[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. XII.[1] Reactions of Some Platinum(II) Complexes with Various Reactants[2]

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Kinetic studies are reported for the reactions of some platinum(II) complexes in aqueous solution with a variety of nucleophilic reagents. The reactions studied fall into two categories: (1) those that are first order in complex but zero order in reactant and all of nearly the same rate; (2) those that are first order in both the complex and the reactant and faster than those of the first category. In general the reactants of category (1) are low in the *trans*-effect series whereas reactants of category (2) have a high *trans*-effect. The significance of the role played by the reactant in reactions of platinum(II) complexes is not involved in the current *trans*-effect theories of Chatt and Orgel. However these theories can be extended to explain the marked correlation between the reactivity of different reactants and their *trans*-directing properties. A "dissociation" mechanism is proposed for substitution reactions of "square" complexes.

The *trans*-effect in platinum(II) complexes, first recognized by Werner[3] and so designated somewhat later by Chernyaev,[4] has received considerable attention in recent years. In a review Quagliano and Schubert[5] have described the qualitative aspects of the *trans*-effect and its practical utility in the preparation of the geometrical isomers of platinum(II) complexes, as well as in some structural investigations. Several theories have been advanced by different authors, *e.g.*, Grinberg,[6] Syrkin,[7] Cardwell,[8] Chatt[9] and Orgel,[10] to account for the *trans*-effect. The theories of Chatt and of Orgel are very similar and are based on quantum mechanical (π-bonding) considerations which can satisfactorily account for the high *trans*-labilizing influence of unsaturated molecules such as C_2H_4, CO, NO, etc.

Quantitative rate data on the subject are lacking in the literature except for a recent publication by Zvyagintsev and Karandasheva[11] who have investigated the kinetics of substitution by pyridine of a halide group in some platinum(II) complexes of the type $Pt(NH_3)XYZ$, where Y and Z are negative groups (Cl^-, Br^- or NO_2^-) and X is the halide group displaced under the *trans*-influence of Z. The reactions were found to be second order as expected for an SN2 mechanism as postulated by Cardwell,[8] Chatt[9] and Orgel.[10] Furthermore the rates decreased in the order $NO_2^- > Br^- > Cl^-$ for the ligand Z in agreement with decreasing *trans*-effects for these groups. The Russian workers also observed that $Pt(C_2H_4)Cl_3^-$ reacts with pyridine too fast to be measurable. This is expected because of the strong *trans*-effect of the olefin.[12] Grantham, Elleman and Martin[13] have studied the rate of acid hydrolysis of $PtCl_4^{2-}$ and its rate of exchange with radioactive chloride ion and found that exchange proceeded by way of the acid hydrolysis step and its reverse.

Except for some further exchange studies on symmetrical complexes which will be referred to later, nothing appears to have been done by way of studying the effect on the rate of the nature of the entering group. This present work furnishes the results of a fairly wide sampling of the kinetics of a variety of nucleophilic reagents and several platinum(II) complexes.

The compounds studied were *cis*- and *trans*-dichlorodiammineplatinum(II), dichloroethylenediamineplatinum(II), chlorotriammineplatinum(II) chloride and potassium tetrachloroplatinate(II). The rates of substitution of chlorine in one or more of these complexes by pyridine, ammonia, glycine, aniline, thiourea, allyl alcohol, water hydroxide ion, nitrite ion, oxalate ion and chloride ion itself have been investigated. In case of the chloride ion the rate of exchange has been followed kinetically by the radio-isotopic tracer method using chloride ion tagged with $^{36}Cl^-$. In the case of the other substituting groups, the progress of the reaction was estimated at intervals by physico-chemical methods such as the change in electrical conductance or change in optical density at a suitable wave length of the reacting solution in question, or by titrating the released chloride ion potentiometrically with standard silver nitrate solution using a glass–Ag/AgCl electrode assembly in acidified acetone–water medium (*cf.* Brown and Ingold[14]).

Experimental

A. Preparation of Materials.—*cis*-Dichlorodiammineplatinum(II) was prepared, from K_2PtCl_4 and ammonia in aqueous solution, following the method of Ramberg.[15] The product was purified by recrystallization from hot water acidified with hydrochloric acid.

trans-Dichlorodiammineplatinum(II) was prepared from tetrammineplatinum(II) chloride by heating the solid salt to 250° for about $^1/_2$ hr., extracting with hot water acidified with hydrochloric acid and cooling. The product which separated was purified by recrystallization from acidified hot water.[16]

Dichloroethylenediamineplatinum(II) was prepared in a pure state from aqueous solution of K_2PtCl_4 and ethylene-

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[1] (1) Previous paper in this series, F. Basolo, W. R. Matoush and R. G. Pearson, THIS JOURNAL, **78**, 4883 (1956).

[2] (2) This investigation was supported by a grant from the U. S. Atomic Energy Commission under contract AT(11-1)-89-project No. 2.

[3] (3) A. Werner, *Z. anorg. allgem. Chem.*, **3**, 267 (1893).

[4] (4) I. I. Chernyaev, *Ann. inst. platine (U. S. S. R.)*, **4**, 243, 261 (1926).

[5] (5) J. V. Quagliano and L. Schubert, *Chem. Revs.*, **50**, 201 (1952).

[6] (6) A. A. Grinberg, *Ann. inst. platine (U. S. S. R.)*, **10**, 58 (1932); *Acta Physicochim. (U. S. S. R.)*, **3**, 573 (1935).

[7] (7) Y. K. Syrkin, *Izvestya Akad. Nauk., U. S. S. R. otdel. Khim. Nauk.*, 69 (1948); *C. A.*, **42**, 5368 (1948).

[8] (8) H. M. E. Cardwell, *Chemistry & Industry*, 422 (1955).

[9] (9) J. Chatt, L. A. Duncanson and L. M. Venanzi, *ibid.*, 749 (1955); *J. Chem. Soc.*, 4456 (1955).

[10] (10) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

[11] (11) O. E. Zvyagintsev and E. F. Karandasheva, *Doklady Akad. Nauk. (S. S. S. R.)*, **101**, 93 (1955).

[12] (12) See refs. 6, 10 and 12; A. D. Gelman and E. F. Karandasheva, *ibid.*, **87**, [4] 597 (1952).

[13] (13) L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., THIS JOURNAL, **77**, 2965 (1955).

[14] (14) D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).

[15] (15) L. Ramberg, *Z. anorg. Chem.*, **83**, 33 (1913).

[16] (16) H. D. K. Drew, *J. Chem. Soc.*, 2328 (1932).

diamine following the method of Drew[16] as modified by Basolo, Bailar and Tarr.[17]

Chlorotriammineplatinum(II) chloride was prepared from *cis*-dichlorodiammineplatinum(II) according to the procedure described by Tschugaev.[18] The purity of the sample was checked by analysis.

Anal. Calcd. for $[\text{Pt(NH}_3)_3\text{Cl}_2]\text{Cl}$: Pt, 61.51; N, 13.24; H, 2.84. Found: Pt, 60.98; N, 13.50; H, 2.90.

B. **Determination of the Rate of Exchange of Radiochloride Ion.**—This has been determined in case of both *trans*-dichlorodiammineplatinum(II) and the chlorotriammineplatinum(II) cation in aqueous solutions 0.2 *M* in potassium nitrate. To an aqueous solution of the desired complex were added the requisite amounts of solid potassium nitrate and hydrochloric acid containing $^{36}\text{Cl}^-$ of known concentration; the solutions were then diluted to the requisite volume and thermostated at 25°. Aliquots of 0.50 cc. were removed at known intervals and to the aliquots were added a constant amount of a solution of potassium chloride (to form a sufficient precipitate of AgCl). The free chloride ion was then precipitated by adding 10% excess of the requisite quantity of silver nitrate solution. The mixture was centrifuged for 10 min. and then an aliquot of the clear supernatant liquid was withdrawn and evaporated on a disc of filter paper in an aluminum tray under strong infrared light. The activity of all these samples were then counted in a Scaling Unit, Model 162, Nuclear Instruments and Chemical Corporation, Inc. Since in $\text{Pt(NH}_3)_2\text{Cl}_2$ there are two equivalent chlorine atoms, it can be shown that the rate constant, *k*, for the constant rate of exchange of chlorine in the complex with the chloride ions in solution will be given by

$$k = \frac{2[\text{Cl}^-] \times 2.303}{\{2[\text{Pt(NH}_3)_2\text{Cl}_2] + [\text{Cl}^-]\}t} \log \frac{(C_\infty - C_0)}{(C_\infty - C_t)} \qquad (1)$$

where C_0, C_t and C_∞ represent the counts per minute of the evaporated samples corresponding to the aliquots of reacting solution treated at zero time, *t* minutes and ∞, respectively. The latter has been calculated assuming complete exchange of both the chlorine atoms in the complex so that the radioactive isotope is distributed equally between the covalent and ionic chlorine in the system. This value was checked experimentally on one sample which was allowed to stand for several days before being treated. From the slopes of the curves obtained by plotting $\log (C_\infty - C_0)/(C_\infty - C_t)$ *vs.* *t*, *k* was calculated using eq. 1. The results are given in Table I.

The experimental procedure in the case of $\text{Pt(NH}_3)_3\text{Cl}^+$ was identical. Since, however, there is only one chlorine in the complex, *k* was evaluated graphically from eq. (2) tion

$$k = \frac{2.303}{t} \log \frac{(C_\infty - C_0)}{(C_\infty - C_t)} \qquad (2)$$

by plotting $\log (C_\infty - C_0)/(C_\infty - C_t)$ *vs.* *t* at two different concentrations of chloride ion. The results are recorded in Table I.

C. **Determination of the Rates of Release of Chloride Ion from the Chloro Complexes of Platinum(II) under the Influence of Water, Ammonia, Aniline, Pyridine, Glycine, Thiourea, Allyl Alcohol, Hydroxide Ion, Nitrite Ion and Oxalate Ion.**—These reactions have been followed by one or more of the several physico-chemical methods described below.

(1) **Change in Conductance.**—The reactions of non-ionic and cationic complexes with neutral molecules like aniline, pyridine, glycine, thiourea and allyl alcohol (freshly prepared solutions were used) were followed by measuring the change in conductance of the solution under investigation, thermostated at 25°, using a Conductivity Bridge (Model RC 16, Industrial Instruments, Inc.). Relatively large excess of the reagent was used to follow the reaction as one of pseudo first-order type, in case it is not truly first order. Rate constants have been evaluated graphically from the equation

$$k = \frac{2.303}{t} \log \left(\frac{R_0 - R_\infty}{R_0}\right)\left(\frac{R_t}{R_t - R_\infty}\right) \qquad (3)$$

where the *R*'s stand for resistances in ohms of the reacting solution measured at different times in the same cell. In the case of $\text{Pt(NH}_3)_3\text{Cl}^+$ the experimental value of R_∞ which agreed closely with the value expected for a compound of the type $[\text{PtA}_4]\text{X}_2$, was used in the calculations. This is also true for the reaction of *trans*-$\text{Pt(NH}_3)_2\text{Cl}_2$ with allyl alcohol, where only one chloride ion is released giving $[\text{PtA}_3\text{Cl}]\text{Cl}$, even after a week. But in the reaction of *trans*-$\text{Pt(NH}_3)_2\text{Cl}_2$ with pyridine, aniline and glycine both chloride ions are ionized successively. Hence, in this case the value of R_∞ used in the calculations was taken as double the observed value of the resistance after three weeks. Determination of the chloride ion at this stage by potentiometric titration (*vide infra*) indicated that both the chlorines were displaced. Results of these determinations are given in Table I. Interestingly enough $\text{Pt(NH}_3)_3\text{Cl}^+$ did not react at all with allyl alcohol, even at 50°. The reaction of *trans*-$\text{Pt(NH}_3)_2\text{Cl}_2$ with thiourea was so fast that the conductivity of the solution reached a value expected for an ionic compound of the type $[\text{PtA}_4]\text{X}_2$ within a few minutes of mixing of the constituents, and hence the rate of the reaction could not be measured.

A conductivity method was utilized in studying the reaction of hydroxide ion with PtCl_4^{2-}. Equimolecular amounts of the reactants were mixed and the change in conductance, due to replacement of OH^- in solution by Cl^- was followed

$$\text{PtCl}_4^{2-} + \text{OH}^- \longrightarrow \text{Pt(OH)Cl}_3^{2-} + \text{Cl}^- \qquad (4)$$

The value of R_∞ could not be determined experimentally, as the solution on standing overnight became turbid due to separation of a bluish-black precipitate. R_∞ was calculated assuming that PtCl_4^{2-} and Pt(OH)Cl_3^{2-} have the same value of the equivalent conductance and using the known values of the equivalent conductance of PtCl_4^{2-}, OH^- and Cl^- ions. Since a first-order plot was obtained for this equimolecular mixture it was concluded that the reaction is independent of the OH^- ion concentration. The value of the rate constant was also checked by following the reaction by titrating the unreacted OH^- ion at different stages potentiometrically as described below.

To check the influence of ionic strength of the medium on the rate constants some of these determinations were repeated in 0.2 *M* potassium nitrate solution using the potentiometric titration technique (*vide infra*) to follow the rate of release of the chlorine ligand from the complex as chloride ion into the solution. These data are also recorded in Table I.

(2) **Potentiometric Titration.**—The rates of displacement of coördinated chloride ion from chloroammineplatinum(II) complexes by ammonia in ammonium nitrate buffer medium (to suppress the basic dissociation of ammonia), water, hydroxide ion, oxalate ion and nitrite ion have been investigated by potentiometric titration of the released chloride ion. Aliquots of 25 cc. of the reacting solution under investigation, thermostated at the desired temperature, were removed at intervals and immediately run into 150 cc. of acidified acetone (25 cc. of concd. nitric acid per 1 kg. of acetone) cooled in ice. The glass–Ag/AgCl electrode assembly was dipped into the solution which was kept cooled in ice and well stirred by a mechanical stirrer during the titration. Titration was carried out by gradually adding from a microburet (5 cc./0.01) a standard solution of silver nitrate (strength 10 times the molar concentration of the total chlorine in the reacting solution) and following the change in potential with a *p*H millivoltmeter (Beckman, model G). The end-point was marked by a very sharp change (decrease) in potential per 0.01 cc. of the titrant. The rate constant was calculated graphically from the usual first-order equation. The value of V_∞ used was calculated from the known concentration of the complex in solution. This calculated value always was checked experimentally and good agreement found in most cases. The results are recorded in Table I.

It is interesting to note that the reaction of the *trans*-dichloro compound with nitrite ion was so fast at 25° that it could not be conveniently followed experimentally. But from the data presented below it appears that the rate is also dependent on the concentration of nitrite ion, as in the case of the corresponding *cis*-compound, or the chlorotriammineplatinum(II) complex cation:

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[17] F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, THIS JOURNAL, **72**, 2433 (1950).

[18] L. A. Tschugaev, *Trans. Chem. Soc.* (*London*), **107**, 1247 (1915).

trans-$Pt(NH_3)_2Cl_2$, 0.0005 *M*, and NO_2^- (KNO_2), 0.02 *M*; 25°

Time, min.	0 (immediately after mixing)	12	Total Cl equiv. to 2.5 cc. of 0.01 *M* $AgNO_3$
Titer/25 cc. (cc. $AgNO_3$, 0.01 *M*)	1.92	2.44	

trans-$Pt(NH_3)_2Cl_2$, 0.0005 *M*, and NO_2^-, 0.001 *M*; 25°

Time, min.	0	15	Total Cl equiv. to 2.5 cc. of 0.01 *M* $AgNO_3$
Titer/25 cc. (cc. $AgNO_3$, 0.01 *M*)	0.76	1.90	

The reaction of OH^- ion with $PtCl_4^{2-}$ has been followed by titration of the free alkali at different stages of progress of the reaction in a solution 0.002 *M* in both K_2PtCl_4 and KOH. An alkali–glass electrode (Beckman E) with a saturated calomel reference electrode was used in conjunction with a Beckman *p*H meter (Model G) to follow the change in *p*H during the course of the titration with 0.01 *M* $HClO_4$. Titration was carried out to a *p*H of 8.0 ± 0.05 to determine the amount of free OH^-. V_∞ was taken as zero, as is expected for the equimolecular mixture. A first-order plot was obtained and the rate constant thus calculated was identical to that obtained by the conductance method.

(3) **Spectrophotometric Method.**—This was applied in studying the reaction of $Pt(NH_3)_3Cl^+$ with nitrite ion. The rate of reaction was followed spectrophotometrically at 260 mμ, where the chloro and nitro compounds have different absorbancy, the latter absorbing more strongly. The selection of wave length was made by first plotting the spectra using a Cary recording spectrophotometer, Model 11, in the region 400–220 mμ. Final measurements at the selected region were made in a Beckman DU quartz spectrophotometer, with thermostated cell compartment. The absorbancy of the nitro compound was obtained by mixing a solution of the chloro compound with excess of potassium nitrite, keeping it overnight and measuring the absorption against a blank of potassium nitrite solution of the same concentration as in the solution under investigation. This was checked daily until a reasonably constant value was obtained. It can be shown that the rate constant, *k*, is given by

$$k = \frac{2.303}{t} \log \frac{(\mathrm{O.D.})_\infty - (\mathrm{O.D.})_0}{(\mathrm{O.D.})_\infty - (\mathrm{O.D.})_t} \qquad (5)$$

where all the optical densities are measured against a blank of potassium nitrite solution of the same concentration as in the reacting solution. The value for $(\mathrm{O.D.})_\infty$ was obtained as described above. The same procedure has been employed in studying the reaction of $PtCl_4^{2-}$ with allyl alcohol. Measurements were carried out at the selected wave length of 300 mμ where the allyl alcohol has practically no absorption while the product of the reaction, presumably $[Pt(CH_3H_6O)Cl_3]^-$, absorbs much more than $PtCl_4^{=}$. The results of some determinations are also presented in Table I.

D. Temperature Dependence.—The effect of temperature on some of these reactions has been studied and the activation energy, E_a has been calculated from the usual Arrhenius equation. These are presented in Table II.

Discussion

The reactions studied fall into two categories. (1) Those that are first order in the complex and zero order in the attacking reagent and (2) those that are first order in both the complex and the reagent. Furthermore, those reactions which are totally first order for a given complex have very nearly identical rates for several reagents. Thus some step other than the reaction with the reagent is rate determining in these cases. This may be a slow SN2 reaction of the complex with water to form the aqua complex

$$PtA_3Cl + H_2O \xrightarrow{\text{slow}} PtA_3H_2O^+ + Cl^- \qquad (6)$$

followed by a rapid reaction of the aqua complex with the reagent Y

$$PtA_3H_2O^+ + Y \xrightarrow{\text{fast}} PtA_3Y^+ + H_2O \qquad (7)$$

Or it may be an SN1 dissociation of the complex followed by rapid reaction of a three-coördinated intermediate with Y and/or water.

$$PtA_3Cl \xrightarrow{\text{slow}} PtA_3^+ + Cl^- \qquad (8)$$

$$PtA_3^+ + Y \xrightarrow{\text{fast}} PtA_3Y^+ \qquad (9)$$

It is possible in a favorable case to distinguish between these two paths by studying the rate of reaction of the aqua complex with Y to see if it is rapid enough to be consistent. In the present studies some experiments were done to check the reactivity of the aqua complexes. If the chloro complexes are dissolved in water and allowed to stand for some time it is found that *cis*-$Pt(NH_3)_2Cl_2$ comes to an equilibrium within a few days in which 45% of the original coördinated chlorine is ionic. The product is assumed to be 90% *cis*-$[Pt(NH_3)_2(H_2O)Cl]Cl$ and 10% unreacted dichloro, since $Pt(NH_3)_3Cl^+$ was found not to release any ionic chloride after several days standing. If alkali is added to a solution of *cis*-$Pt(NH_3)_2Cl_2$, both chlorines are replaced. Upon acidifying with perchloric acid, a little over one-half of the chlorine very rapidly re-enters the complex, giving the same equilibrium mixture as before.

The *trans*-isomer of $Pt(NH_3)_2Cl_2$, on standing in solution for several weeks does not form any ionic chloride as judged by titration of the chloride ion and by conductivity. This is in disagreement with the conductivity data reported by others[19] who claimed that the *trans*-complex over a period of several hours attained an appreciable conductivity. However, our results were checked several times on different preparations of the complex obtained by heating $[Pt(NH_3)_4]Cl_2$ to 250°. An attempt to make *trans*-$Pt(NH_3)_2Cl_2$ by the method used by Drew gave a material with quite different properties from that obtained by thermal decomposition. Furthermore the analysis of this material did not agree with a dichlorodiammine of platinum(II). If the *trans* complex is treated with alkali, all of the chlorine is replaced. Upon acidifying, 75% of the chlorine rapidly returns to the coördinated form. That this is not due to a mixture of *cis*-$[Pt(NH_3)_2(H_2O)Cl]Cl$ and *trans*-$Pt(NH_3)_2Cl_2$ being formed has been proven by measuring the optical density of the solution at three different wave lengths (220, 230 and 240 mμ) where the *cis*- with *trans*-compounds absorb differently, the *trans* isomer having the greater optical density. It has been found that the solution under investigation had an optical density even higher than that expected for the pure *trans*-compound. This indicates the existence of a different species, presumably a polynuclear one, in solution, which is formed from the aqua complexes reacting with Cl^- ion. The nature of this polynuclear species is not known but it cannot be the dimer, $[Pt(NH_3)(NH_2)Cl]_2$, said to be isolated from the reactions of *cis* and of *trans*-$Pt(NH_3)_2Cl_2$ individually with sodium hydroxide followed by hydro-

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[19] H. D. K. Drew, F. W. Pinkard, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, 988 (1932); I. I. Chernyaev and M. M. Yakshin, *Ann secteur platine, Inst. chim. gen* (*U.S.S.R.*), **17**, 29, 42 (1940).

TABLE I

RATES OF REACTIONS OF SOME PLATINUM(II) COMPLEXES

Reactant, Y	Concn. of Y in soln. M	Added substance	Rate const., k, min.$^{-1c}$
trans-$Pt(NH_3)_2Cl_2$, 0.0005 M; 25°; $Pt(NH_3)_2Cl_2 + Y \rightarrow Pt(NH_3)_2YCl + Cl^-$			
$^{36}Cl^-$(HCl)	0.005	0.2 M KNO_3	2.1×10^{-3}
	.01	.2 M KNO_3	2.1×10^{-3}
OH^- (KOH)	.00096	....	6.1×10^{-3}
	.0064	....	6.1×10^{-3}
	.016	....	6.1×10^{-3}
NH_2CH_2COOH	.01	....	4.6×10^{-3}
	.02	....	4.6×10^{-3}
$C_6H_5NH_2$^{a}	.01	....	5.7×10^{-3}
	.02	....	5.7×10^{-3}
C_5H_5N^{a}	.005	0.2 M KNO_3	6.5×10^{-3}
	.01	.2 M KNO_3	6.5×10^{-3}
	.01	....	5.0×10^{-3}
NH_3	.009	0.1 M NH_4NO_3	1.1×10^{-2}
	.018	.1 M NH_4NO_3	2.1×10^{-2}
$CH_2{=}CHCH_2OH$	.005	....	3.8×10^{-3}
	.01	....	7.5×10^{-3}
	.015	....	10.8×10^{-3}
$C_2O_4^{2-}$ ($Na_2C_2O_4$)	.01	....	4.8×10^{-3}
	.02	....	9.0×10^{-3}
NO_2^- (KNO_2)			Extremely rapid
$SC(NH_2)_2$			Extremely rapid
trans-$Pt(NH_3)_2(OH)Cl$, 0.0005 M; 40°; $Pt(NH_2)_2(OH)Cl + OH^- \rightarrow Pt(NH_3)_2(OH)_2 + Cl^-$			
OH^- (KOH)	0.008	....	2.3×10^{-3}
	.016	....	2.3×10^{-3}
cis-$Pt(NH_3)_2Cl_2$, 0.0005 M; 25°; $Pt(NH_3)_2Cl_2 + Y \rightarrow Pt(NH_3)_2YCl + Cl^-$			
H_2O	Aq. soln.	0.01 M HNO_3	2.3×10^{-3}
OH^-	0.008	....	2.3×10^{-3}
	.016	....	2.3×10^{-3}
cis-$Pt(NH_3)_2(OH)Cl$, 0.0005 M; 25°; $Pt(NH_3)_2(OH)Cl + OH^- \rightarrow Pt(NH_3)_2(OH)_2 + Cl^-$			
OH^- (KOH)	0.016	....	1.3×10^{-3}
	.032	....	1.3×10^{-3}
cis-$[Pt(NH_3)_2(H_2O)Cl]^+$, 0.0005 M; 25°; $Pt(NH_3)_2(H_2O)Cl^+ + Y \xrightarrow{\text{fast}} Pt(NH_3)_2YCl + H_2O$; $Pt(NH_3)_2YCl + Y \rightarrow Pt(NH_3)_2Y_2 + Cl^-$			
1. C_5H_5N	0.01	....	1.5×10^{-3}
	.02	....	1.5×10^{-3}
2. NO_2^- (KNO_2)	.0032	....	3.9×10^{-3}
	.005	....	5.8×10^{-3}
$Pt(en)Cl_2$, 0.0005 M; 25°; $Pt(en)Cl_2 + Y \rightarrow Pt(en)YCl + Cl^-$			
1. H_2O	Aq. soln.	0.01 M HNO_3	3.2×10^{-3}
2. OH^- (KOH)	0.008	....	3.2×10^{-3}
	.016	....	3.2×10^{-3}
$Pt(en)(OH)Cl$, 0.0005 M; 25°; $Pt(en)(OH)Cl + OH^- \rightarrow Pt(en)(OH)_2 + Cl^-$			
OH^-	0.008	....	1.5×10^{-3}
	.016	....	1.5×10^{-3}
$[Pt(NH_3)_3Cl]^+Cl^-$, 0.0005 M; 25°; $Pt(NH_3)_3Cl^+ + Y \rightarrow Pt(NH_3)_3Y + Cl^-$			
1. $^{36}Cl^-$ (HCl)	0.0045	0.2 M KNO_3	0.9×10^{-3}
	.0105	.2 M KNO_3	$.9 \times 10^{-3}$
2. C_5H_5N	.01	....	1.3×10^{-3}
	.01	0.2 M KNO_3	1.0×10^{-3}
	.02	....	1.3×10^{-3}
3. NH_3	.009	0.2 M NH_4NO_3	1.9×10^{-3}
	.009	.1 M KNO_3, 0.1 M NH_4NO_3	1.7×10^{-3}
	.009	.15 M KNO_3, 0.05 M NH_4NO_3	1.5×10^{-3}
	.036	.1 M KNO_3, 0.1 M NH_4NO_3	2.1×10^{-3}
	.036	.1 M NH_4NO_3	2.7×10^{-3}
4. NO_2^- (KNO_2)	.005	....	3.2×10^{-3}
	.01	....	5.8×10^{-3}

TABLE I—(*continued*)

Reactant, Y	Concn. of Y. in soln. M	Added substance	Rate const., k, min.$^{-1c}$
5. $SC(NH_2)_2$	.005	....	2.5×10^{-2}
	.01	....	4.7×10^{-2}
	.015	....	8.4×10^{-2}
6. $CH_2{=}CHCH_2OH$			No reaction
	K_2PtCl_4, 0.002 *M*; 25°; $PtCl_4^{=} + Y^- \rightarrow PtYCl_3 + Cl^-$		
OH^- (KOH)	0.002	....	1.9×10^{-3} min.$^{-1}$
$CH_2{=}CHCH_2OH$	.06	....	1.6×10^{-3}
	.12	....	3.0×10^{-3}
	.30	....	8.5×10^{-3}
$^{36}Cl^-$	..	....	2.3×10^{-3b}

[a] The value of k given is $^1/_2$ the observed k. See Discussion. [b] This is the result of Grantham, Elleman and Martin, ref. 13. [c] First order or pseudo-first order.

chloric acid.[20] Thus these experiments, while incomplete, indicate that the aqua complexes are very reactive, at least to chloride ion. This means that it is not possible to distinguish between the SN2 and SN1 mechanisms in these cases.

TABLE II

VARIATION OF THE RATE CONSTANTS FOR $[Pt(NH_3)_3Cl]^+$ WITH TEMPERATURE, $[Pt(NH_3)_3Cl]Cl$, 0.0005 *M*

	Rate constant × 10³, min.$^{-1}$			*Ea*, kcal./mole
Temp., °C.	18	25	35	
C_5H_5N (0.01 *M*)	0.5	1.3	3.9	20.6
$SC(NH_2)_2$ (0.005 *M*)	11.5	25.3	51.0	14.7

The reagents which give second-order rates follow the reactivity sequence $SC(NH_2)_2 > NO_2^- > NH_3 > CH_2{=}CHCH_2OH > C_2O_4^{2-}$. Ammonia is second order with *trans*-$Pt(NH_3)_2Cl_2$ but not with $Pt(NH_3)_3Cl^+$. Also $Pt(NH_3)_3Cl^+$ does not appear to react at all with allyl alcohol. This is not surprising since the product would be of a cationic type that is known not to be stable, $Pt(NH_3)_3$olefin$^+$. Thus, it may be an unfavorable equilibrium constant and not an unfavorable rate which is responsible. The following approximate sequence of ligands in order of decreasing *trans* effect has been given[12]: $CN^- \sim C_2H_4 \sim CO \sim NO > SC(NH_2)_2 \sim R_2S \sim R_3P \sim NO_2^- \sim I^- \sim CNS^- > Br^- Cl^- >$ pyridine $> NH_3 > OH^- > H_2O$. It is striking that it is just the ligands which have a large activating influence when in a *trans* position to a replaceable group, which react rapidly and bimolecularly when taking the role of external reagents. Furthermore, the poor reagents, H_2O, OH^-, pyridine and Cl^- are down near the bottom in *trans* activating influence. It is indeed remarkable that OH^-, which is such a powerful reagent for organic halides and for the complexes of cobalt(III) and chromium(III), is so *ineffective* as a reagent for the planar complexes of platinum(II). On the other hand, the relatively great reactivity of allyl alcohol (reacting as an olefin) is unusual since the nucleophilic and basic properties of the double bond are very small. It is also known from the work of Jensen[20] and of Chatt and Wilkins[21] that trialkyl phosphines, arsines and stibines react very rapidly with the corresponding dichloroplatinum(II) complexes.

The picture given by Chatt[9] and by Orgel[10] for the mode of reaction of systems containing *trans* activating groups can be extended to accommodate these new observations on the effect of the nature of the reagent. It has been postulated by them that π-bonding occurs in which electrons from a filled d orbital of platinum are donated in part to a π-orbital in unsaturated ligands such as C_2H_4, CO, NO_2^-, etc., or to a ligand with empty d orbitals such as R_2S and R_3P. This is shown schematically in Fig. 1 in which the four groups attached to platinum lie in the *xy*-plane and the filled d_{xz} orbital forms a π-bond to the ligand. The resulting decrease in electron density allows a nucleophilic reagent to approach the opposite side from above or below the plane. The transition state will then approximate a trigonal bipyramid with the entering group, the departing group and the group *trans* to it all in the trigonal plane. Also in the trigonal plane will be two d orbitals belonging to platinum and filled with two electrons each. These will be the d_{xz} and $d_{x^2-z^2}$ as shown in Fig. 2 where the three groups and the two orbitals lie in the *xz*-plane. It is clear that π-bonds can be formed from either of the two d orbitals with any of the three groups in the plane. If the entering group can form a π-bond, this will be a factor stabilizing the transition state and hence causing an increase in the rate of reaction as observed. As in the theories of Chatt[9] and Orgel,[10] a group in the *trans* position to the leaving group stabilizes the transition state by removing electrons from the regions in which the entering and departing groups are placed. It also may be argued that π-bonding by the group being

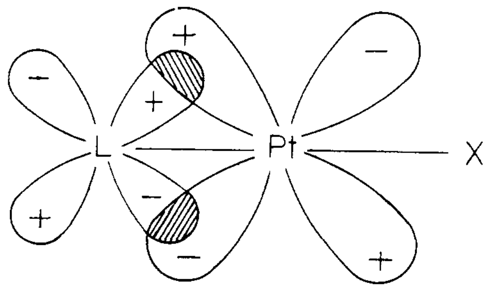

Fig. 1.—d-d-π-Bonding in platinum(II) complexes. If ligands L and X lie in the *xy*-plane than the d orbitals shown are either d_{xz} or d_{yz}.

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(20) K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 252 (1936).

(21) J. Chatt and R. G. Wilkins, "Symposium on Coördination Compounds," Danish Chemical Society, Copenhagen, 1953, pp. 57–60.

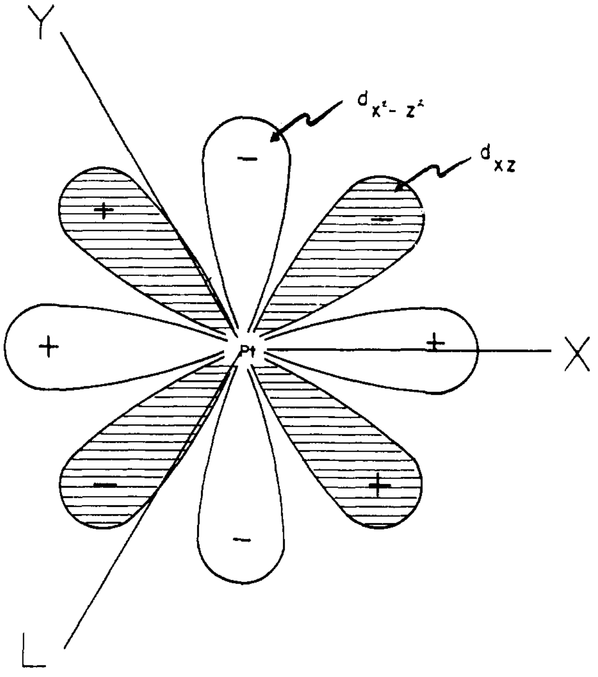

Fig. 2.—Trigonal xz-plane of trigonal bipyramid intermediate, PtA_2LXY, where the two A groups are at the apical position on the y-axis. Diagram shows the d_{xz} and $d_{x^2-z^2}$ orbitals of platinum(II) in the xz-plane which can π-bond with the ligands in this trigonal plane.

replaced stabilizes the system in the same way, but opposed to this are the facts that only two π-bonds can be formed at any one time in the trigonal plane (two additional π-bonds can be formed with the groups on the diagonal or y-axis), and double-bonding of the leaving group will hinder its leaving.

It also may be noted that in the original square planar form only three π-bonds involving metal d orbitals[22] can be formed, with d_{xz}, d_{yz} and d_{xy}. Hence if platinum is coördinated to four potential π-bonding groups, there will be an extra driving force to add a fifth group and become a trigonal bipyramid, since now four π-bonds can be formed. This explains the puzzling phenomenon observed by Grinberg and Nikolśkaya.[23]

These workers, in studying the rate of exchange of PtX_4^{2-} with labeled X^-, found the rates to increase in the order $Cl^- < Br^- < I^- < CN^-$. Since this is the order of increasing stability of the complexes as well, it implies that the most stable complex is also the most labile. The order given is also that of increasing *trans*-effect, which explains the rates. Thus in spite of the strength of the Pt–CN bond, the transition state is sufficiently stabilized by four cyano groups which can form π-bonds.

Another factor which should be considered in evaluating the stability of various transition states for platinum(II) is the change in crystal field stabilization energy in going from the original square planar configuration. The crystal field stabilization energy (CFSE) is a property of a complex ion resulting from the preferential occupation by d electrons of the central atom of the orbitals which point away from the ligands.[24]

The energies of the various d orbitals for square planar and trigonal bipyramid complexes have been calculated by Ballhausen and Klixbüll Jørgensen.[25] There are some approximations that must be made in applying these calculations to any real system but a result good enough for the present purposes can be obtained. Thus for a symmetrical, square planar complex containing eight d electrons, the CFSE is about 25 Dq, less the energy required to couple two electrons in one orbit. The parameter Dq can be obtained from spectral data and is about Dq = 4.5 kcal. in order of magnitude for a divalent, third transition series element.[26] For a symmetrical trigonal bipyramid structure, the corresponding stabilization energy is only 14 Dq and if the complex remains diamagnetic the electron coupling energy remains constant. Hence there is a loss of about 11 Dq or 50 kcal. in CFSE in a reaction going by the S_N2 mechanism postulated above. Although a calculation cannot be made easily, it is certain that π-bonding by any of the groups in the trigonal plane will appreciably reduce the loss in CFSE by the process already discussed.

As opposed to this path, an S_N1 mechanism in which one group leaves and the remaining three groups maintain their original positions, leads to only a small decrease in CFSE, of the order of 2 Dq. Such a reaction path might be favored by a reagent which cannot form π-bonds, *e.g.*, H_2O, NH_3 and oxalate ion. In such a case, however, it is difficult to account for the second-order kinetics observed with the last two reagents and *trans*-$Pt(NH_3)_2Cl_2$. Also an inspection of Table I shows that the reactions which are independent of the concentration of entering reagent are remarkably insensitive to the net charge on the platinum complex. Thus the ions *cis* and *trans*-$Pt(NH_3)_2Cl_2$, $PtenCl_2$, $Pt(NH_3)_3Cl^+$, *cis*-$Ptpy(NH_3)_2Cl^+$ and $PtCl_4^{2-}$ all react at the same rate within a factor of about three. By comparison $Co(NH_3)_5Cl^{2+}$ reacts slower than *trans*-$Co(NH_3)_4Cl_2^+$ by a factor of about 1000.

Such an insensitivity to coulombic effects is quite incompatible with an S_N1 mechanism which goes predominantly by bond breaking. It is instead what one would expect if both bond making and bond breaking were of comparable importance. Furthermore both mechanisms described above for a square planar complex ignore a fact which has become quite apparent from recent experimental work and from elementary energetic considerations. This fact is that a square planar complex invariably will have two further groups coördinated above and below the plane at a greater distance than the four primary ligands.[27] These groups may be solvent, or solute, molecules in solution, and anions, solvent of crystallization or even

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[22] G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

[23] A. A. Grinberg and L. E. Nikolśkaya, *Zhur. Priklad. Khim.*, **22**, 542 (1949); **24**, 893 (1951).

[24] See L. E. Orgel, *J. Chem. Soc.*, 4756 (1956); *J. Chem. Phys.*, **23**, 1819 (1955).

[25] C. J. Ballhausen and C. Klixbüll Jørgensen, *Kgl. Danske Videnskab Selskab*, **29**, No. 14 (1955).

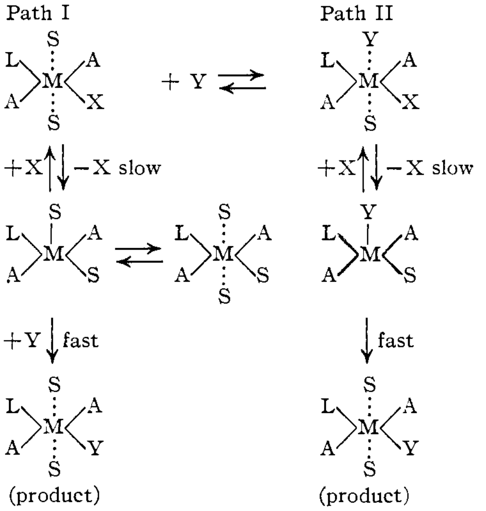
[26] C. Klixbüll Jørgensen, *Acta Chem. Scand.*, **10**, 517 (1956).

[27] L. Tschugaeff, *Compt. rend.*, **161**, 563 (1915); A. K. Sundaram and E. B. Sandell, THIS JOURNAL, **77**, 855 (1955); L. Malatesta and L. Vallarino, *J. Chem. Soc.*, 1867 (1956); C. M. Harris and R. S. Nyholm, *ibid.*, 4375 (1956).

metal atoms from another complex in the solid state.

Accordingly the following mechanism is proposed for reactions of "square planar" complexes in solution

$$MLA_2X + Y \longrightarrow MLA_2Y + X \qquad (10)$$



Thus the reaction goes by a dissociation mechanism of a tetragonal complex in which two groups above and below the plane move in to help displace the group X. The five-coördinated intermediate will probably rearrange to a trigonal bipyramid, particularly if L or Y is a π-bonding group. In path II, Y can directly enter the square plane. Otherwise the aqua (or corresponding) complex will be an intermediate in a further sequence of dissociations until Y is picked up.

Such a reaction scheme accounts for (1) the over-all stereospecificity of such reactions (2) the activating influence of a π-bonding group on the ligand *trans* to it, (3) the reactivity and second-order kinetics of π-bonding reagents, (4) the small influence of electrostatic factors on the rates and (5) the second-order kinetics observed for some non π-bonding reagents such as NH_3 and oxalate ion. Furthermore it is in agreement with the almost certainly tetragonal structure of the complexes.

The mechanism also can be correlated with those postulated for the reactions of cobalt(III) complexes. These are SN1 dissociations for acid hydrolyses with usually a square pyramid structure for the five-coördinated intermediate, and SN1CB dissociations for base hydrolyses with rearrangement to a trigonal bipyramid intermediate.[28] There are two differences between the platinum(II) and cobalt(III) systems and each leads to important differences in the observed kinetics of their reactions. One difference is that platinum(II) is a d^8-system whereas cobalt(III) is a d^6-system. The extra pair of electrons in the case of platinum (originally in the d_{z^2} orbital) would lie in the trigonal plane, if a trigonal, pyramid is formed, occupying the $d_{x^2-z^2}$ orbital. In the case of cobalt(III), this orbital would be empty. This means that only ligands that are unsaturated, or have empty d or p orbitals, can stabilize the trigonal form in the case of platinum, whereas only ligands with unshared pairs of electrons (OH^- and NH^-) can stabilize the cobalt system. This is in agreement with the observed rates of reaction of these systems. Thus in platinum(II) the electron donation in π-bonding is from metal to ligand and in cobalt(III) it is from ligand to metal. Because of the original position of the extra pair of electrons on platinum, only the *trans* ligand can enter the trigonal plane and stabilize it. A *cis* ligand, even if a potential π-bonder such as $P(C_2H_5)_3$, would form a higher energy system if it became part of an *xy* trigonal plane because the extra pair of electrons would no longer be in this plane. This restriction does not hold for cobalt and in fact *cis* electron donors are more effective than *trans*.

The second difference is that all six groups in the case of cobalt are firmly held, their identity is fixed and the remaining bond distances remain nearly constant during the dissociation of one of the groups. In platinum, two of the groups are labile and can be replaced by other ligands in the solution. Further these two labile groups are believed to move in closer to platinum during the dissociation of the leaving group. This means that an external reagent, Y, can easily influence the rate of reaction of platinum complexes but not of cobalt complexes. Also cobalt complexes will react primarily by bond breaking, with very little help from bond making, whereas in platinum there will be contributions from both.[29] All of this is in agreement with the experimental facts on these systems.

The tetragonal structure of the platinum system also guarantees stereospecificity in that the entering group Y will always take up the position vacated by X. This is because the two groups labeled A always maintain a *trans* position to each other and hence hold the configuration in the square plane. A *trans* configuration for the two A groups does not fix the stereochemistry in an octahedral complex. Hence rearrangement is possible for cobalt(III) reactions.[28]

The rates of reaction for platinum complexes studied in this work are about as expected for varying *trans* ligands. Table I shows that for complexes of the same electrical charge the rates run $Cl^- > NH_3 > OH^-$, the same order as in the *trans* effect series listed above.

The reactions of *trans*-$Pt(NH_3)_2Cl_2$ with aniline and pyridine require special considerations. The experimentally observed rate of release of Cl^- was found to be approximately twice that of the hydroxide ion or glycine reactions. This can be accounted for on the basis of the mechanism

$$Pt(NH_3)Cl_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Pt(NH_3)_2(H_2O)Cl^+ + Cl^- \quad (11)$$

$$Pt(NH_3)_2(H_2O)Cl^+ + Y \xrightarrow{k_3} Pt(NH_3)_2YCl^+ + H_2O \quad (12)$$

$$Pt(NH_3)_2YCl^+ + H_2O \underset{k_5}{\overset{k_4}{\rightleftharpoons}} Pt(NH_3)_2Y(H_2O)^{++} + Cl^- \quad (13)$$

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[28] R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).

[29] It is also possible that, in some cases, reaction of square planar complexes may be completely determined by bond making. That is, addition of Y to the platinum atom even in a weakly held position may be sufficient to ensure that the reaction will go to completion.

$$Pt(NH_3)_2Y(H_2O)^{++} + Y \xrightarrow{k_6} Pt(NH_3)_2Y_2^{++} + H_2O \qquad (14)$$

By using the steady-state assumption for the concentration of the intermediates $Pt(NH_3)_2(H_2O)Cl^-$, $Pt(NH_3)_2YCl^+$ and $Pt(NH_3)_2Y(H_2O)^{++}$, the rate equation reduces to

$$\frac{d[Cl^-]}{dt} = 2k_1\left(1 - \frac{k_2[Cl^-]}{k_2[Cl^-] + k_3[Y]}\right)[Pt(NH_3)_2Cl_2] \qquad (15)$$

It actually has been observed that the initial, rather rapid, rate of liberation of Cl^- drops to a much lower value even before half of the total chlorine has been liberated, and that the smaller the concentration of the incoming group, Y, in the solution, the earlier this drop off occurs. Furthermore, if chloride ion is added to the solution to begin with, then for the same concentration of Y, the slowing down takes place earlier. Addition of more Y at this stage again speeds up the reaction. These are all expected on the basis of eq. 15. Eventually all of the chloride ion is replaced by pyridine or aniline (see Experimental). Hence, the rate constant for the initial rate has been divided by two for the data given in Table I for these two reagents, namely, aniline and pyridine in their reaction with *trans*-$Pt(NH_3)_2Cl_2$.

EVANSTON, ILL.

[CONTRIBUTION FROM THE INSTITUTE OF GENERAL CHEMISTRY, THE UNIVERSITY OF PALERMO]

Studies in Coördination Chemistry. I. The Effect of Solvents on Some Bis-(N-alkylsalicylaldimine)-nickel(II) Complexes

BY LUIGI SACCONI, PIERO PAOLETTI AND GIUSEPPE DEL RE

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A series of bis-(N-alkylsalicylaldimine)-nickel(II) complexes in the solid state and in solution of organic solvents was submitted to magnetic, spectrophotometric and electric moment measurements. The results of dipole moment determination afford evidence against the hypothesis of a tetrahedral structure of such complexes when dissolved in "non-coördinating" solvents. The paramagnetism developed in such solutions and some characteristic features of the absorption spectra can be understood with the hypothesis of an equilibrium involving an "outer orbital" $4s4p^24d$ planar configuration. The magnetic behavior and the absorption spectral data of these complexes in the solid state are discussed in terms of this concept. Observations on the influence of the length of the *n*-alkyl chains attached to the nitrogen atoms on these properties are reported. The zigzag shape of the curves of magnetic moments, atomic polarizations and melting points for this series of complexes are correlated with changes of base strength and coördination power of the parent amines. The smaller the coördination power of the amine, the greater the polarity and thus the "outer orbital" character of the coördinate bonds of the complex. This is also accompanied by a greater ease of bending vibrations of the chelate rings and a greater tendency for interactions between the polarizable molecules in the crystals.

The magnetic behavior of nickel complexes has proved of considerable value in obtaining useful information concerning the bond type and the stereochemistry of such compounds.

Generally magnetic measurements have been carried out on metal complexes in the solid state. However, some measurements also have been made on complexes dissolved in organic solvents. French, Magee and Sheffield,[1] postulate that the weak paramagnetism (1.9 B.M.) exhibited by a methanol solution of diamagnetic bis-(formylcamphor)-ethylenediaminenickel(II) is caused by a partial conversion of the planar complex to a tetrahedral form. Subsequently Willis and Mellor[2] found that a number of tetracovalent nickel(II) complexes, diamagnetic in the solid state, exhibit paramagnetism in various solvents such as pyridine, alcohols, dioxane, chloroform and benzene. The paramagnetism observed in pyridine solutions, corresponding to two unpaired electrons, was attributed to an expansion of the coördination number to six. This solvation reaction was confirmed by Basolo and Matoush[3] through the isolation of the corresponding paramagnetic complexes containing two molecules of pyridine.

Some complexes such as bis-(formylcamphor)-ethylenediaminenickel(II), bis-(salicylaldoxime)-nickel(II) and bis-(N-methylsalicylaldimine)-nickel-(II), diamagnetic in the solid state, exhibit paramagnetism even in "non-coördinating" solvents such as benzene and chloroform.[2] In such cases, where the magnetic moment is intermediate between 0 and 3.2 B.M., it was suggested that a proportion of the molecules of the complex is converted from a planar to a tetrahedral configuration.[2]

In this connection Basolo and Matoush[3] found that no direct correlation exists between the magnetic moment of bis-(formylcamphor)-ethylenediaminenickel(II) in methylbenzenes and the base strength of these solvents. They concluded that the paramagnetism must therefore not be due to solvation but rather to formation of tetrahedral nickel(II) compounds.

Nyholm[4] recently suggested that the intermolecular crystalline forces in solids may sometimes favor the square configuration, whereas in solution, the tetrahedral arrangement of lowest potential energy may be adopted by the isolated molecule.

The magnetic measurements by Fujii and Sumitani[5] and by Clark and Odell[6] on solutions of such complexes in non-coördinating solvents over a

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(1) H. S. French, M. Z. Magee and E. Sheffield, THIS JOURNAL, **64**, 1924 (1942).

(2) J. B. Willis and D. P. Mellor, *ibid.*, **69**, 1237 (1947).

(3) F. Basolo and W. R. Matoush, *ibid.*, **75**, 5663 (1953).

(4) R. S. Nyholm, *Chem. Revs.*, **53**, 263 (1953).

(5) S. Fujii and M. Sumitani, *Sci. Repts. Tôhoku Imp. Univ., First Series*, **37**, 49 (1953).

(6) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955).