Cis-dichlorodiammineplatinum(II). Aquation Equilibria and Isotopic Exchange of Chloride Ligands with Free Chloride and Tetrachloroplatinate(II)*

K. W. LEE and D. S. MARTIN, Jr.

Ames Laboratory, USERDA and the Chemistry Department, Iowa State University, Ames, 1A.50010, U.S.A.

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The equilibrium quotients for the first and second aquation steps of c-Pt(NH₃)₂Cl₂ have been determined by a titration technique. At 25.0° C and an ionic strength of 0.318 M the first and second aquation equilibrium constants are: $K_1 = 3.63 \pm .22 \times 10^{-3} M$, $\Delta H^\circ_1 = 3.4$ kcal and $K_2 = 1.11 \pm .14 \times 10^{-4} M$, $\Delta H^\circ_2 = 10$ kcal.

The kinetics of isotopic exchange of chlorine was investigated in the ternary system: c-Pt(NH₃)₂Cl₂, PtCl₄²⁻, Cl⁻. In addition to exchange via the route of aquation, a direct exchange of chloride between c-Pt(NH₃)₂Cl₂ and PtCl₄²⁻ occurred which is described by the rate expression:

$$R = [c\text{-}Pt(NH_3)_2Cl_2][PtCl_4{}^{2-}](k_{ac}{}' + k_{ac}{}''[Cl^-]^{-1}).$$

At 25° C the rate constants were $k_{ac}{}' = 3.0 \times 10^{-4} M^{-1} sec^{-1}$ and $k_{ac}{}'' = 9.0 \times 10^{-5} sec^{-1}$.

Introduction

A series of investigations from this Laboratory have described the isotopic exchange of chlorine between chloride and the chloride ligands of the complete set of square-planar chloro–ammine complexes of platinum (II).[1-7] These studies have shown that the isotopic exchange has occurred by normal processes in which the chloride ligand is replaced in a reversible aquation of the ligands or by the direct nucleophilic attack of chloride upon the complex. The exchange processes are, accordingly, first order in the complex.

In contrast, it has been found that with the corresponding bromide complexes a portion of the exchange frequently occurs by anomalous processes which involve dimeric transition states.[8-12] With chloride ligands such an anomalous exchange process has only been observed[13] for the case of the anion of Zeise's salt, Pt(C₂H₄)Cl₃⁻. Cis-dichlorodiammineplatinum(II) has assumed special importance because of its recently discovered biological and antitumor activity.[14, 15] The present work was undertaken to provide a more complete

characterization for c-Pt(NH₃)₂Cl₂ and to determine if it participates in an anomalous process in the ternary exchange system, c-Pt(NH₃)₂Cl₂:PtCl₄²⁻:Cl⁻. Also, since present automatic titration equipment can provide titrations which are far superior to those of the earlier studies, the equilibria quotients for the two aquation reactions have been redetermined.

Experimental

Materials

The K₂PtCl₄ was prepared from iridium-free platinum[16] by the method described previously.[1] The cis-Pt(NH₃)₂Cl₂ was prepared by the method of Lebedinskii and Golovaya.[17] However, their method was modified in that the hot filtered solution was cooled only to 35° C for the recrystallization. Only one recrystallization was required under these conditions to prepare very pure c-Pt(NH₃)₂Cl₂. The residue from a thermogravimetric analysis: 65.01% found, 65.02% calcd. The ultraviolet absorption spectrum provides a sensitive criterion of purity for c-Pt(NH₃)₂Cl₂. Figure 1 illustrates the spectrum recorded by a Cary Model 14
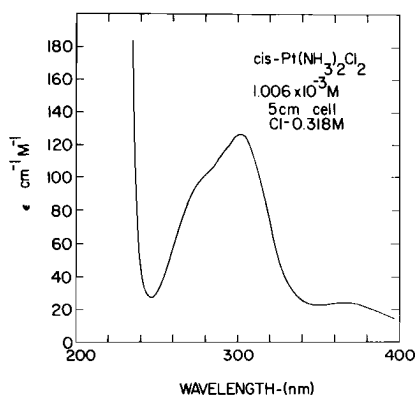

Figure 1. Absorption spectrum of *cis*-Dichlorodiammineplatinum(II).

spectrophotometer for a sample of c-Pt(NH$_3$)$_2$Cl$_2$ of representative purity. In general, the absorbance ratio between the peak at 300 nm and the valley at 247 nm was greater than 4.5 for the preparations under the conditions indicated in Figure 1.
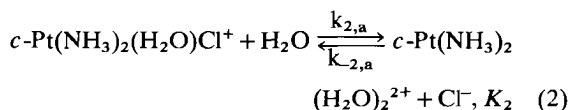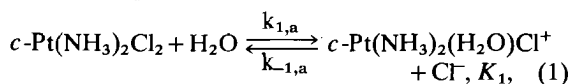
Radioactive ^{36}Cl was purchased in the form of 2.68N HCl from New England Nuclear Corporation, Boston. Dowex 1 × 8 anion exchange resin, 50–100 mesh in the nitrate form, served for the ion exchange resins.

Other materials were of analytical reagent grade. Demineralized water, distilled from alkaline permanganate, was used for all the solutions.

Procedures

Equilibrium Quotients

The c-Pt(NH$_3$)$_2$Cl$_2$ in aqueous solution undergoes the stepwise replacement of the chloride ligands by H$_2$O according to the reactions

$$c\text{-Pt(NH}_3)_2\text{Cl}_2 + \text{H}_2\text{O} \underset{k_{-1,a}}{\overset{k_{1,a}}{\rightleftharpoons}} c\text{-Pt(NH}_3)_2(\text{H}_2\text{O})\text{Cl}^+ + \text{Cl}^-, K_1, \quad (1)$$

$$c\text{-Pt(NH}_3)_2(\text{H}_2\text{O})\text{Cl}^+ + \text{H}_2\text{O} \underset{k_{-2,a}}{\overset{k_{2,a}}{\rightleftharpoons}} c\text{-Pt(NH}_3)_2$$
$$(\text{H}_2\text{O})_2{}^{2+} + \text{Cl}^-, K_2 \quad (2)$$

Each H$_2$O ligand can be titrated for one acidic proton with an endpoint pH of $ca.$ 9. Such titrations from a range of concentration provided therefore the extent of hydration from which the equilibrium quotients could be calculated. The ionic strength for the titrations was adjusted to 0.318M by KNO$_3$. The solutions were aged for periods ranging from 6 to 16 days in thermostats which maintained constant temperature to ±0.05° C. The flasks in which the solutions were aged were covered with black opaque tape to exclude light. Samples for titration were pipetted from the aging flasks into jacketed taped titration cells. The cell cover with the saturated calomel electrode and the glass electrode was attached, and Grade A nitrogen was bubbled through the sample for 4 to 5 minutes with constant mechanical stirring. The titrations were performed by means of a Radiometer Model SBR 2C/ABUc/TTTIc automatic titrator with a 0.2500 ml ±(1μ1+0.07%) capacity. The titer to reach the end point pH for blank solutions, from which only the platinum complex was omitted, was subtracted from the sample titers.

Exchange Studies

The procedure of Reishus and Martin[4] for the separation of ^{36}Cl from the c-Pt(NH$_3$)$_2$Cl$_2$ was utilized except that Hg$_2$Cl$_2$ was precipitated rather than AgCl. Hg$_2$Cl$_2$ has the advantages that its precipitates are more uniform in particle size, it is not so sensitive to photodecomposition and it has a higher equivalent weight than AgCl. The procedure utilizes an anion exchange separation to remove Cl$^-$ and PtCl$_4{}^{2-}$ from

the solutions of c-Pt(NH$_3$)$_2$Cl$_2$ and c-Pt(NH$_3$)$_2$(H$_2$O) Cl$^+$. Rather high Cl$^-$ concentrations were used in these exchange systems to suppress the formation of c-Pt (NH$_3$)$_2$(H$_2$O)Cl$^+$. With these solutions it should be emphasized that very careful control of the elution rate from the resin columns is required to remove the Cl$^-$ to a sufficient level yet permit the elution of a major portion of the c-Pt(NH$_3$)$_2$Cl$_2$.

In the absence of tagged PtCl$_4{}^{2-}$, weighed quantities of c-Pt(NH$_3$)$_2$Cl$_2$, KCl, KNO$_3$ and K$_2$PtCl$_4$, if it were included, were dissolved in a 200 ml volumetric flask. The solution was aged three days in the dark in a thermostat. The exchange was initiated by the addition of the HCl tracer solution. At measured time intervals 20 ml aliquots were withdrawn for the anion exchange separation.

For exchange of c-Pt(NH$_3$)$_2$Cl$_2$ in the presence of tagged PtCl$_4{}^{2-}$, two solutions of equal volume were prepared. One of these was prepared by dissolving weighed amounts of KCl, KNO$_3$ and c-Pt(NH$_3$)$_2$Cl$_2$ in a 100 ml volumetric flask and the other by dissolving the same amounts of KCl and KNO$_3$ and the desired amount of K$_2$PtCl$_4$. Into the K$_2$PtCl$_4$ solution was added 25 μl of the HCl tracer solution. This solution was allowed to stand in the dark for at least 3 days and in some cases as long as 30 days. The exchange was started by mixing the two solutions.

Results and Discussion

Aquation Equilibria for c-Pt(NH$_3$)$_2$Cl$_2$

The titer, T, for an aged solution prepared by dissolving a mol c-Pt(NH$_3$)$_2$Cl$_2$ to give a liter of solution is related to the equilibrium quotients by the equation[18]

$$T^3 + K_1 T^2 + (K_1 K_2 - aK_1)T - 2aK_1 K_2 = 0 \quad (3)$$

The titers measured for a series of concentrations, a, are listed in Table I. At high dilution, values of $T/a > 1$ were found so that the second aquation, equation 2, occurred to an appreciable extent. The equilibrium quotients were computed by an iterative weighted nonlinear least squares procedure in which the quantity S was minimized.

$$S = \Sigma w_i (T_{i\text{-obsd}} - T_{i\text{-calcd}})^2 \quad (4)$$

The weights, w_i, were taken as $1/\sigma_i{}^2$ where σ_i was the standard deviation for the titrations made with the concentration a_i. K_1 and K_2 obtained from the least squares treatment for 25° and 35°C together with the indicated $\Delta H°$ are included in Table I together with the calculated value of the titer.

With the wider range of concentrations in the present work and the number of titrations for statistical treatment possible with the automatic titrator, the values for K_1 and K_2 are much more reliable than those of

TABLE I. Titration Data for the Aquation Equilibrium Quotients of c-Pt(NH$_3$)$_2$Cl$_2$, K_1 and K_2, for Ionic Strength of $0.318\,M$.

Number Titrations	Total c-Pt(NH$_3$)$_2$Cl$_2$ a (mM)	Equilibrium Titer, T (mM)	
		Obsvd.	Calcd.
		25°C	
8	0.1202	0.162 ± .003	.1642
9	.2004	.255 ± .003	.2501
8	.3989	.440 ± .006	.4376
9	.4007	.425 ± .005	.4392
8	.9972	.876 ± .010	.9052
10	1.0018	.930 ± .005	.9084
8	1.3960	1.157 ± .011	1.1716
7	1.9944	1.482 ± .019	1.5291
10	2.0037	1.558 ± .009	1.5343
13	4.0073	2.504 ± .021	2.5123

$$K_1 = 3.63 \pm .22 \times 10^{-3}\,M$$
$$K_2 = 1.11 \pm .14 \times 10^{-4}\,M$$

		35°C	
8	0.2994	0.357 ± .005	.3771
8	.2997	.373 ± .003	.3774
9	.4791	.550 ± .002	.5495
9	.4795	.557 ± .004	.5499
9	.7187	.759 ± .005	.7565
9	.7192	.764 ± .004	.7569
12	1.1978	1.111 ± .005	1.1223
11	1.1986	1.126 ± .006	1.1229
12	1.4972	1.334 ± .005	1.3284
11	1.4980	1.332 ± .006	1.3290
14	2.9944	2.202 ± .009	2.2041
12	2.9970	2.200 ± .010	2.2055

$$K_1 = 4.37 \pm .13 \times 10^{-3}\,M$$
$$K_2 = 1.88 \pm .08 \times 10^{-3}\,M$$

$$\Delta H^{\circ}_1 = 3.4 \pm 1.2 \text{ kcal}$$
$$\Delta H^{\circ}_2 = 10 \pm 2 \text{ kcal}$$

Reishus and Martin[4] who were required to use a fresh sample for each point on a potentiometric titration curve.

The upper limit on the ranges of concentrations, a, was the solubility of the c-Pt(NH$_3$)$_2$Cl$_2$, while the lower limit was set by the loss of accuracy in the potentiometric endpoint. Even so, the present values of K_1 were in fair agreement with the earlier ones. However, the present values of K_2 are much smaller. The values of ΔH° are positive and no more than 10 kcal and rather typical for aquation reactions of halide ligands in platinum(II) complexes. Both K_1 and K_2 for the c-Pt(NH$_3$)$_2$Br$_2$ complex[12] are very nearly one third the value for the chloride complex which is consistent with the assignment of Pt^{II} as a Class B metal by Ahrland, Chatt and Davies[19] or a soft acid by Pearson.[20]
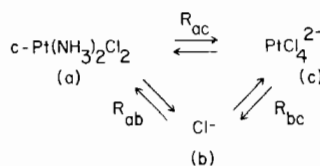

Figure 2. Exchange scheme for the three component system c-Pt(NH$_3$)$_2$Cl$_2$, PtCl$_4^{2-}$, Cl$^-$.

Chloride Ligand Exchange

For all of the exchange studies the chloride ion component comprised the largest fraction of chlorine. The chloride ion concentration was maintained at high levels to suppress the extent of aquation of the complexes. Both complexes undergo aquation of the chloride ligands; and, indeed, the aquation process contributes to isotopic exchange. However, with the lowest chloride concentration employed (67 mM), less than 6% of the c-Pt(NH$_3$)$_2$Cl$_2$ and less than 18% of the PtCl$_4^{2-}$ would have undergone aquation at equilibrium. Very great complications in the treatment are avoided by utilization of the approximation that the aquation is negligible. In this case the exchanging system contains only significant concentrations of the three components shown in the scheme of Figure 2. Isotopic exchange between any pair of components can occur so a description of such exchange requires the evaluation of the three indicated rates R_{ab}, R_{bc}, R_{ac} mol l^{-1} sec^{-1}. The three-component exchange requires two independent differential equations for characterization, viz:

$$\frac{du_a}{dt} = R_{ab}(S_b - S_a) + R_{ac}(S_c - S_a) \tag{5}$$

$$\frac{du_c}{dt} = R_{bc}(S_b - S_c) + R_{ac}(S_a - S_c) \tag{6}$$

The subscripts refer to the components indicated and u represents a concentration of radioactive ^{36}Cl, normally specified in units of cts m^{-1} l^{-1}. The S quantities represent the specific activities of the indicated component (cts m^{-1} mol^{-1}) and are defined by the following,

$$S_a = u_a/2a; \quad S_c = u_c/4c; \quad S_b = (I - u_a - u_b)/b \tag{7}$$

where I is the total concentration of ^{36}Cl.

For treatment of data the quantity, F_a, was calculated from each determined value of u_a,

$$F_a = (u_a - u_{a,o})/(u_{a,\infty} - u_{a,o}), \tag{8}$$

where the subscripts o and ∞ correspond to zero and infinity time. The values for infinity time were obtained by the collection and count of the total chloride of a solution aliquot together with the relation,

$$S_\infty = I/(2a + b + 4c). \tag{9}$$

In a two component exchange F_a is considered the fraction of exchange. However, for a three component

TABLE II. Isotopic Exchange Experiments. 25°C, Ionic Strength 0.318M.

No. Expts.	c-Pt(NH$_3$)$_2$Cl$_2$ a (mM)	Cl⁻ b (mM)	PtCl$_4^{2-}$ c (mM)	$S_c°$	Time of Half-Exchange min.	
					Obsvd.	Calcd.
2	5.00	134	0	–	903 ± 45	936
6	2.50	134	0	–	984 ± 40	970
6	2.50	134	10	2 $S_b°$	612 ± 27	636
4	2.50	134	20	2 $S_b°$	517 ± 33	491
2	2.50	67	10	2 $S_b°$	524 ± 6	528
2	2.50	134	10	0	774 ± 35	727

system, the value of F_a can in certain circumstances be greater than 1. For a two component exchange the quantity, $(1-F_a)$, is an exponential function in time so the plot of $\log(1-F_a)$ is linear in time; and from such a plot a half-time of exchange can be evaluated. For a three component exchange $(1-F_a)$ is the sum or difference of two exponential functions, and the plot of $\log(1-F_a)$ will not be linear over all time. For the conditions of all the exchange reactions listed in Table II, the plots of $\log(1-F_a)$ could be followed to values of 0.2–.35 for $(1-F_a)$. Over this region the plots did not deviate from straight lines by more than the uncertainties in the points. A plot for a typical experiment is presented in Figure 3. Accordingly, observed times for half-exchange for each experiment were calculated as (log 2) divided by the slope of the weighted linear least squares fit to the experimental points. Average values for the observed times of half-exchange in the experiments under each set of experimental conditions are included in Table II.

From Table II it is seen that the times of half-exchange for experiments in which PtCl$_4^{2-}$ was absent were greater than 900 min. These times were significantly reduced by the presence of PtCl$_4^{2-}$, so it was
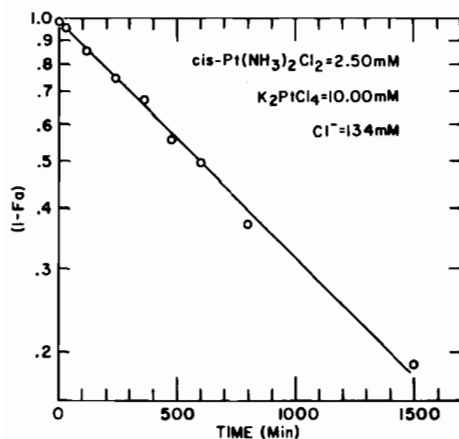

Figure 3. Typical exchange experiment. Observed time of half-exchange = 609 ± 14 min.

concluded that PtCl$_4^{2-}$ influences the isotopic exchange for c-Pt(NH$_3$)$_2$Cl$_2$. The two rates, R_{ab} and R_{bc}, indicated in Figure 2, can each be resolved into two components.

$$R_{ab} = R_{ab}° + R_{ab}' \qquad (10)$$

$$R_{bc} = R_{bc}° + R_{bc}' \qquad (11)$$

The components with the zero superscripts correspond to rate processes in the absence of the other complex, whereas a primed component corresponds to a catalysis of the exchange process between one complex and the free chloride by the other complex. The $R_{ab}°$ values were obtained from the exchange experiments in the absence of PtCl$_4^{2-}$ by means of the following equation.

$$R_{ab}° = \frac{2ab \ln 2}{(b+2a)\tau_{1/2}} \qquad (12)$$

If the exchange between c-Pt(NH$_3$)$_2$Cl$_2$ and Cl⁻ occurs primarily by the aquation process, equation 1, with negligible formation of c-Pt(NH$_3$)$_2$(H$_2$O)Cl⁺, $R_{ab}°$ is described by the equation:

$$R_{ab}° = k_{1,a}[c\text{-Pt(NH}_3)_2\text{Cl}_2] \qquad (13)$$

The value of $k_{1,a}$ indicated by the experiments in the absence of PtCl$_4^{2-}$ are given in Table III. This value of $2.30 \pm .11 \times 10^{-5}$ sec⁻¹ for 25° C was slightly smaller than the value of 2.5×10^{-5} reported by Reishus and Martin,[4] but the agreement was within a reasonable limit from the uncertainty of the experiments. The value of $k_{1,c}$ was taken as the aquation rate constant for PtCl$_4^{2-}$ of Grantham et al.[1].

For an initial treatment of data the catalysis of exchange for each complex by the other complex was

TABLE III. Rate Constants for Exchange Processes in the System c-Pt(NH$_3$)$_2$Cl$_2$: PtCl$_4^{2-}$: Cl⁻.

$k_{1,}$[a]	$2.30 \pm .11 \times 10^{-5}$ sec⁻¹
$k_{1,}^{ca}$	$3.9 \pm .2 \times 10^{-5}$ sec⁻¹ [*]
k_{ac}'	$3.0 \pm .2 \times 10^{-4}$ sec⁻¹ M^{-1}
k_{ac}''	$9.0 \pm .6 \times 10^{-5}$ sec⁻¹

[a] From Reference 1.

considered to be negligible, *i.e.*, $R_{ab}' = R_{bc}' = 0$. The time of half-exchange for $c\text{-Pt(NH}_3)_2\text{Cl}_2$ was decreased by the increase in PtCl_4^{2-} concentration and by the decrease in Cl^- concentration. Therefore, following the treatment for the $c\text{-Pt(NH}_3)_2\text{Br}_2$ system[12], the exchange rate, R_{ac}, was represented by the function,

$$R_{ac} = (k_{ac}' + k_{ac}''/([\text{Cl}^-])[c\text{-Pt(NH}_3)_2\text{Cl}_2] \\ [\text{PtCl}_4^{2-}] \quad (14)$$

With various trial values of k_{ac}' and k_{ac}'' and the indicated values of $k_{1,c}$ and $k_{1,a}$, the differential equations 5 and 6 were solved numerically by the Runge–Kutta method.[21] The times of half-exchange were evaluated from the numerical solutions. In this way it was possible to determine by an iterative computation the values for the constants k_{ac}' and k_{ac}'' which minimized the quantities, $\Sigma(\tau_{1/2\text{-calcd}} - \tau_{1/2\text{-obsd}})^2$ for the three sets of conditions with initially tagged PtCl_4^{2-}. The computed values for the times of half-exchange are included in Table II, and they agree quite satisfactorily within the experimental uncertainty with the observed times. Values for the indicated rate constants are included in Table III.

In the experiments for which the PtCl_4^{2-} was initially not tagged, the time of half-exchange was somewhat longer than for the experiments with comparable concentrations in which the PtCl_4^{2-} was tagged. With the assumption that $R_{ab}' = 0$ and with the rate constants of Table III a computed value for the time of half exchange was actually slightly smaller than the observed time of half-exchange. However, the difference between the computed and the observed values was well within the reasonable uncertainty. It was concluded therefore that there is negligible catalysis of the exchange between $c\text{-Pt(NH}_3)_2\text{Cl}_2$ and Cl^- by PtCl_4^{2-}. Rather, the enhancement of the exchange rates involves a trading of chloride ligands between the two different complexes without the formation of a free chloride intermediate.

The rate constant, k_{ac}', was only 4% as large and k_{ac}'' was 17% as large as the corresponding constants for the system with bromide ligands at 25° C. The lower values for the chloride system likely reflect the reduced stability of the chloride bridges so the formation of the dimeric transition state will contribute a higher component to the activation enthalpy. The values of R_{ac} for the experimental conditions were scarcely more than 10% of the contribution of aquation to R_{bc} in any experiment. Hence, the contribution of the ligand trading to the R_{ac} should not cause an experimentally detectable change in the time of half-exchange for PtCl_4^{2-}.

The chloride-dependent process, characterized by k_{ac}'' was more than twice as rapid as the chloride-independent process under any of the experimental conditions. A possible mechanism for the chloride-independent process, following the proposal for the
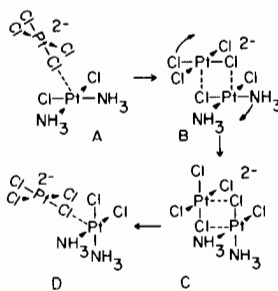

Figure 4. Possible double bridged mechanism for trading of ligands between $c\text{-Pt(NH}_3)_2\text{Cl}_2$ and PtCl_4^{2-}.

corresponding bromide systems,[11,12] is shown in Figure 4. It was found for $c\text{-Pt(NH}_3)_2\text{Br}_2$ that a portion of the bromide-dependent process occurred by a process which presumably involved a singly bridged intermediate, $\text{Br}_3\text{Pt–Br–Pt(Br)(NH}_3)_2$. However, this process did not account for the total bromide-dependent process. A portion of the process was accordingly presumed to occur by a similar transition state as shown in Figure 4 except one of the non-bridging halide ligands was replaced by an aquo group. It has not been possible to characterize the chloride system as completely as the bromide system and possibly the chloride-dependent process could involve either or both of the processes proposed for the bromo complexes. The poorer characterization for the chloride system results from the lower values in R_{ac} which can be obtained in comparison to R_{ab}. Thus, in none of the experimental conditions was R_{ac}, which must be obtained by differences, as large as R_{ab}. In part, this was because of the higher stability constants for bromide complexes; so it was possible to work with lower bromide concentrations than chloride and therefore to achieve a higher contribution in the halide-dependent process. Although the trading of chloride ligands between complexes has been demonstrated, the limitations in the accuracy which it has been possible to achieve here indicated that meaningful activation parameters would not be obtained from temperature dependence studies, and they were not attemped.

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