ , whilst the rate of interchange varies inversely as the activity of the hydrogen ion. From the later pH measurements, the true  $[\text{H}^+]$  in each of the experiments in the series has been calculated (Col. 4, Table I), and thence the velocity constants in Col. 6. These values, and values of  $k$  in subsequent tables, are obtained by multiplying the observed first-order velocity constants by  $[\text{H}^+]$ . Within the limits of experimental uncertainty, the velocity of interchange is independent of the concentration of ammine.

TABLE I.

Expt.	Concn. of ammine, g./l.	$t_4$ , mins.	True pH.	$[\text{H}^+] \times 10^6$ .	$k \times 10^8$ .	Expt.	Concn. of ammine, g./l.	$t_4$ , mins.	True pH.	$[\text{H}^+] \times 10^6$ .	$k \times 10^8$ .
P1	48.3	35	5.54 <sub>1</sub>	2.88	5.70	P3	12.0	26.5	5.68 <sub>2</sub>	2.08	5.43
P2	24.0	31.5	5.61 <sub>0</sub>	2.45	5.39	P4	6.1	22.5	5.74 <sub>7</sub>	1.79	5.52
Mean 5.49											

(b) *The temperature coefficient of the reaction.* A standard weight (0.72 g.) of 81% heavy salt was dissolved in 30 c.c. of buffer solution, of original pH 5.91 (true pH in presence of that concentration of ammine = 5.61<sub>0</sub>). Interchange experiments were carried out at 0°, 7°, 14°, and 20°, with the results collected in Table II. From the variation of  $\log k$  with temperature, the critical increment at constant pH is calculated as 25,200 cal.

TABLE II.

Expt.	Temp.	$t_4$ , mins.	$k \times 10^8$ .
P2	20°	31.5	5.40
Q2	14	80	2.13
Q3	7	250	0.681
Q4	0	820	0.207

$k_{20^\circ}/k_{10^\circ} = 4.76$   
 $k_{10^\circ}/k_{0^\circ} = 5.47$   
 $E = 25,200 \text{ cal.}$

(ii) *Tetramminopalladous Chloride.*—(a) *Dependence of the velocity of interchange upon the concentration of the ammine.* The velocity of interchange of 78.8% heavy tetramminopalladous chloride was measured at 0° in  $m/15$ -phosphate buffer solution of pH 7.168,  $[\text{H}] = 0.679 \times 10^{-7}$ , complex salt concentrations varying from 0.0124 to 0.0955 g.-mol./l. being used. Under these conditions it was estimated that about 97% of the interchange proceeded *via* the true ammine type interchange (see Table V) so that the results obtained are

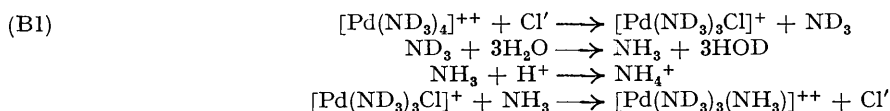
comparable with those for the cobalt and platinum amines studied. Detailed results, given in Table III, show that in this case the measured first-order velocity constant of the interchange reaction is nearly independent of the initial concentration of complex salt. This was to be expected, for owing to the much higher ionic strength of the buffer mixture of pH 7.168 ( $I = 0.160$ ) used in these experiments than that of pH 5.906 ( $I = 0.080$ ) used with tetramminopalladous chloride, salt effects should be correspondingly less. In agreement with this, electrometric measurements showed that the change in pH of the buffer mixture on addition of the tetramminopalladous chloride used in the interchange experiments up to a concentration of 0.04M was almost negligible.

TABLE III.

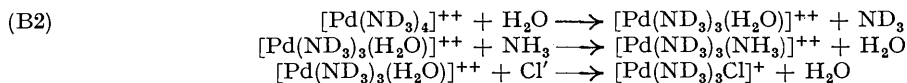
Expt.	Concn., g.-mol./l.	$k_{\text{obs.}} \times 10^3$ , min. <sup>-1</sup> .	$t_{1/2}$ , mins.	$k \times 10^{10}$ .	Expt.	Concn., g.-mol./l.	$k_{\text{obs.}} \times 10^3$ , min. <sup>-1</sup> .	$t_{1/2}$ , mins.	$k \times 10^{10}$ .
12	0.0124	14.4	48.1	9.78	15	0.0674	14.6	46.5	9.91
13	0.0243	14.1	49.0	9.57	16	0.0955	16.1	43.0	10.93
14	0.0486	13.7	50.0	9.30		Mean	14.6	47.5	9.90

(b) *The effect of hydrogen-ion concentration on the rate of interchange.* Table IV summarises the results of measurements made at 20°, 10°, and 0° on 0.0673M-solutions of 78.8% heavy tetramminopalladous chloride in various M/15-phosphate buffer mixtures of pH 5.288 to 7.731. Runs 1, 2, and 3 show that, in any case, the rate of interchange is not a linear function of the hydrogen-ion concentration: for a fourfold increase in hydrogen-ion concentration, from pH 5.91 to pH 5.29, the time of half-change increases by only 30%. This behaviour is in contrast with the results obtained with the cobaltamines, and the most immediate explanation would be the possibility of interchange by some mechanism peculiar to the palladous ammine. Consonant with this hypothesis was the observation that, whereas in buffer solutions of pH 6.8—7.0 tetramminopalladous chloride dissolves to give a completely colourless solution, yet in buffers of pH 5.3—5.9 the solutions are yellow. Moreover, from the most acid solution used (pH 5.29) there separated a small amount of a pale yellow, insoluble solid, which was identified as  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ . From its colour and reaction with potassium iodide, we believe the diammine chloride prepared under these very mild conditions to be the *cis*-compound, first isolated by Grünberg and Schulman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 5, 218). This, however, was not unambiguously established.

It is clear that, in the more acid solutions investigated (pH 5.3—5.9), the degradation of the tetrammine complex to the diammine chloride is incipient. Hence, deuterium may be transported from the heavy ammine to the solvent not only by the typical ammine mechanism (A),  $[\text{Pd}(\text{ND}_3)_3\text{ND}_3]^{++} \rightleftharpoons [\text{Pd}(\text{ND}_3)_3\text{ND}_2]^+ + \text{D}^+$ , discussed in relation to the cobaltamines, but also through the direct degradative transfer of ammonia from the ammine complex to the solution. Two possible mechanisms suggest themselves, according as a chloro-ammine (B1) or an aquo-ammine (B2) is the immediate product of substitution. In either case, the formation of a triammine complex, as shown, will presumably precede the formation of diammine, this second stage being very incomplete at the hydrogen-ion concentrations under consideration.



Alternatively,

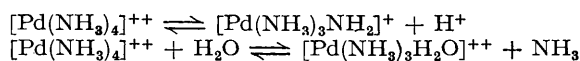


That the degradation proceeds by the scheme (B2) appears probable when the stability and solubility of the mixed palladous amines are taken into account. Furthermore, King (J., 1938, 1338) has shown that the platinum diammines may give rise to aquo-ammines in solution, and it has been repeatedly emphasised (*e.g.*, Drew, J., 1934, 57) that the halogen, particularly in the *cis*-diammine chloride, is more reactive in solution than would be expected.

Since, according to both schemes, (B1) and (B2), the isotope interchange depends on the dynamic equilibrium between tetrammine and triammine, which is displaced by conversion of ammonia molecules into ammonium ions, according to either scheme of reactions, the velocity of interchange of deuterium and hydrogen by this degradative mechanism would be proportional to the hydrogen-ion concentration. Hence the total rate of interchange will be given by the sum of dissociative and degradative mechanisms, *i.e.*, we may define a total velocity constant by

$$k = k_1[\text{H}^+] + k_2/[\text{H}^+].$$

This is a quadratic expression in  $[\text{H}^+]$ , and it may at once be seen by differentiation that  $k$  passes through a minimum. In terms of the reaction mechanisms, at that hydrogen-ion concentration where the two equilibria



furnish equivalent amounts of hydrogen ion and ammonia, the rate of the reaction is independent of small changes in the hydrogen-ion concentration.

At sufficiently low hydrogen-ion concentrations, the first reaction ( $\propto k_1[\text{H}^+]$ ) should be effectively suppressed, and interchange should occur only by the typical ammine mechanism. It was with this in mind that we extended the measurements to solutions of comparatively high pH, where a linear relation between rate of interchange and hydrogen-ion concentration might be expected. As may be seen from Fig. 2, this is borne out; up to a concentration of  $[\text{H}^+] = 0.8 \times 10^{-7}$  the curve is linear. Above that acidity, the decomposition of the complex becomes appreciable, and the interchange occurs also by the degradative mechanism just considered.

TABLE IV.

Expt.	Temp.	pH.	$[\text{H}^+] \times 10^7$ .	$k_{\text{obs.}} \times 10^3$ , min. <sup>-1</sup> .	$t_4$ , mins.	$t_4$ at 0° (calc.), mins.
1	20.00°	5.288	51.5	53.9	12.9	315
2	"	5.589	25.8	58.6	11.8	288
3	"	5.906	12.4	67.0	10.4	254
4	10.00	5.589	25.8	12.5	55.4	—
5	0.00	6.643	2.28	5.76	120.0	—
6	"	6.813	1.54	7.60	91.2	—
7	"	6.979	1.05	9.81	70.7	—
8	"	7.168	0.679	14.60	47.5	—
9	"	7.381	0.416	23.8	29.1	—
10	"	7.731	0.186	52.6	13.2	—

The addition of ammonium ions to a solution of pH 6.64<sub>3</sub>, in which interchange by the degradative mechanism is marked, suppressed this mode of reaction, as might be anticipated. In Fig. 2 the point *X* represents

the value found for the time of half-change in a solution containing 1 mol. of ammonium nitrate per mol. of ammine. The point *X* falls on the linear extrapolation of the curve through the points corresponding to expts. 8, 9, and 10, representing the velocity of interchange by the typical acid dissociation of the ammine only. The deviation of the point from the linear extrapolation ( $t_4$ , calc. = 161 mins.; obs. = 162 mins.) is within the experimental error, and is of the same order of magnitude as was found for the primary salt effect of ammonium nitrate and potassium chloride on the interchange in hexaminocobaltic chloride (Part I, p. 363).

One of the two mechanisms of interchange can thus be satisfactorily isolated, and its velocity constant derived, from the experimental data. The similar quantitative evaluation of the second mechanism is less readily achieved, owing to the large amount of ancillary data requiring investigation. We have therefore been content to establish only the order of magnitude of the relevant velocity constant. From the value for the total velocity

constant given above, it may be seen that if  $[\text{H}^+]_0$  denotes the hydrogen-ion concentration at which the net velocity is a minimum (*i.e.*,  $t_4$  is a maximum), then at  $[\text{H}^+]_0$   $dk/d[\text{H}^+] = 0$ , and  $k_2 = k_1[\text{H}^+]_0^2$ . From the measured temperature coefficient and critical increment of the total reaction (runs 2 and 4, Table III), the experimental data of runs 1, 2, and 3 may be recalculated to give the times of half-change at 0°. It is clear from the plot that the run in the most strongly acid solution (run 1) is approaching the value of  $[\text{H}^+]_0$  (Fig. 2), and rough extrapolation gives  $[\text{H}^+]_0$  about  $50 \times 10^{-7}$ , with  $t_4$  about 300 mins. (A direct experimental repetition of run 2 at 0° was invalidated by an experimental error, which introduced an uncertainty of unknown magnitude in  $t_4$ .) Even if the above estimate of the maximum value of  $t_4$  be in error by 10–20%, the shape of the curve remains qualitatively the same, and the value estimated for  $[\text{H}^+]_0$  is not greatly altered. A second method of evaluating  $k_1$  is to fit the experimental data of the runs 5, 6, 7, 8, 9, and 10, at the commencement of the range where the reaction becomes composite, to the expression  $k = k_1[\text{H}^+] + 9.78 \times 10^{-10}/[\text{H}^+]$ . The best fit for these runs is given by  $k_1 = 6.26 \times 10^3$ , and the closeness of fit with the experimental data is indicated by Table V. The values of  $k_1$  relate to the interchange *via* the acid dissociation mechanism above and are thus comparable with constants derived from measurements on platinum and cobalt amines.

From the value for the total velocity constant given above, it may be seen that if  $[\text{H}^+]_0$  denotes the hydrogen-ion concentration at which the net velocity is a minimum (*i.e.*,  $t_4$  is a maximum), then at  $[\text{H}^+]_0$   $dk/d[\text{H}^+] = 0$ , and  $k_2 = k_1[\text{H}^+]_0^2$ . From the measured temperature coefficient and critical increment of the total reaction (runs 2 and 4, Table III), the experimental data of runs 1, 2, and 3 may be recalculated to give the times of half-change at 0°. It is clear from the plot that the run in the most strongly acid solution (run 1) is approaching the value of  $[\text{H}^+]_0$  (Fig. 2), and rough extrapolation gives  $[\text{H}^+]_0$  about  $50 \times 10^{-7}$ , with  $t_4$  about 300 mins. (A direct experimental repetition of run 2 at 0° was invalidated by an experimental error, which introduced an uncertainty of unknown magnitude in  $t_4$ .) Even if the above estimate of the maximum value of  $t_4$  be in error by 10–20%, the shape of the curve remains qualitatively the same, and the value estimated for  $[\text{H}^+]_0$  is not greatly altered. A second method of evaluating  $k_1$  is to fit the experimental data of the runs 5, 6, 7, 8, 9, and 10, at the commencement of the range where the reaction becomes composite, to the expression  $k = k_1[\text{H}^+] + 9.78 \times 10^{-10}/[\text{H}^+]$ . The best fit for these runs is given by  $k_1 = 6.26 \times 10^3$ , and the closeness of fit with the experimental data is indicated by Table V. The values of  $k_1$  relate to the interchange *via* the acid dissociation mechanism above and are thus comparable with constants derived from measurements on platinum and cobalt amines.

TABLE V.

Expt.	$[\text{H}^+] \times 10^7$ .	$k \times 10^3$ , min. <sup>-1</sup> , obs.	$t_4$ , mins., obs.	$k_1 \times 10^3$ , min. <sup>-1</sup> , calc.	$k_2 \times 10^3$ , min. <sup>-1</sup> , calc.	$k \times 10^3$ , min. <sup>-1</sup> , calc.	$t_4$ , mins., calc.
5	0.186	52.6	13.2	52.6	0.1	52.7	13.2
6	0.416	23.8	29.1	23.5	0.3	23.8	29.1
7	0.679	14.6	47.5	14.4	0.4	14.8	46.8
8	1.05	9.8	70.7	9.3	0.7	10.0	69.3
9	1.54	7.6	91.2	6.4	1.0	7.4	93.7
10	2.28	5.76	120	4.29	1.48	5.77	120

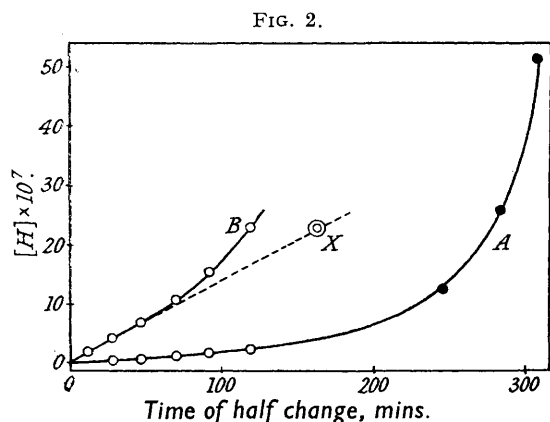


FIG. 2.

Open circles—measurements at 0°; solid circles—calculated from measurements at 20°. For curve B, the scale of the ordinates is increased tenfold.

At hydrogen-ion concentrations higher than  $2.3 \times 10^{-7}$ , however, the calculated curve turns over too rapidly, giving for  $[H^+]_0$  about  $4 \times 10^{-7}$ , and for  $t_{\frac{1}{2}}$ , 139 mins. Inclusion of a further term in the velocity constant, to take account of the second stage in the degradation reaction (triammine  $\rightarrow$  diammine) would decrease the maximum value of  $t_{\frac{1}{2}}$  still further. The discrepancy between the calculated values and the results of runs 1, 2, and 3 may, however, be subject to two sources of uncertainty. In the first place, the data of runs 1, 2, and 3 were reduced to  $0^\circ$  by a method involving the mean temperature coefficient  $k_{20^\circ}/k_{10^\circ}$ . If the temperature coefficients and critical increments of the two concurrent reactions are very different, the time of half-change so calculated may be considerably in error. Secondly, the effect of tetramminopalladous chloride on the pH of phosphate buffer solutions, in that range of pH where decomposition is incipient, has not been fully investigated. For unavoidable reasons, the effect of the palladous ammine was investigated by us only in a buffer solution of original pH 7.16, where the change in activity of the hydrogen ions was negligible. On the other hand, the repetition at  $0^\circ$  of run 2, although attended with a large experimental uncertainty, indicates that at  $[H^+] = 25.8 \times 10^{-7}$ ,  $t_{\frac{1}{2}}$  is at least 219 mins.

Much further work would be necessary to elucidate this composite interchange process. The results we have obtained suffice, however, to establish the existence in the case of tetramminopalladous chloride of two distinct processes, and to indicate the nature of the process operative in more acid solutions. We may, perhaps, designate the mechanisms of hydrogen isotope interchange as the ammine and the ammoniate types of dissociation respectively. The point of interest is that the tetramminopalladous complex can represent no special case; it is, however, unusual in that both types of reactive function are displayed under our experimental conditions. In chemical properties also, this complex stands between the metal ammoniates and the true amines of the luteo-cobaltic type. The analogous tetramminoplatinous complex, although more stable than the palladous salt, is decomposed in fairly concentrated hydrochloric acid solution. The ammoniate type of dissociation is thus much diminished as compared with the ammine type, but its occurrence is clear. If the interchange experiments were extended to much higher hydrogen-ion concentrations, it is probable that departure from the linear relationship between hydrogen-ion concentration and rate of interchange would be found. The extremes of stability are represented by hexamminocobaltic chloride, in which the ammoniated function is completely suppressed, and the highly dissociable ammoniates of bivalent cobalt, nickel, copper, etc., in which any typical ammine functions are masked. The possession of both typical functions by such salts as tetramminopalladous chloride is strong presumptive evidence, however, that the gradation between the two extreme types of complex salt is continuous rather than—as is sometimes assumed—a question of fundamentally distinct types of chemical binding.

One may, perhaps, regard the results as having some bearing on the old problem of the relation of the metal ammonies to the ammonium salts. There is, in fact, a kernel of truth in the older conception of Blomstrand and Jørgensen, that the amines can be regarded as substituted ammonium salts. In considering the constitution of co-ordination compounds, concentration upon the rôle of the metal atom as the central atom of the complex tends to obscure the reciprocal nature of the phenomenon—*i.e.*, that the nitrogen atom of each ammonia molecule might legitimately be taken as a co-ordination centre, since it forms one co-ordinate link in virtue of the fact that it thereby acquires its stable co-ordination number, 4, and passes into the same valency state as in the ammonium ion.

A substituted ammonium ion,  $[NH_3R]^+$ , might be capable of dissociation by either of the mechanisms  $NH_3R^+ \rightleftharpoons NH_3 + R^+$  or  $NH_3R^+ \rightleftharpoons NH_2R + H^+$ , the equilibrium actually set up in solution being then dependent on the relative magnitudes (i) of the electron affinities of the  $R^+$  and  $H^+$  ions, and (ii) of the energies of the N-H and N-R links. With alkylammonium salts ( $R =$  alkyl group), these factors operate so as to set up only one equilibrium, *viz.*, that between amine and hydrogen ion, but with metal amines ( $R =$  metal atom, or metallic complex residue) the first of these factors is of similar order of magnitude for both reactions: the experimental evidence shows that the amino-ions are bases comparable in strength with ammonia. The second factor is sensitive to structural and other influences, as is shown by the variation in acid strength of amines of different metals, or amines involving other substituents (cf. ethylenediamine compounds). Moreover, herein lies the reason for the much greater acidity of oxonium compounds (such as aquopentamminocobaltic chloride) as compared with the ammonium compounds. Metal amines may therefore dissociate, as substituted ammonium salts, in either manner, and may even—under appropriate conditions of pH, where the equilibria are shifted sufficiently—display reactions belonging to both dissociation mechanisms simultaneously. It is this state that is realised, in our experimental conditions, for the tetramminopalladous complex.

In conclusion, the experimental data for the two salts discussed in this paper are compared in Table VI, together with the relevant data for hexamminocobaltic chloride, which are included since (see Part I) the

TABLE VI.

Salt.	$10^8 k$ at $0^\circ$ .	$10^8 k_0$ .	$E$ , cal.
$[Pd(NH_3)_4]Cl_2$ .....	0.978*	1.17	(25,300) †
$[Pt(NH_3)_4]Cl_2$ .....	2.07	2.48	25,200
$[Co(NH_3)_6]Cl_3$ .....	7.67	13.8	28,400

$k = k_{obs.} \times [H^+]$ ;  $k_0 = k \times$  number of exchangeable hydrogen atoms.

\* Velocity constant for true ammine-type interchange only.

† Overall value for both mechanisms of interchange.

values of  $k$  multiplied by the number of interchangeable hydrogen atoms should be comparable even for amines of different types. Two effects may be discerned in the above data. First, it is clear that, as we have supposed, the velocity constant of hydrogen interchange does run parallel with the stability of complex amines; and secondly, an increase in the valency of the central atom of the complex is accompanied by a very definite increase in the acid strength of the complex-bound ammonia, as was postulated by Grünberg and Faermann (*Z. anorg. Chem.*, 1930, **193**, 230); the existence of such an effect was predicted by Kossel in his original application of electronic ideas to the problem of valency (*Ann. Physik*, 1916, **49**, 323).

We are glad to record our indebtedness to the Mond Nickel Co. Ltd., for the generous loan of the precious metal used in this investigation.

IMPERIAL COLLEGE, SOUTH KENSINGTON, LONDON, S.W.7.  
UNIVERSITY OF MELBOURNE, MELBOURNE, N.3, VICTORIA.

[Received. January 4th, 1943.]

---