The preparation and kinetic studies of some rhodium(III) complexes.

Stephen Richard Koprich
University of Windsor

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THE PREPARATION AND KINETIC
STUDIES OF SOME RH(III) COMPLEXES

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UNIVERSITY OF WINDSOR

STEPHEN RICHARD KOPRICH, B.A. (WESTERN ONTARIO)

Chemistry Department
University of Windsor
Windsor 11, Ontario

February, 1970
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He who spares his words is truly wise.

Proverbs. XVII. 27
ACKNOWLEDGMENT

I wish to thank my committee, Dr. A. Gnyp, Dr. D. J. McKenney, Dr. R. C. Rumfeldt, and my external examiner, Dr. A. R. Norris (Queen's), for their reading and comments on this dissertation. Especially, I wish to thank Dr. E. J. Bounsall for the conception and direction of this work.
A series of complexes of the type Rh(cyclam)X^2+ and Rh(cyclam)XY^R+ have been prepared and characterized, where cyclam represents 1,4,8,11-tetraazacyclotetradecane, and X and Y represent OH^-, H_2O, Cl^-, Br^-, I^-, N_3^-, NCS^-, and NO_2^- . The infrared and electronic spectra are discussed to assign the cis and trans isomers, the linkage isomers, and the Rh-ligand stretching frequencies above 250 cm\(^{-1}\). The thermodynamic trans effect is related to shifts in the Rh-ligand stretching frequencies and the acid strengths of the aquo complexes. The intensities of the d-d transitions are related to distortion of the octahedral field to support the cis and trans assignments, and compared to show the decrease in bond constraint for propylene linkages in place of ethylene. Steric constraint accounts for the single case of stereoisomerization by cis-Rh(cyclam)I^2+ . Catalytic approaches to Rh(III) syntheses and the advantages of the hydroxo intermediate pathway as a convenient preparatory technique are discussed. Some attempted preparations are given with explanations for their failures.

The experimental technique for spectrometric kinetic studies, and a pooled variance method for determining the standard error on the temperature dependent data, are given. The kinetic results for the acid hydrolysis of the trans-dihalo complexes are presented and related to the trans effect, both in terms of the nonreactive ligand and the leaving group. The interference by base hydrolysis is shown, and its elimination by the use of acid media is described. The additional problem of interference by tri-iodide formation in acid iodide media is also shown with an explanation of how it can be minimized.
The expected I > Br > Cl order for the kinetic trans effect, and the Cl > Br > I order for the leaving group, are found. A brief discussion of the mechanism is included, although acid hydrolysis studies, by themselves, do little to elucidate the intimate mechanism in terms of displacement versus dissociation. The base hydrolysis reactions are discussed and related to the trans effect.

Suggestions for further study are made on the basis of the scope provided by the large number of cyclam complexes successfully prepared and characterized, and their unexpected sensitivity to base hydrolysis.
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I. INTRODUCTION

1. Preparation of Rhodium(III) Complexes

Macro cyclic quadridenate ligands such as 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,7,10-tetraazacyclododecane (cy clen) have become important since they provide a substrate for octahedral substitution mechanistic studies with two advantages over the more commonly studied bisethylenediamine systems.

First, the rigidity of the quadridenate structure is a barrier to stereoisomerization during substitution reactions making the acid hydrolysis studies of Co(III) simpler. Poon and Tobe\(^1\) found that all the substitutions (acid hydrolysis, anation, and base hydrolysis) of some trans-diacidocyclamcobalt(III) complexes occurred with complete retention of configuration. In addition, they\(^2\) found that the cis isomers also retained the less stable cis configuration on substitution, although a slow subsequent isomerization was observed. This cis to trans isomerization was shown to go by way of the labile cis-Co(cyclam)-(OH)(H\(_2\)O)\(^{2+}\) cation\(^3\). The isomerization of the cis-hydroxoaquo complex is accompanied by exchange of two of the four amine protons, which was assumed to be necessary for the inversion of the configurations of the nitrogen atoms. The configurational requirements of the nitrogen...
donors are the most important barrier to stereochemical change. There is only one possible cis configuration:

\[
\begin{array}{c}
+ \text{N-3-N} \\
\frac{1}{2} \frac{1}{2} \\
\text{N-3-N} \\
+ \\
\end{array}
\]

The plus represents a proton which points above the plane. However, there are five possible nonenantiomorphic trans forms. There has been only one form detected, and it was assigned as a meso form on the basis of the diaquo complex n.m.r., ring strain arguments, and analogy with the known structure of Ni(cyclam)Cl₂, determined by x-ray diffraction⁴. The two possibilities for meso configurations are:

\[
\begin{array}{c|c}
+ \text{N-3-N} & + \text{N-3-N} \\
\frac{1}{2} \frac{1}{2} & \frac{1}{2} \\
\text{N-3-N} & \text{N-3-N} \\
+ & - \\
\end{array}
\]

It can be seen that cis to trans isomerization involves the inversion of two of the nitrogens regardless of which trans configuration is present. The most likely mechanism for the inversion is proton exchange, which, as mentioned, was found to accompany the stereochemical reaction studies by Poon and Tobe³.

Secondly, bis(ethylenediamine) complexes can form either a trigonal bipyramid or a square pyramid activated complex depending on the crystal field activation energy involved. Although the crystal field activation energy is large for the Rh(III) and Ir(III) congeners, and therefore, favors the square pyramid, compensating factors such as π-bond stabilization can favor the trigonal bipyramid for Co(III). The steric restrictions imposed by cyclam favor a square pyramid¹.
In addition, cyclam complexes are much simpler than naturally occurring quadridentate cyclic ligands such as the porphyrins. The four substituted pyrrole rings linked by four methine bridges add the complications of substituent, steric, and conjugative effects, not present in cyclam.

Although cyclen is more symmetric than cyclam, the former does not yield both the unfolded (trans) and folded (cis) configurations, while the latter does. This property is valuable for cis and trans effect comparisons, and therefore, cyclam is a more important ligand. Fortunately, cyclam is also the more stable compound in the uncoordinated form, which is important for preparatory convenience. The stability of cyclam is explained by Tobe as the result of diagonal hydrogen bridging by two of the amine hydrogens:

This is made possible by a folded configuration of the free cyclam molecule. This structure leaves two lone pairs of electrons available for direct protonation, which agrees with the two fast and the two slow protonations of the four nitrogens, found by Curtis. In comparison, the protonation of the open chain follows a regular four step sequence.

Recent work has produced some cyclen complexes and several cyclam complexes. Collman and Schneider have prepared some cis-Co(cyclen)X₂⁺ complexes, and also, cis-Rh(cyclen)Cl₂⁺. Allen and Pedwell have prepared cis-Cr(cyclam)Cl₂⁺ as well as some cyclam complexes of several other metals; Cu(II), Zn(II), Cd(II), and Pd(II). Tobe and coworkers
have prepared several cis\textsuperscript{2} and trans\textsuperscript{5}-Co(cyclam)X\textsubscript{2}\textsuperscript{2+} complexes, a few Ni(cyclam)X\textsubscript{2} complexes\textsuperscript{9}, and some cis and trans-Co(cyclam)XY\textsuperscript{2+} complexes\textsuperscript{2}, which were used to study the mechanism and steric course of octahedral acid hydrolysis\textsuperscript{1,2,3}. Bounsall and Pedwell\textsuperscript{10} have attempted to prepare some diacidocyclamiridium(III) complexes by the direct reaction of IrCl\textsubscript{3}·3H\textsubscript{2}O and cyclam in water and also methanol. Even the use of a NaBH\textsubscript{4} catalyst did not give a well-defined product.

In addition to these cyclic ligands, the linear quadridentate analogs have received recent study. The triethylenetetramine (trien) complexes of Co(III) and Rh(III) were reported by Gillard and Wilkinson\textsuperscript{11}, and also, by Sargeson\textsuperscript{12}. The even more similar analog to cyclam, 1,4,8,11-tetraazaundecane (2,3,2-tet), was studied by Alexander\textsuperscript{13} and Gillard\textsuperscript{14}. Gillard termed these open chain ligands as facultative, based on their ability to assume different configurations. The two stable cis configurations as opposed to one for cyclam, make these systems more complicated and less desirable as simple substrates for mechanistic studies.

Since Rh(III) complexes are relatively inert, causing preparations to be time-consuming, attempts have been made to use catalysts. Several successful ones have been reported by Gillard and coworkers\textsuperscript{15}. A series of reducing agents including ethanol, sodium borohydride, formic acid, hypophosphorous acid, and hydrazine catalyzed the direct reaction of rhodium trichloride and weakly basic ligands such as pyridine, \textgamma-picoline, and bipyridyl. However, the direct reaction was not successful for more strongly basic ligands such as ammonia and ethylenediamine, because a hydrated rhodium oxide is the only product. An indirect approach was successful, since a tetrapyridine complex
can be substituted with the more strongly basic ligands using the same catalysts.

Gillard originally explained this catalytic behavior in terms of hydride transfer with the intermediate formation of labile hydrides. However, in subsequent work, he argued in favor of reduction to Rh(I), since the catalysts are reducing agents as well as hydride transfer agents. This reduction is then followed by bridged complex formation with an unreduced Rh(III) complex and subsequent interchange of oxidation states, strongly labilizing the trans ligand, since Rh(I) is square planar.

\[
\text{Rh(I)}-\text{Cl-Rh(III)}-\text{Cl} \ (\text{inert}) \rightarrow \text{Rh(III)}-\text{Cl-Rh(I)}-\text{Cl} \ (\text{labile})
\]

The hydrazine complexes were readily isolated and were found to be relatively inert, which ruled out the possibility of labilization by hydrazine complex formation. However, the hydrazine complexes are labilized in an acid solution, but this is due to hydrazinium formation, which is then a labile ligand.

Recent work by Rund has supported the reduction theory over the hydride transfer labilization theory. Catalysts containing Rh(I) compounds were found to be more active than those containing reducing and hydride-producing agents. Hydrido complexes of Rh(III) did not exhibit catalytic activity, and hydrido complexes of Rh(I) were not formed under the reaction conditions used for the pyridination reaction, which was studied. o-Phenanthroline inhibited the pyridination reaction, and this was interpreted as the result of its scavenger property for catalytic Rh(I). The substitution rate dependence of the reactants for
one of the catalyzed Rh(III) reactions was determined. However, the results did not unambiguously support one mechanism.

Basolo and Bauer$^{18}$ have prepared several diacidobis(ethylene-diamine)iridium(III) complexes using hypophosphorous acid as a catalyst, and some mixed chloroacid complexes of the type trans-$M$(en)$_2$$C$$L$X$^+$ ($M$ is Rh or Ir) by a new photochemical method starting with trans-$M$(en)$_2$Cl$^+$. This method involves the photo (Vycor-filtered GEUAll, 1200 W mercury arc lamp) acid hydrolysis of the dichloro complex in water at 25° C, followed by anation with the desired anion. The method is complicated by the need to remove chloride using silver nitrate, since the chloride present is expected to interfere with the desired anion, and sometimes, by unreacted dichloro complex removal.

Although the reactions of Co(III) have received more attention than those of Rh(III) and Ir(III), mainly because more cobalt complexes have been prepared, the latter are becoming more important as new approaches to the preparatory techniques are making more rhodium and iridium complexes available for study.

2. The Trans Effect

One of the more interesting features of substitution reactions, subject to kinetic studies, is the activation by nonreactive groups. If the activation is by a trans group, it is called the trans effect, a term introduced by Chernyaev in 1926, and if it is cis activation, it can be called the cis effect. This activation can be a destabilizing effect, in which case it can be called a thermodynamic trans effect, or it can be a labilizing effect, in which case it can be called a kinetic trans effect. Of course, as is generally true, there is no
requirement that the kinetic and thermodynamic effects are in the same direction. Any theory of the trans effect (or cis effect) must make clear whether it is explaining a ground state or a transition state effect, and the same for experimental determinations. When the trans effect is mentioned by itself, a kinetic effect is meant as is clearly stated in a definition by Basolo as "the effect of a coordinated group upon the rate of substitution reactions of ligands opposite it in a metal complex". This usage has developed because of the historical predominance of Pt(II) kinetic trans effect studies.

The substitution reactions, which are most conveniently studied in aqueous media are acid hydrolysis, base hydrolysis, and anation. The hydrolysis terms describe the reaction depending on the product. Acid hydrolysis gives an aquo product and has also been called aquation; base hydrolysis gives a hydroxo product, and was formerly called simply hydrolysis. Basolo suggested that the simple term, hydrolysis, be applied to a reaction giving an equilibrium mixture of aquo and hydroxo products. Of course, the product is determined by the pH of the reaction medium and the acidity of the aquo complexes. The predominant reaction is nucleophilic attack by water because of its overwhelming concentration relative to other nucleophiles in aqueous solution. The third reaction, anation, refers to substitution of water by any anion.

The kinetic activation effects can be studied by means of any substitution reaction, although acid hydrolysis has been most commonly used. Since water is the common entering group in high concentration (i.e. the solvent), these studies are of little direct value mechanistically due to a pseudo-first order rate law. However, by isolating
two ligands through the occupation of four positions by an amine, preferably chelated to increase inertness, the labilizing effects of the two relatively more labile ligands can be studied conveniently.

The trans effect for octahedral complexes follows a similar order to that of square planar complexes with respect to \( \sigma \)-donors, while \( \pi \)-bonders can give rise to some differences. In comparing ambident ligands such as nitro and thiocyanato, the particular bond which is present must be kept in mind. The square planar Pt(II) data is by far the most extensive and gives the order\(^23\): \( \text{CO}, \text{CN}^-, \text{C}_2\text{H}_4 > \text{PR}_3, \text{H}^- > \text{CH}_3^- \), \( \text{C}_6\text{H}_5^-, \text{NO}_2^-, \text{I}^-, \text{SCN}^- > \text{Br}^-, \text{Cl}^- > \text{py}, \text{NH}_3, \text{OH}^-, \text{H}_2\text{O} \). A tentative order for Pt(IV), based on isolated products\(^24\) as well as rate data\(^25\) is: \( \text{I}^- > \text{Cl}^- > \text{NO}_2^- > \text{NCS}^- > \text{OH}^- > \text{NH}_3 \). However, the substitution reactions of Pt(IV) are catalyzed by light, single electron reducing agents\(^26\), and Pt(II). An order for Co(III) based on rate data\(^27\) for the acid hydrolysis of Co(en)\(_2\text{Cl}^+ \) is \( \text{OH}^- > \text{NO}_2^- > \text{N}_3^- > \text{CN}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 > \text{NCS}^- \). This is changed to \( \text{NO}_2^- > \text{CN}^- > \text{N}_3^- > \text{NH}_3 > \text{Br}^- > \text{Cl}^- > \text{OH}^- > \text{NCS}^- \), based on activation energies. However, two different mechanisms appear to be involved depending on the \( \pi \)-donor or acceptor properties of the trans ligand (see p. 14).

For square planar Pt(II) complexes, the trans effect is more important than the cis effect, while octahedral Co(III) exhibits both effects strongly depending on the bonding characteristics of the ligands. The Pt(II) trans effect is "one of the most dramatic effects on the rates of substitution reactions in metal complexes, spanning many orders of magnitude"\(^28\). Zvyagintsev and Karandasheva\(^29\) showed quantitative evidence for the degree of the effect with the rate constants and activation energies for the substitution of chloro by pyridine.
in the reaction

\[
\begin{align*}
\text{NH}_3 & \quad \text{NH}_3 \\
\text{L-Pt-Cl} + \text{py} & \rightarrow \text{L-Pt-py} + \text{Cl}^- \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

There was a hundred-fold increase in rates from L = Cl\(^-\) to L = C\(_2\)H\(_4\), and a decrease of 8 kcal mole\(^{-1}\) from L = Cl\(^-\) to L = NO\(_2\). Basolo and coworkers\(^{30}\) found an even greater range of rates for the reaction of trans-Pt(P\(_3\)Et\(_3\))\(_2\)Cl with pyridine. A 10\(^5\)-fold increase in rates was observed from L is Cl\(^-\) to L is P\(_3\)Et\(_3\), H\(^-\), or CH\(_3\). In comparison, the cis effect was very small as determined by the range of rates for the reaction of cis-Pt(P\(_3\)Et\(_3\))\(_2\)Cl with pyridine. There was only a three-fold increase from L is Cl\(^-\) to L is CH\(_3\).\(^{-30}\) However, when the trans effect is very small, the cis effect can become relatively important.

Martin and coworkers\(^{31}\) have shown that the hydrolysis rates of the PtCl\(_4\)\(^2-\) to Pt(NH\(_3\))\(_2\)Cl\(^+\) series can be explained in terms of a cis effect instead of the classical trans effect and bond strength argument.

For Co(III), the cis effect can be very pronounced, and greater than the trans effect even for good trans activators. From a study by Tobe and coworkers\(^{32}\), it is evident that \(\pi\)-bonding plays an important role in Co(III) reactions, and can account for the relative importance of the cis and trans effects. The acid hydrolysis of cis and trans-Co(en)\(_2\)Cl\(^+\) at 25\(^0\) C was used to compare cis and trans rate data (Fig. 1). It was found that there was a stronger cis effect for \(\pi\)-donors, and a stronger trans effect for \(\pi\)-acceptors. The most inert complexes involved L being NH\(_3\) or H\(_2\)O, which are neither \(\pi\)-donors nor \(\pi\)-acceptors.

The overall labilization, both cis and trans, by \(\pi\)-acceptors is explained by the withdrawal of t\(_{2g}\) electron density\(^{33}\). This reduces the
electron density around the trans ligand, and to a lesser extent around the cis ligands, which facilitates nucleophilic cis attack, that is, solvent assistance in chloro bond breaking. Since the trans electron density decrease is greater, \( \pi \)-acceptors display a greater trans effect, and involve more bond making in the activated complex.

L is \( \pi \)-acceptor

Fig. 1. Acid Hydrolysis Rates of Co(en)_2LCl^+
On the other hand, a π-donor puts more negative charge on the metal facilitating dissociation. This is more strongly a cis effect, since a cis ligand can more effectively π-donate to the vacated orbital with less rearrangement in the activated complex with a tetragonal pyramid configuration. The trans ligand cannot do this as illustrated. The vacated orbital is in dashes, in the diagrams below.

For a trans effect, rearrangement to a trigonal bipyramid is necessary for similar π-donation and stabilization of the activated complex.

The diagram shows efficient overlap with the vacant $d_{x^2-y^2}$ (dashed) in a trigonal bipyramid activated complex. The crystal field activation energy for rearrangement to a trigonal bipyramid is high for Co(III), and even higher for Rh(III) and Ir(III). Therefore, the cis effect is expected to be stronger for the cobalt congeners. However, the displacement mechanism is more important for the heavier metals, and as such, the π-donor mechanism for activated complex stabilization may not be operative. This would make the σ-donor ability of L more important, and result in a stronger trans than cis effect.
The duality of mechanism, which was used to explain the relative magnitude of the cis and trans effects, was not supported by Tobe\textsuperscript{34} in detailed kinetic studies over a wide range of non-solvolytic conditions. Langford\textsuperscript{35} suggested that the mechanism for Co(III) reactions is essentially unimolecular, and the duality of behavior arises from the two possible configurations of the dissociated activated complex, the trigonal bipyramid and the tetragonal pyramid. This contradicts the $\pi$-acceptor theory, but trans labilization can be explained in terms of a $\sigma$-donor theory.

Inductive effects using the $\sigma$-bonding metal orbitals with directional properties results in a trans effect. The $s$ and $e_g$ metal orbitals have an equal cis and trans inductive effect, while the $p$ orbitals have only a trans effect. Therefore, the $\sigma$-inductive effect is an overall trans effect\textsuperscript{36}. This can also be considered as covalent competition for the $\sigma_x$ M.O., by which $L$ takes a larger share of the molecular orbital leaving less for the leaving group, $X$.

\begin{center}
\begin{tabular}{c}
\textbf{L} \textcircled{\textbf{C}} \textbf{Pt} \textcircled{\textbf{C}} \textbf{X} \\
Equal sharing of $\sigma_x$
\end{tabular}
\hspace{1cm}
\begin{tabular}{c}
\textbf{L} \textcircled{\textbf{C}} \textbf{Pt} \textcircled{\textbf{C}} \textbf{X} \\
Competition by $L$ for $\sigma_x$
\end{tabular}
\end{center}

The use of cyclam complexes prevents trigonal bipyramid formation, which is supported by retention of configuration during substitution reactions. As such, the trans $\pi$-donor mechanism cannot be operative. This is supported by the observation that cis-Co(cyclam)Cl\textsubscript{2} is 15000 times as labile as the trans isomer at 25\textdegree C. In comparison, there is only a seven-fold increase in rates at 25\textdegree C from the cis to trans bisethylenediamine analogs. In addition, there is 35\% steric change.

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for trans-Co(en)$_2$Cl$_2^+$, and none for the cis isomer, which supports the two configurations for the activated complex, a trigonal bipyramid for trans and a tetragonal pyramid for cis. Another result of this study was only a thirty-fold decrease of rate from trans-Co(en)$_2$Cl$_2^+$ to trans-Co(cyclam)Cl$_2^+$, which suggests that the $\pi$-bond stabilization of the activated complex is almost cancelled by the crystal field activation energy for rearrangement. Further evidence for the similarity of energy for the two configurations is given by the presence of both for Ni(CN)$_5^{3-}$ in the [Cr(en)$_3$][Ni(CN)$_5$]$\cdot\frac{1}{2}$H$_2$O unit cell.

Some evidence for the increased importance of the $\sigma$-trans effect for Rh(III) is provided by the base hydrolysis rates\(^{38}\) of Rh(NH$_3$)$_5$Cl$_2^+$ and cis-Rh(en)$_2$Cl$_2^+$, which are faster in base, while the trans-Rh(en)$_2$Cl$_2^+$ rate is the same in acid and base. This means that the cis effect of NH$^-$ formed by the SNICB mechanism in the latter complex is small and superseded by the trans effect which can operate in the former two complexes in which NH$_2^-$ and NH$^-$ are trans to the leaving group, Cl$^-$. In addition, the ratio $k_{OH^-}/k_{H_2O}$ is very much less for cis-Rh(en)$_2$Cl$_2^+$ than for cis-Co(en)$_2$Cl$_2^+$. These results indicate that activation by $\pi$-donation is decreased for Rh(III) as expected.

The $\sigma$-inductive effect is related to the polarizability of the trans activator as well as of the central metal. A more polarizable or softer ligand can transfer more charge to the metal, and in turn, a softer metal can accept more charge from the ligand. This accounts for the halo trans effect order (I > Br > Cl). Changing the central metal should not change this order, but it is expected that a softer metal will increase the differences in trans activation. In fact, the whole substrate should be considered, since the inert ligands contribute to
the overall polarizability of the central metal. On this basis, the Ir(en)$_2$L$^{2+}$ substrate is softer than the Rh(en)$_2$L$^{2+}$ substrate, and should demonstrate a greater trans effect. A comparison of the activation enthalpies$^{39}$ of the acid hydrolysis of trans-Ir(en)$_2$LCl$^+$ and trans-Rh(en)$_2$LCl$^+$ shows equal trans effects, while the acid hydrolysis of trans-Ir(en)$_2$LBr$^+$ shows a lesser effect than trans-Rh(en)$_2$LBr$^+$. While this result is unexpected, the substitution reactions of square planar complexes do show the intensified trans effect for the softer Pt(II) system opposed to the harder Pd(II) and Ni(II) systems. Since the Ir(III) work is very new, no explanation has, as yet, been made of its unexpected behavior.

In summary, the activation by nonreactive ligands in octahedral substitution reactions, from a kinetic point of view, can be attributed to a cis $\pi$-donor effect, a trans $\pi$-acceptor effect, and a trans $\sigma$-inductive effect. Each effect has an overall labilizing influence, and therefore, the terms cis and trans are used to denote the greater relative directional effect. Originally, the effect was observed for Pt(II) reactions, in which only the trans effect was seen due to the small degree of $\pi$-bonding and the high degree of polarizability favoring the $\sigma$-inductive trans effect. The observation of a cis effect in Co(III) reactions does not detract from the trans effect theories, but is a logical extension of the $\pi$-donor theory.

The polarization theory of Grinberg$^{40}$ is rather naive, but provides a useful introduction to the M.O. theory of $\sigma$-induction. The primary

![Diagram](attachment:image.png)
charge on M induces a dipole on L, which in turn induces a dipole on the metal, which ends the sequence by repelling the primary negative charge of the leaving group, X. The theory suffers from two serious objections. First, the induced dipole on the metal should depend on the net charge of L more strongly than the induced moment; secondly, the effect should be greater for shorter bond lengths, which gives the wrong order for Cl and I.

However, it is clear that trans labilization is related to the ground state destabilization of the leaving group bond, which, as mentioned, can be called a thermodynamic trans effect. There are several ways to determine the leaving group bond strength experimentally: stability constants, x-ray studies, infrared spectra, nuclear magnetic resonance, acid strengths of aquo complexes, molar refraction using additive atomic refractions, and dipole moments. The experimental evidence does clearly demonstrate the differential bond weakening property of trans activators. Of course, the thermodynamic order is expected to correspond to the kinetic order only if the assumptions of the linear free energy relations are met, namely that the Morse potential curves are parallel for related compounds and that the free energies can be directly related to enthalpies, that is, constant entropies are found. If the entropies of activation vary, the choice of temperature can give contradictory results.

The M.O. theory of the $\sigma$-inductive trans effect, which was described, is more internally consistent than the Grinberg theory, and is not restricted to polarizability as the basic determinant of trans activating ability. In the case of Pt(II), the polarizability is important, since softer activators are expected to compete for a larger covalent
share of the $\sigma_x$ M.O. of a soft metal ion. However, the M.O. theory is
not restricted to a discussion of polarizability, and may be interpreted
on the basis of any factor affecting covalent bond strength.

The $\pi$-acceptor trans effect is clearly a transition state pheno-
menon, since it is generally accepted that it has a stabilizing effect
on all the bonds in the ground state through $\sigma$-donor charge removal from
the central metal ion. The activation can be explained assuming the
displacement mechanism for a diamagnetic $d^8$ system with a trigonal
bipyramid intermediate in two ways. First, there is the argument already
used for the octahedral trans effect, that is, facilitation of nucleo-
philic attack through preferential trans $\pi$-electron density removal.
This was applied to square planar Pt(II) by Orgel\textsuperscript{43}. Secondly, there is
the $\pi$-bond stabilization of a trigonal bipyramid intermediate as described
by Chatt and coworkers\textsuperscript{44}. This is similar to the $\pi$-bond stabilization
described for the trigonal bipyramid formation from octahedral dissoc-
iation. The cis effect resulting from a square pyramid activated complex
is not expected for Pt(II), and only a very small cis effect is found.

Langford and Gray\textsuperscript{45} also discuss trigonal bipyramid stabilization
both as a $\sigma$-trans effect and as a $\pi$-trans effect on the basis of M.O.
bonding. Although the trigonal bipyramid activated complex is of far
lesser importance for octahedral reactions, the principles should be
applicable to other configurations. The $\sigma$-trans effect is attributed
to the repulsion of trans $\sigma$ electrons by an activator, which can put
a great deal of negative $\sigma$ charge in the $p_x$ orbital of the metal consider-
ing the $x$-axis as the reaction coordinate. This is similar to the
covalent competition ground state theory. In addition, Langford and
Gray predict a transition state stabilization effect. The three groups
in the trigonal plane, the trans activator, the entering group, and the leaving group can share two p orbitals, while four ligands must share the same two p orbitals in the square plane. Therefore, good σ-bonders (H\(^-\), CH\(_3\)^-) can stabilize the trigonal bipyramid by stronger σ-bonding to the extra available metal σ orbitals. It is important to keep in mind that the p orbitals involved have trans directional properties, and therefore, the activation is specifically trans. This does not preclude overall cis and trans activation by the same mechanism using the other metal σ orbitals, namely \(d_{x^2-y^2}\), \(d_{z^2}\), and \(s\).

The \(\pi\)-trans effect, discussed from M.O. theory, does not add much to the previous discussion. It accounts for overall stabilization through the increased use of \(\pi\) M.O.'s in the activated complex, but mainly by the equatorial ligands which include the trans activator resulting in a trans effect. The addition of the tetragonal pyramid intermediate and an explanation of the cis effect would make this theory more complete and applicable to octahedral reactions, especially Co(III).

Good trans activators can be placed in three categories\(^4\) on the basis of their bonding characteristics regardless of the particular theories proposed to account for the mechanisms. There are strong σ-bonders (H\(^-\), CH\(_3\)^-), strong \(\pi\)-bonders (C\(_2\)H\(_4\), CO), and moderate σ and \(\pi\)-bonders (I\(^-\), tu). Weak trans activators (NH\(_3\), OH\(^-\)) do not fit in any of the three categories.

Parshall\(^5\) has given support to this classification, at least from the thermodynamic or bond weakening point of view, to show that the trans effect is both a σ and π-effect. The \(^{19}\)F n.m.r. shielding parameters of m-fluorophenyl complexes are sensitive to the trans σ-donors in a Pt(II) complex. By varying the σ-donor, it was found that the n.m.r.
shifts corresponded roughly to the basicities of the trans activator. On the other hand, the p-fluorophenyl complexes had shielding parameters, after correction for the \( \sigma \) inductive effects, which indicated the degree of \( \pi \)-acceptance by a trans activator. The strong \( \pi \)-acceptance of \( \text{CN}^- \), \( \text{SnCl}_3^- \), and \( \text{C}_2\text{H}_4 \) as well as the weaker \( \pi \)-donation of the halides was demonstrated by the para \( ^{19}\text{F} \) chemical shifts.

The increased availability of far infrared spectrometers has resulted in more ligand-metal stretching frequency data. The variations of the M-N (\( \sim 500 \text{ cm}^{-1} \)), the M-Cl (\( \sim 300 \text{ cm}^{-1} \)), and the M-Br (\( \sim 200 \text{ cm}^{-1} \)) stretching frequencies on changing the trans activating ligand has provided thermodynamic trans effect data. The bond weakening in the ground state by good activators is clearly shown by the large variations. The Pt(II)-Cl stretching frequency\(^{47}\) varies from 340 \( \text{ cm}^{-1} \) for trans-chloro to 270 \( \text{ cm}^{-1} \) for trans-hydrido. The Rh(III)-Cl frequencies\(^{48}\) in solid trans-\([\text{Rh(en)}_2\text{ClX}]\text{ClO}_4\) change from 343 \( \text{ cm}^{-1} \) for trans-chloro to 343 or 333 \( \text{ cm}^{-1} \) for trans-bromo to 311 \( \text{ cm}^{-1} \) for trans-iodo. The trans bond weakening is also shown by the Rh(III)-Br frequencies in solid trans-\([\text{Rh(en)}_2\text{BrX}]\text{ClO}_4\). The value decreases from 223 \( \text{ cm}^{-1} \) for trans-bromo to 196 \( \text{ cm}^{-1} \) for trans-iodo.

The aquo complex acid strength data is limited, and must be carefully interpreted. However, it does provide an indirect measure of the M-O bond strength, assuming that a stronger acid and weaker O-H bond mean a stronger M-O bond. Of course, complexes of equal charge should be compared. The comparison is expected to be fairly good for weak \( \pi \)-bonders. Cis-Pt(\( \text{NH}_3 \))\(_2\)(\( \text{H}_2\text{O} \))\(_2\)\(^{2+}\) is a weaker acid (\( pK_{a1} = 5.6 \)) than the trans isomer (\( pK_{a1} = 4.3 \)), which agrees with the greater trans effect of \( \text{NH}_3 \) relative to \( \text{H}_2\text{O}\).\(^{49}\)
The presence of a \( \pi \)-activator causes complications, which do not fit into a simple ground state bond weakening discussion. Although \( \text{C}_2\text{H}_4 \) is much higher in the trans effect series than \( \text{Cl}^- \), the bond weakening effect is in the opposite direction as indicated by acid strengths. Trans-Pt(\( \text{C}_2\text{H}_4 \))(\( \text{H}_2\text{O} \))Cl\(_2\) (pK \( \sim \) 5) is a stronger acid than cis-Pt(\( \text{NH}_3 \))(\( \text{H}_2\text{O} \))Cl\(_2\) and, as such, \( \text{C}_2\text{H}_4 \) would be said to have a weaker trans effect than chloro. However, the reduction of \( \pi \)-density on Pt(II) by a strong \( \pi \)-acceptor such as \( \text{C}_2\text{H}_4 \) is expected to decrease the electrostatic proton attraction increasing the acidity.

X-ray analysis studies were not undertaken in this work, but the recent work of Skapski and Troughton\(^{50}\) is noteworthy. Their study involved one of the first examples of a transition metal alkyl in the presence of low-field ligands with no \( \pi \)-acceptor properties. RhEt(\( \text{NH}_3 \))\(^2+\) was isolated by Wilkinson and coworkers\(^{51}\), who demonstrated strong ethyl trans activation in solution as expected. The x-ray study showed the cis Rh-N bond lengths to be 2.072 \( \text{\AA} \), which is close to the sum of the covalent radii, 2.06 \( \text{\AA} \). However, the trans Rh-N bond length of 2.256 \( \text{\AA} \) is one of the largest cases of relative lengthening observed for an octahedral \( \text{d}^6 \) complex.

Although the entering group in acid hydrolysis studies is common and in large excess, namely the solvent, and therefore, does not provide direct mechanistic information, the leaving group can be varied. By keeping the trans activator constant, the acid hydrolysis rates are a measure of the leaving group effect. It is expected that an inverse relationship between bond strengths and the rates of acid hydrolysis is an indication of bond breaking in the activated complex.

This work is concerned with halo ligands both as trans activators...
and as leaving groups. The relative bond strengths of the halo leaving groups should fall in a class (a) or a class (b) order\(^{52}\) depending on the polarizability\(^{53}\) of the central metal ion or the substrate. Often the polarizability of the substrate is strongly influenced by the other ligands present. For class (a) metals the halo stability order is \(\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-\), while the class (b) order is just the reverse. This is the result of the generalization that hard acids prefer to associate with hard bases, and soft acids prefer soft bases. Polarizability is a convenient property on which to base such a generalization, since other properties such as ionization potential, electronegativity, and unsaturation can be related to it. Of course, polarizability is only one factor among many which determine stability, such as chelation, steric, and resonance effects.

The use of a polar solvent poses this type of problem in determining the relative halo stabilities from activation enthalpies. Poe and Vaidya\(^{54}\) have presented heat of halo substitution data that show that even for class (b) metals the bond strength order is \(\text{Cl}^- > \text{Br}^- > \text{I}^-\). They explain the difference in class (b) behavior as a narrowing of the class (a) bond strength differences rather than a reversal. The apparent reversal is attributed to factors which contribute to the overall reaction enthalpy change other than bond strength, namely changes in the solvation enthalpies of the complex ions and of the halide ions. Of the two changes in solvation enthalpies, it is expected that the latter be more important. A polar solvent will more effectively solvate an ion with a larger charge to radius ratio. Therefore, even though the chloro bond strength is greater than the iodo, the hydration enthalpy can give an apparent reversal of order, when the relative

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differences in bond strength are smaller than the relative differences in solvation. By separating the solvation effects, Poe and Vaidya showed that the bond strength order is always $\text{Cl}^- > \text{Br}^- > \text{I}^-$ irrespective of the stability constant order, and their conclusion is supported by Raman spectra force constants.

Bott and Poe\textsuperscript{55} demonstrated that the $\text{Rh(en)}_2X^{2+}$ substrate is on the borderline between class (a) and class (b). Allowing for statistical effects the equilibrium constants at $85^\circ\text{C}$ for the first and second bromo substitution on the trans-dichloro complex ($K_1' = 0.9 \pm 0.1$; $K_2' = 1.6 \pm 0.2$) indicate that the first substitution is borderline, while the second is slightly class (b).

Bounsall and Poe\textsuperscript{48} have done temperature dependent studies of the relative stabilities of the halo complexes of bis(ethylenediamine)-rhodium(III). From the relative enthalpies of bonding of the dihalo complexes in aqueous solution the stability order was trans-$\text{I}_2 > \text{IBr} > \text{ICl} > \text{Br}_2 > \text{BrCl} > \text{Cl}_2$. The enthalpy change for complete chloro substitution by bromo is $0 \pm 1$ kcal mole$^{-1}$, and for complete bromo substitution by iodo is $-6.0 \pm 0.5$ kcal mole$^{-1}$, which indicates borderline behavior for the former and class (b) behavior for the latter equilibrium.

Bounsall and Poe\textsuperscript{48} also showed the increase in class (b) character of the $\text{Rh(en)}_2X^{2+}$ substrate as $X$ changes, from chloro to bromo to iodo, through the use of a linear enthalpy relation using enthalpies corrected for solvation, with $H^0$ for trans-$\text{Rh(en)}_2\text{I}_2^+$ taken as zero. By relating the enthalpies of trans-$\text{Rh(en)}_2XY^+$ to trans-$\text{Rh(en)}_2\text{ClY}^+$, the slopes for $X$ is Cl, Br, and I were 1.0, 0.85, and 0.65 (Fig. 2). This is a quantitative measure of the decrease in relative halo bond strengths as $X$ is changed along the halo series, and shows the increase of class...
(b) character. It is interesting to note that this result is not apparent, as explained, from the corrected enthalpy order, which is completely reversed for the class (b) halo order.

Of course, the narrowing of the halo enthalpy differences is expected to be intensified by the trans effect. The trans destabilization of mixed complexes results in higher enthalpies than predicted from an average of the appropriate unmixed ones. It has long been recognized for the Pt(II) trans effect that the relative magnitude of trans activation is decreased by weaker bonds. This means that the relative trans activation is greatest for the strongest bond, namely chloro in this series. Therefore, destabilization by this effect acts in the same direction as the decrease of class (b) character or the increase in hardness of the complex.

The same type of discussion can be applied to kinetic activation,
when ground state destabilization is more important than activated complex stabilization. In the absence of \( \pi \)-effects, it is expected that the ground state effect is more important, since stronger bonds are involved than in the transition state. Bott, Bounsall, and Poe\(^{56} \) discuss this with respect to the results of the kinetic studies of some trans-dihalobis(ethylenediamine)rhodium(III) complexes. The activation enthalpies for trans-\( \text{X} \), where \( \text{X} \) is Cl, Br, and I, are 21.1, 23.1, and 25.3 kcal mole\(^{-1} \), indicating the increasing inertness with the increasing polarizability of the leaving group. This was called kinetic class (b) behavior by analogy to the thermodynamic classification. These results did not show that the relative trans effects depended on whether the leaving halo group was chloro or bromo. There is a difference of 2.1 kcal mole\(^{-1} \) between trans-iodo and bromo for either leaving group.

However, it is expected that the relative trans effect is dependent on the leaving group. Greater differences are predicted for stronger bonds of the trans leaving group. This result was obtained by Bott and Poe\(^{57} \) from the results of the anation reactions of some trans-haloaquobis(ethylenediamine)rhodium(III) complexes. A comparison of the activation enthalpy data for the anation reactions with the acid hydrolysis data gives larger relative trans effects for an aquo than for a halo leaving group. Bauer and Basolo\(^{39} \) also found this for the acid hydrolysis of some dihalobis(ethylenediamine)iridium(III) complexes. The trans effects of bromo and iodo differed by 1.8 kcal mole\(^{-1} \) with a chloro leaving group, but only by 0.1 kcal mole\(^{-1} \) with a bromo leaving group.

In summary, the trans activation trends can be related to mutual
trans destabilization effects. The observed results indicate that softer ligands are more effective trans destabilizers, but in turn, are the least susceptible to trans destabilization.

3. Mechanism of Octahedral Substitution

The anation studies provide more direct evidence for the mechanism of substitution reactions than the acid hydrolysis studies, since the latter are pseudo-first order. Bott and Poe found that the relative nucleophilic character of the halides towards the trans-Rh(en)$_2$L(H$_2$O)$_2$$^{2+}$ complexes shows a small, but definite trend in the order $I^- > Br^- > Cl^-$ on the basis of the activation enthalpies. However, this effect could be explained in terms of ion pairing, since iodide forms ion pairs with slightly more favorable enthalpies than chloride. This does not clear up the ambiguity and the results of the studies of Rh(III) complexes made so far do not, unfortunately, allow an unambiguous assignment of the mechanism.

The insensitivity of the acid hydrolysis rates of Rh(III) to charge on the complex has been offered as evidence for bond making in the activated complex. Basolo and coworkers showed that the rates of acid hydrolysis of Rh(NH$_3$)$_5$Cl$^{2+}$ ($4.3 \times 10^{-5}$ sec$^{-1}$), trans-Rh(NH$_3$)$_4$Cl$_2$$^{2+}$ ($4.7 \times 10^{-5}$ sec$^{-1}$), and Rh(C$_2$O$_4$)$_2$Cl$_2$$^{3-}$ ($1.6 \times 10^{-5}$ sec$^{-1}$) at 80°C are very nearly the same. Since assistance by water is expected to have a lesser effect on rates than a primarily dissociative mechanism, such as for Co(III), which has a large degree of charge dependence, the data was interpreted as evidence for bond making in the transition state. It was argued that dissociation involves charge separation, while displacement involves charge separation and neutralization.
Therefore, a dissociative mechanism is expected to be more charge 
dependent. However, this type of comparison assumes that there are 
small kinetic cis and trans effects, since the nonreactive ligands 
are different in the complexes of different charge. The presence of 
large trans effects for Rh(III)\textsuperscript{56} has been demonstrated. In addition, 
the acid hydrolysis rates\textsuperscript{57} of Rh(NH\textsubscript{3})\textsubscript{5}I\textsubscript{2}\textsuperscript{2+} (2 X 10\textsuperscript{-7} sec\textsuperscript{-1}) and 
Rh(en)\textsubscript{2}I\textsubscript{2}\textsuperscript{2+} (1.3 X 10\textsuperscript{-4} sec\textsuperscript{-1}) at 50° C, and those\textsuperscript{58} of Rh(en)\textsubscript{2}Cl\textsubscript{2}\textsuperscript{2+} 
(1.4 X 10\textsuperscript{-6} sec\textsuperscript{-1}) and RhCl\textsubscript{6}\textsuperscript{3-} (5.2 X 10\textsuperscript{-2} sec\textsuperscript{-1}) show that the re-
results obtained by Basolo are due to the particular choice of examples, 
which may be subject to compensating cis and trans effects.

The base hydrolysis reaction can take place in two ways. First, 
there is the anation reaction with hydroxide acting the same as any 
other nucleophile, subsequent to the rate determining acid hydrolysis 
step. Basolo and coworkers\textsuperscript{38} showed that this occurs for several amine 
complexes of Rh(III) of the type trans-RhA\textsubscript{4}Cl\textsubscript{2}\textsuperscript{2+}, for which the rates 
of hydrolysis are the same at pH 1 and 13. However, the hydrolysis 
rates of Rh(NH\textsubscript{3})\textsubscript{5}Cl\textsubscript{2}\textsuperscript{2+}, cis-Rh(en)\textsubscript{2}Cl\textsubscript{2}\textsuperscript{2+}, and cis-Rh(trien)Cl\textsubscript{2}\textsuperscript{2+} increase 
with increasing pH. Moreover, k\textsubscript{OH}/k\textsubscript{H\textsubscript{2}O} < 10 for the trans complexes, 
but is \approx 2 X 10\textsuperscript{3} for cis-Rh(en)\textsubscript{2}Cl\textsubscript{2}\textsuperscript{2+} and \approx 10\textsuperscript{4} for cis-Rh(trien)Cl\textsubscript{2}\textsuperscript{2+}. 
These results can be explained in terms of a second mechanism, the 
SNICB (substitution, nucleophilic, unimolecular, conjugate base) mech-
anism, which involves the rapid deprotonation of a nonreactive amine, 
changing a poor cis and trans activator, the amine group, into an 
 excellent activator, the amido group. For Co(III) the amido group is 
a remarkable activator giving k\textsubscript{OH}/k\textsubscript{H\textsubscript{2}O} from 5 X 10\textsuperscript{5} for Co(NH\textsubscript{3})\textsubscript{5}Cl\textsubscript{2}\textsuperscript{2+}\textsuperscript{59} 
to 1.3 X 10\textsuperscript{9} for cis-Co(trien)Cl\textsubscript{2}\textsuperscript{2+}\textsuperscript{60}. It is apparent that the \textalpha-donor 
activation found for the amido group in Co(III) reactions is not
nearly as important for Rh(III), since the cis effect is very small. However, there is a large trans effect, which indicates the increased importance of the $\sigma$-inductive effect in Rh(III) reactions. Another interesting illustration of the greater amido trans effect relative to cis for Rh(III) is the complex Rh(tren)$\text{Cl}_2^+$

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH}_2 \\
\text{N} & \quad \text{Rh} \\
\text{Cl} & \quad \text{NH}_2 \\
\text{Cl} &
\end{align*}
\]

Only one chloro ligand is susceptible to base hydrolysis.$^{61}$

Another explanation for the greater activation by a trans amido group is the greater acidity of an amine trans than cis. The n.m.r. chemical shifts of the N-H protons in Co(NH$_2$)$_2$$^+X^{2+}$ show that they are 100 times more acidic trans to X (halo, carboxylato) than cis.$^{62}$

There is no necessity for the base hydrolysis mechanism to be SN1CB for Rh(III), since solvent assistance probably plays more or less the same role as in the acid hydrolysis mechanism. The mechanism could be SN2CB or more likely, some mechanism between the two extremes. Unambiguous evidence in this respect is, as yet, unavailable.

On the other hand, the major difference between acid hydrolysis and base hydrolysis is that only hydroxide shows second order kinetics in aqueous solution, and this behavior is best explained by a conjugate base mechanism. A simple SN2 mechanism cannot account for this unique behavior, since other strong nucleophiles such as $\text{N}_3^-$ and NCS$^-$ do not show similar behavior.$^{63}$ In addition, there is convincing evidence for the conjugate base mechanism for Co(III). First, complexes without
acidic protons cannot form the required conjugate base, and should not react rapidly with hydroxide. This was found for the hydrolysis rates of Co(CN)$_5$Br$^{3-}$ and Co(CN)$_5$I$^{3-}$, which are independent of pH in basic media$^{59}$. Another example of complex, not negatively charged, is trans-Co(dipy)$_2$(OAc)$_2^+$ which has the same rates at pH 11-12 as at pH 6-8$^{64}$. There are more examples, too numerous to mention here, and the one or two examples of rate increase in base without acidic protons are special cases, such as chelate effects$^{65}$.

Secondly, the conjugate base intermediate should react with other nucleophiles in nonaqueous media, making hydroxide a catalyst. Pearson$^{66}$ and coworkers observed this catalytic behavior in dry DMSO. The substitution of chloride in trans-Co(en)$_2$Cl$^{+}$ by nitrite is slow in dry DMSO, and independent of nitrite concentration. Hydroxide ion equal to 10% of the complex ion concentration reduces the half-life from 5-6 hours to ~2 minutes, yielding the trans dinitro product rather than the nitrohydroxo. This cannot involve rapid nitro substitution of an intermediate hydroxo complex, since this reaction is too slow. In addition, other bases, such as piperidine, act as catalysts, and the rates are independent of nucleophilic character, being the same for NO$_2^-$, NCS$^-$, and N$_3^-$.

More evidence for the conjugate base mechanism is the sensitivity of the rates to the nature of the amido group. A secondary amido group is a much better activator than a primary amido group. Direct nucleophilic attack by hydroxide would show the opposite behavior due to the increased steric hindrance of a secondary amido group. Poon and Tobe$^1$ found $k_{OH}/k_{H_2O} = 6 \times 10^{10}$ l. mole$^{-1}$ for trans-Co(cyclam)Cl$_2^+$ and $9 \times 10^7$ l. mole$^{-1}$ for Co(en)$_2$Cl$_2^+$ at $25^\circ$.
Although there is, as yet, only a small amount of data for Rh(III) base hydrolysis, it is evident that the rates increase significantly only for a trans amine group, on the basis of the data already given. This difference is more consistent with a strong activator such as amido, which is expected to give large cis and trans differences. The direct nucleophilic attack by hydroxide involves amine as the activating group, and therefore, is not expected to give large differences, since amines show small cis and trans differences (see Fig. 2). In addition amine activation of leaving groups is very weak both as a cis and as a trans effect.
II. PREPARATION OF SOME DIACIDOCYCLAMRHODIUM(III) COMPLEXES

1. Experimental

RhCl$_3$·3H$_2$O (J. Bishop and Co. Platinum Works) was used without further purification as a source of Rh(III) for the cis and trans-dichloro preparations, which were the starting materials for all the other preparations. 99.9 Mol % pure methanol and ion exchanged distilled water were used as solvents. Reagent grade sodium salts were used as a source of the anions for substitution and precipitation.

The electronic spectra were recorded on a Bausch and Lomb Spectronic 505, using water as the solvent for all samples except those with a hydroxo ligand, for which 0.1 M NaOH was used; the infrared spectra were recorded on a Beckman IR 10 using 1.0% KBr pellets; and the ORD spectra were recorded on a Cary 60 spectropolarimeter, through the courtesy of Dr. Kirschner (Wayne State University). The analyses were obtained from Midwest and Spang Microanalytical Laboratories.

2. Successful Preparations

The larger number of different diacido and mixed diacidocyclam-rhodium(III) complexes compared to the bis(ethylenediamine) analogs broadens the scope for kinetic and trans effect studies. In addition, cis and trans-Rh(cyclam)Cl$_2^+$ are easier to separate, and the faster base hydrolysis rates coupled with the ease of hydroxo complex isolation provide an excellent pathway for the otherwise difficult and time-consuming preparations. The total retention of configuration during all the substitution reactions of the cyclam complexes made the separation of the stereoisomers unnecessary after the initial dichloro separation, since the dichloro complex was the starting material for all the other preparations. The only exception to this was the cis-diido preparation,
since a slow isomerization was observed. Limiting the reflux time of the cis-dichloro complex in iodide solution minimized the problem, and the pure cis-diiodo complex could be prepared.

The preparation of cyclam was carried out according to the method of Tobe with two modifications which simplified the procedure and improved the yield from 2.5 to 3.5 g. The cyclam product was pre-

\[
2 \text{NH}_2(\text{CH}_2)_2\text{NH}_2 + \text{Br(CH}_2)_2\text{Br} \rightarrow \text{EtOH} \rightarrow \text{NH}_2(\text{CH}_2)_2\text{NH(CH}_2)_2\text{NH(CH}_2)_2\text{NH}_2
\]

pitated directly from the reaction solution, after most of the ethanol was removed by distillation, rather than being sublimed along with an added amount of 1,9-diamino-3,7-diazaheptane. It was found that absolute ethanol was best for the precipitation, since the presence of water prevented the precipitation. However, the water could be removed by evaporation followed by the addition of absolute ethanol. Secondly, the crude product was purified by vacuum sublimation rather than recrystallization from dioxane, which improved the yield, since the sublimation was more efficient. The method of Stetter and Mayer is more elegant, but was not used because of its length and similar yield. However, the m.p. of 186° (sealed tube) was closer to that reported by Stetter and Mayer (185°) than that by Tobe (173°). Recrystallization from dioxane was also used by Stetter and Mayer for purification.

Cyclam was observed to be very stable in air. It was quite soluble in water in contradiction to the observation of Stetter and Mayer. However, the infrared spectrum corresponded exactly with their spectrum.

The preparation of the 1,5,9,13-tetraazacycloclohexadecane analog of
cyclam was attempted, since it is a more symmetric ring with four propylene linkages. While a crude product was isolated, it was not stable in air, turning brown, and it was quite viscous. Apparently the stability and high m.p. of cyclam are not shared by this analog. Other close analogs also have low melting points (1,3,7,10-tetraazacyclo-
dodecane, 35°; 1,4,8,11-tetraazacyclotridecane, 41°)\(^67\). The ring folding, which permits diagonal intramolecular hydrogen bonding seems to be peculiar to cyclam.

The preparation of the dichloro complex from RhCl\(_3\cdot3\)H\(_2\)O and cyclam in water gave almost entirely the cis isomer. On the other hand, if the same preparation was carried out in methanol, the trans isomer predominated (60% trans; 30% cis isolated). Although the mechanism for

\[
\text{RhCl}_3\cdot3\text{H}_2\text{O} + \text{cyclam} \xrightarrow{\text{water}} \text{cis-Rh(cyclam)Cl}_2^+ \quad \text{(red)} \\
\text{RhCl}_3\cdot3\text{H}_2\text{O} + \text{cyclam} \xrightarrow{\text{MeOH}} \text{trans-Rh(cyclam)Cl}_2^+ + \text{cis-[Rh(cyclam)Cl}_2\text{]}\text{Cl}^- \quad \text{(red)} \quad \text{(yellow)}
\]

this difference is uncertain, it is likely that the two solvents stabilize different configurations of the cyclam molecule, since different nitrogen configurations are present in the cis and trans isomers as described in the introduction. The stereoisomers were very easy to separate, since the cis isomer precipitated from the reaction solution as the chloride salt, with no evidence of any trans impurity. All the remaining cis isomer was removed by adding large volumes of conc. HCl, which did not precipitate the trans isomer. After the methanol and HCl were removed by evaporation, the trans isomer residue could be readily purified by recrystallization from a HCl solution. The large difference
in solubilities of the two stereoisomers was not found in water, and as such, the small amounts of trans in the cis-dichloro product, prepared in water, gave an impure cis product relative to that prepared in methanol. The purity of the isomers was determined spectrometrically.

Most of the cis and trans-Rh(cyclam)X₂⁺ complexes were prepared from the respective cis or trans-dichloro complex by heating at reflux temperature in an aqueous solution of the desired anion (0.1 - 1.0 M) for various periods of time from 3 hours to 3 days, depending on the solubilities of the products. This was possible since only the cis-diodo complex showed any tendency to isomerize. However, even the cis-diodo complex could be prepared by carefully limiting the reflux period, as mentioned. The cis and trans diisothiocyanato complexes could not be prepared in this way because of the weak cis and trans effects of the isothiocyanato ligand. The substitution reaction stopped after the formation of the chloroisothiocyanato complex. However, the products could readily be prepared by anating cis and trans-Rh(cyclam)(OH)(H₂O)²⁺. The anation rates are very fast relative to the acid hydrolysis rates in 1.0 M solutions of the anion.

The mixed diacid complexes of the type trans-Rh(cyclam)XY⁺, where X and Y are different unidentate ligands, were prepared in two ways depending on the nature of the product. If the trans effect difference of X was much greater than Y, trans-Rh(cyclam)X₂⁺ could be substituted with Y, and the kinetic mixed product, which was desired,

\[ \text{e.g. } \text{trans-Rh(cyclam)Cl}_2^+ + \text{SCN}^- \rightarrow \text{trans-Rh(cyclam)Cl(NCS)}^+ \]

could be isolated. The following trans-Rh(cyclam)XY⁺ were prepared by this method: ClI, Cl(N₃), Cl(NCS), Br(N₃), and I(N₃). The method was
not possible when X and Y were close in their trans effects, such as chloro and bromo, since the substitution did not stop at the mixed product, but went to the disubstituted product.

The second method was made possible by the use of the trans-Rh(cyclam)X(OH)\(^+\) complexes. The cyclam complexes of Rh(III), relative to the bis(ethylenediamine) analogs, were very sensitive to base hydrolysis, and gave complete dihydroxo formation in less than one hour in approx. 0.1 M NaOH at reflux temperature, with indications of the usual second order rate dependence. The relatively rapid formation of hydroxo complexes provided an excellent pathway for the preparation of mixed diacido complexes, which were not possible by the first method, and was used in preference to the photochemical method developed by Basolo. Moreover, the speed and purity of the products made this a desirable method for all the preparations (see Revised Preparations).

By carefully limiting the reflux period of trans-Rh(cyclam)X\(^2+\) in \(~1\text{ M NaOH}\) from 3 to 10 minutes, it was found that the solution contained only the mono and dihydroxo products with no trans-Rh(cyclam)X\(^2+\) remaining. The longer reflux times were necessary for the more insoluble complexes such as diido. The monohydroxo product could be precipitated in very pure form (~50% yields) with perchlorate, since the dihydroxo complex was too soluble to be precipitated with perchlorate.

\[
e.g. \quad \text{trans-Rh(cyclam)}\text{Cl}_2^+ + 0.1 \text{ M NaOH} \rightarrow \text{trans-[Rh(cyclam)Cl(OH)]ClO}_4^- + \text{trans-Rh(cyclam)}(\text{OH})_2^+ + \text{Cl}^- \\
\text{(yellow)} \quad \text{ClO}_4^- \quad \text{(paler yellow)}
\]

The procedure was made possible by the relatively small hydroxo trans effect. The monohydroxo complex was acidified to give the monoaqauo,
which was also precipitated with perchlorate, and which was readily

\[
\text{e.g. } \text{trans-Rh(cyclam)I(OH)}^+ + \text{H}^+ \rightarrow \text{trans-Rh(cyclam)I(H}_2\text{O)}^2+ \\
\text{Cl}^- \rightarrow \text{trans-Rh(cyclam)ICl}^+ + H_2\text{O}
\]

\text{(orange)} \quad \text{(red)}

anated with several different anions to give the desired mixed diacido complexes. The appropriate reactions were chosen after preliminary consideration of the relative trans effects of the two ligands in the mixed complex. For example, the anation of the iodoaquo complex by chloride was used to give the chloroiodo product rather than the anation of chloroaquo by iodide. This was necessary, since even under the mild reaction conditions used for anation, some diiodo formation was observed if the latter reaction pathway was attempted, due to the greater trans effect of I\(^-\) relative to Cl\(^-\). The following trans-Rh(cyclam)XY\(^+\) complexes were prepared by this method: ClBr, ClI, BrI, Br(NCS), I(NCS), and (N\(_3\))(NCS).

The cis and trans-Rh(cyclam)(OH)(H\(_2\)O)\(^2+\) complexes were special cases. The base hydrolysis reaction was carried out to completion by refluxing the cis-dichloro complex for 5 minutes in .2 M NaOH, and the trans-dichloro complex for 60 minutes in .5 M NaOH. NaClO\(_4\)\cdot H\(_2\)O was added and the solutions were neutralized with dilute HClO\(_4\), until the hydroxoaoquo complex precipitated. This was made possible by the very
great solubility of the dihydroxo and diaquo complexes, neither of which could be precipitated with perchlorate. Therefore, the hydroxoaquo product was free of any diaquo or dihydroxo impurities.

Most of the complexes were isolated as the perchlorate salts, since first, the perchlorato ligand has a very slight tendency to serve as a donor in aqueous solution, and therefore, does not interfere in the substitution reaction\(^{68}\); and secondly, the perchlorate ion is large enough to act as a good precipitating agent, which is necessary for the aquo and hydroxo products, which are quite soluble in aqueous solution. On the other hand, the dichloro complex was isolated as the chloride salt, since the cis and trans isomers could be easily separated from the methanol reaction medium. The dibromo and diiodo complexes were isolated as the bromide and iodide salts respectively, because of their limited solubilities in the bromide and iodide reaction media.

The experimental procedures and analyses of the successful preparations are presented, starting with the cyclam preparation, and then giving the complex preparations in sufficient detail to facilitate repetition of the experiments. Each experiment was performed at least twice, and sometimes as many as ten times to insure reproducibility of the results. The analysis are single determinations on the best sample obtained as indicated by the spectral ratios of extinction coefficients.

**1,11-Diamino-4,8-diazaundecane**

(202 g, 1.00 mole, 102 ml) 1,3-dibromopropane was added dropwise to (371 g, 5 moles, 420 ml) 1,3-diaminopropane in 250 ml ethanol. The dropwise addition was necessary, since the reaction was very exothermic. The yellow solution was heated under reflux for 1 hour. (300 g, 5.3 moles) KOH was added to precipitate the bromide. The KOH was added to
the hot solution and stirred for 30 minutes. The KBr and excess KOH were removed by filtration. The ethanol (78.5° C) and 1,3-diaminopropane (135.5° C) were removed by distillation at atmospheric pressure. The 1,11-diamino-4,8-diazaundecane was separated by vacuum distillation (120° C, 50 µ Hg) as a clear liquid (87 g, 90 ml, 46%). This is the intermediate for the attempted 1,5,9,13-tetraazacyclohexadecane preparation.

1,4,8,11-Tetraazacyclotetradecane (cyclam)

The open chain, 1,9-diamino-3,7-diazanonane, was prepared according to the method of Van Alphen. (250 g, 1.2 moles, 126 ml) 1,3-dibromo-propane was added dropwise to (360 g, 6.0 moles, 400 ml) ethylene-diamine in 300 ml ethanol. The addition was dropwise because the reaction was very exothermic. The yellow solution was heated under reflux for one hour. (300 g, 5.3 moles) KOH was added and the reaction mixture was stirred for 30 minutes. The KBr and excess KOH were removed by filtration. The ethanol (78.5° C) and excess ethylenediamine (116-117° C) were removed by distillation. The 1,9-diamino-3,7-diazanonane (138° C, 4 mm Hg) was separated by distillation as a clear viscous liquid (90 g, 56 moles, 47%).

Cyclam was prepared according to Tobe and coworkers with some modifications. (50 g, .25 moles) 1,3-dibromopropane and (40 g, .25 moles) 1,9-diamino-3,7-diazanonane were added to 4 liters of absolute ethanol, and heated under reflux for 24 hours, during which the solution turned yellow. 3 liters of ethanol were removed by distillation. The solution was cooled and the KBr was removed by filtration. The volume was reduced to 150 ml during which the excess KOH was removed by
decantation. The viscous yellow solution was cooled overnight to precipitate the white product (3.5 g, 7%), which was filtered, washed with acetone, and purified by vacuum sublimation (120° C, 2 mm Hg). The melting point in a sealed tube was 186° C.


Cis-[Rh(cyclam)Cl₂]Cl

(7.5 g, 28 mmoles) RhCl₃·3H₂O and (7.5 g, 37 mmoles) cyclam were dissolved in 300 ml methanol and heated under reflux for 5 minutes during which the red mixture turned to a yellow solution with a yellow precipitate. The reaction mixture was cooled and filtered. The yellow product (3.1 g, 27%) was washed with ethanol and ether, and dried under vacuum for 2 hours.


Trans-[Rh(cyclam)Cl₂]Cl

The filtrate from the preparation of cis-[Rh(cyclam)Cl₂]Cl in methanol was treated with 25 ml conc. HCl to precipitate the excess cyclam as the tetrahydrochloride (analyzed as 3.5 HCl), and any cis isomer left in the reaction solution. After filtration, the yellow solution was evaporated to dryness. The yellow residue was recrystallized from 75 ml water and 25 ml conc. HCl, washed with acetone and ether, and dried under vacuum for 2 hours (5.8 g, 50%).

Cis-[Rh(cyclam)Cl₂]ClO₄

(2.0 g, 7.6 mmoles) RhCl₃·3H₂O, (1.5 g, 7.6 mmoles) cyclam, and (2.0 g, 34 mmoles) NaCl were added to 50 ml water and heated under reflux for 30 minutes, during which the red mixture changed to a yellow solution. 5 ml 70% HClO₄ were added to precipitate the product. The yellow product (2.4 g, 70%) was recrystallized by repeating the procedure, washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)Cl₂]ClO₄: C, 25.36; H, 5.11; N, 11.83; Cl, 22.46. Found: C, 25.57; H, 5.29; N, 11.91; Cl, 22.47.

Cis-[Rh(cyclam)Br₂]Br

(500 mg, 1.22 mmoles) cis-[Rh(cyclam)Cl₂]Cl and (2.5 g, 24 mmoles) NaBr were dissolved in 50 ml water and heated under reflux for 3 hours. The solution turned from yellow to orange, with the formation of an orange precipitate. The reaction mixture was cooled to precipitate the orange product, which was recrystallized by repeating the procedure (450 mg, 68%), washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)Br₂]Br: C, 22.12; H, 4.46; N, 10.32; Br, 44.15. Found: C, 22.26; H, 4.47; N, 10.34; Br, 43.86.

Trans-[Rh(cyclam)Br₂]Br

Starting with the trans-dichloro complex, the procedure was the same as that of the cis isomer with a 5 hour reflux period and (4.6 g, 44 mmoles) NaBr in 50 ml water. The trans isomer (240 mg, 41%) was also orange.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)Br₂]Br: C, 22.12; H, 4.46; N,
Cis-\([\text{Rh(cyclam)} \text{I}_2]\) I

(500 mg, 1.22 mmoles) cis-\([\text{Rh(cyclam)} \text{Cl}_2]\) Cl was dissolved in 50 ml 0.33 M NaI and heated under reflux for 30 minutes. The solution turned from yellow to orange. It was cooled to precipitate the product, which was recrystallized by repeating the procedure twice. The orange product (370 mg, 45%) was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for \([\text{Rh(C}_{10}\text{H}_{24}\text{N}_4}\text{I}_2]\) I: C, 17.56; H, 3.54; N, 8.19; I, 55.66. Found: C, 18.07; H, 3.77; N, 8.43; I, 55.66.

Trans-\([\text{Rh(cyclam)} \text{I}_2]\) I

(504 mg, 1.06 mmoles) trans-\([\text{Rh(cyclam)} \text{Cl}_2]\) ClO_4 and (3.2 g, 21 mmoles) NaI were added to 150 ml water and heated under reflux for 3 hours, during which a brown precipitate was formed. The solution was cooled and the brown product was recrystallized by heating in 2 liters of water and (3.2 g, 21 mmoles) NaI for 3 days, followed by slow evaporation to 200 ml. The product (610 mg, 84%) was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for \([\text{Rh(C}_{10}\text{H}_{24}\text{N}_4}\text{I}_2]\) I: C, 17.56; H, 3.54; N, 8.19; I, 55.66. Found: C, 17.38; H, 3.77; N, 8.20; I, 55.74.

Cis-\([\text{Rh(cyclam)} (\text{N}_3)_2]\) ClO_4

(500 mg, 1.22 mmoles) cis-\([\text{Rh(cyclam)} \text{Cl}_2]\) Cl and (1.0 g, 15 mmoles) NaN_3 were dissolved in 25 ml water and heated under reflux for 3 hours. The yellow solution became golden. 5 ml 70% HClO_4 were added to precip-
itate the yellow product, which was recrystallized by repeating the procedure. The product (460 mg, 78%) was washed with ethanol and ether, and dried under vacuum. The product was protected from light to prevent decomposition to a brown compound, resulting from the oxidation of the azido ligands.

Anal. Calculated for $[\text{Rh}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{N}_3)_2]\text{ClO}_4$: $C$, 24.68; $H$, 4.97; $N$, 28.78; $\text{Cl}$, 7.28. Found: $C$, 24.70; $H$, 5.12; $N$, 29.02; $\text{Cl}$, 7.40.

Trans-$[\text{Rh(cyclam)}(\text{N}_3)_2]\text{ClO}_4$

Starting with the trans-dichloro complex, the trans diazido complex was prepared using the same procedure as described for the cis. The golden yellow product (390 mg, 73%) was also protected from light.

Anal. Calculated for $[\text{Rh}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{N}_3)_2]\text{ClO}_4$: $C$, 24.68; $H$, 4.97; $N$, 28.78. Found: $C$, 24.88; $H$, 4.96; $N$, 28.73.

Cis-$[\text{Rh(cyclam)}(\text{NO}_2)_2]\text{ClO}_4$

(500 mg, 1.05 mmoles) cis-$[\text{Rh(cyclam)}\text{Cl}_2]\text{ClO}_4$ and (1.7 g, 24 mmoles) NaNO₂ were dissolved in 50 ml water and heated under reflux for 3 hours. The solution turned paler yellow. 5 ml 70% HClO₄ were added to precipitate the product, which was recrystallized by repeating the procedure. The pale yellow product (400 mg, 76%) was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for $[\text{Rh}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{NO}_2)_2]\text{ClO}_4$: $C$, 24.28; $H$, 4.89; $N$, 16.99. Found: $C$, 24.44; $H$, 4.93; $N$, 16.64.

Trans-$[\text{Rh(cyclam)}(\text{NO}_2)_2]\text{ClO}_4$

(719 mg, 1.75 mmoles) trans-$[\text{Rh(cyclam)}\text{Cl}_2]\text{Cl}$ and (3.5 g, 51
mnoles) NaNO₂ were added to 50 ml water and heated under reflux for 20 hours. 5 ml 70% HClO₄ were added to precipitate the product, which was recrystallized by repeating the procedure. The white powder (484 mg, 58%) was washed with ethanol and ether, and dried under vacuum.


Cis-[Rh(cyclam)(NCS)₂]ClO₄

(375 mg, .697 mmoles) trans-[Rh(cyclam)(OH)(H₂O)](ClO₄)₂, (2.0 g, 25 mmoles) NaSCN, and (10 g, 72 mmoles) NaClO₄·H₂O were dissolved in 25 ml water and heated under reflux for 2 hours during which the solution became darker yellow. The solution was cooled to precipitate the product. The yellow-white product (165 mg, 46%) was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)(NCS)₂]ClO₄: C, 27.78; H, 4.66; N, 16.20; S, 12.36. Found: C, 27.84; H, 4.57; N, 16.20; S, 12.29.

Trans-[Rh(cyclam)(NCS)₂]ClO₄

(218 mg, .405 mmoles) trans-[Rh(cyclam)(OH)(H₂O)](ClO₄)₂ and (1.0 g, 12 mmoles) NaSCN were added to 25 ml water and 5 drops dilute HClO₄. The yellow solution was heated under reflux for 50 hours. (10 g, 72 mmoles NaClO₄·H₂O was added to precipitate the product. The pale yellow complex was added to 50 ml 1.0 M NaSCN, heated under reflux for 10 hours, and precipitated with NaClO₄. The product (72 mg, 34%) was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)(NCS)₂]ClO₄: C, 27.78; H, 4.66; N, 16.20; S, 12.36. Found: C, 27.56; H, 4.57; N, 15.96; S, 12.44.
Trans-[Rh(cyclam)Cl(OH)]ClO₄

(306 mg, .747 mmoles) trans-[Rh(cyclam)Cl₂]Cl and (1 pellet, ~2.5 mmoles) NaOH were dissolved in 20 ml water and heated under reflux for 3 minutes. (5.0 g, 36 mmoles) NaClO₄·H₂O was added to precipitate the white complex (153 mg, 45%), which was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)Cl(OH)]ClO₄: C, 26.39; H, 5.54; N, 12.31; Cl, 15.58. Found: C, 26.36; H, 5.48; N, 12.07; Cl, 15.71.

Trans-[Rh(cyclam)Cl(H₂O)](ClO₄)₂

(510 mg, 1.24 mmoles) trans-[Rh(cyclam)Cl₂]Cl and (1 pellet, ~2.5 mmoles) NaOH were dissolved in 25 ml water and heated under reflux for 4 minutes. The pale yellow solution was cooled on ice and slightly acidified with dilute HClO₄. (10 g, 72 mmoles) NaClO₄·H₂O was added to precipitate the yellow product (387 mg, 56%), which was washed with ethanol and ether, and dried under vacuum for 2 hours.


Trans-[Rh(cyclam)Br(OH)]ClO₄

(203 mg, .374 mmoles) trans-[Rh(cyclam)Br₂]Br and (1 pellet, ~2.5 mmoles) NaOH were dissolved in 15 ml water and heated under reflux for 3 minutes, during which the solution turned paler yellow. (5.0 g, 36 mmoles) NaClO₄·H₂O was added to precipitate the pale yellow complex (95 mg, 51%), which was washed with 1:1 ethanol and ether, and dried under vacuum.
Anal. Calculated for \([\text{Rh(C}_{10}\text{H}_{24}\text{N}_4}\text{Br(OH)}]\text{ClO}_4\): C, 24.04; H, 5.04; N, 11.21; Br, 15.99; Cl, 7.10. Found: C, 24.23; H, 4.94; N, 11.12; Br, 16.04; Cl, 7.08.

Trans-[\text{Rh(cyclam)}\text{Br(H}_2\text{O)}]\text{(ClO}_4\text{)}_2$

(214 mg, 0.394 mmoles) trans-[\text{Rh(cyclam)}\text{Br}_2]\text{Br}$ and (1 pellet, ~2.5 mmoles) NaOH were dissolved in 15 ml water and heated under reflux for 3 minutes. The yellow solution was cooled and acidified with dilute HClO$_4$. (5.0 g, 36 mmoles) NaClO$_4$·H$_2$O was added to precipitate the pale orange complex (127 mg, 54%), which was washed with 1:1 ethanol and ether, and dried under vacuum.

Anal. Calculated for \([\text{Rh(C}_{10}\text{H}_{22}\text{N}_4}\text{Br(H}_2\text{O)}]\text{(ClO}_4\text{)}_2\): C, 20.01; H, 4.37; N, 9.34; Br, 13.32; Cl, 11.82. Found: C, 20.42; H, 4.18; N, 9.49; Br, 12.94; Cl, 11.66.

Trans-[\text{Rh(cyclam)}\text{I(OH)}]\text{ClO}_4$

(268 mg, 0.392 mmoles) trans-[\text{Rh(cyclam)}\text{I}_2]\text{I}$ and (1 pellet, ~2.5 mmoles) NaOH were added to 15 ml water and heated under reflux for 10 minutes. The solution was filtered and heated under reflux for an additional 2 minutes. (5.0 g, 36 mmoles) NaClO$_4$·H$_2$O was added to precipitate the orange complex (51 mg, 24%), which was washed with 1:1 ethanol and ether, and dried under vacuum.

Anal. Calculated for \([\text{Rh(C}_{10}\text{H}_{24}\text{N}_4}\text{I(OH)}]\text{ClO}_4\): C, 21.97; H, 4.61; N, 10.25; I, 23.22; Cl, 6.49. Found: C, 22.12; H, 4.49; N, 10.10; I, 23.16; Cl, 6.39.

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Trans-[Rh(cyclam)I(H₂O)](ClO₄)₂

(292 mg, 0.427 mmol) trans-[Rh(cyclam)I₂]I and (1 pellet, ~2.5 mmol) NaOH were added to 25 ml water and treated according to the trans-iodohydroxo preparation. The yellow solution was cooled on ice and slightly acidified with dilute HCIO₄ which made the solution red. (5.0 g, 36 mmol) NaClO₄ H₂O was added to precipitate the red complex (75 mg, 27%), which was washed with 1:1 ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)I(H₂O)](ClO₄)₂: C, 18.56; H, 4.05; N, 8.65; I, 19.61; Cl, 10.96. Found: C, 18.31; H, 4.11; N, 7.99; Cl, 11.04; I, 19.55.

Trans-[Rh(cyclam)(N₃)(OH)]ClO₄

(203 mg, 0.417 mmol) trans-[Rh(cyclam)(N₃)₂]ClO₄ and (1 pellet, ~2.5 mmol) NaOH were dissolved in 25 ml water and heated under reflux for 10 minutes, which made the solution paler yellow. (5.0 g, 36 mmol) NaClO₄·H₂O was added to precipitate the pale yellow complex (76 mg, 39%), which was washed with 1:1 ethanol and ether, dried under vacuum, and wrapped in aluminum foil to protect against photo-decomposition.


Trans-[Rh(cyclam)(N₃)(H₂O)](ClO₄)₂

(233 mg, 0.458 mmol) trans-[Rh(cyclam)(N₃)₂]ClO₄ were treated with NaOH as described for the hydroxo preparation. The yellow solution
was cooled on ice and slightly acidified with dilute HClO$_4$, which made it turn very slightly darker yellow. (5.0 g, 36 mmoles) NaClO$_4$·H$_2$O was added to precipitate the yellow complex (140 mg, 54%), which was washed with 1:1 ethanol and ether, dried under vacuum, and wrapped in aluminum foil to protect against photo-decomposition.

Anal. Calculated for [Rh(C$_{10}$H$_{24}$N$_4$)($N_3$)(H$_2$O)](ClO$_4$)$_2$: C, 21.36; H, 4.66; N, 17.44. Found: C, 21.45; H, 4.42; H, 17.27.

Cis-[Rh(cyclam)(OH)(H$_2$O)](ClO$_4$)$_2$

(496 mg, 1.21 mmoles) cis-[Rh(cyclam)Cl$_2$]Cl and (2 pellets, ~5 mmoles) NaOH were added to 25 ml water and heated under reflux for 5 minutes during which the solution turned paler yellow. (10 g, 72 mmoles) NaClO$_4$·H$_2$O was added, and the solution was neutralized with dilute HClO$_4$. Excess acid caused dissolution of the product, and therefore was avoided. The very pale yellow product (429 mg, 66%) was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C$_{10}$H$_{24}$N$_4$)(OH)(H$_2$O)](ClO$_4$)$_2$: C, 22.32; H, 5.24; N, 10.41; Cl, 13.18. Found: C, 22.42; H, 5.15; N, 10.44; Cl, 13.20.

Trans-[Rh(cyclam)(OH)(H$_2$O)](ClO$_4$)$_2$

(698 mg, 1.70 mmoles) trans-[Rh(cyclam)Cl$_2$]Cl and (5 pellets, ~12 mmoles) NaOH were dissolved in 20 ml water and heated under reflux for 100 minutes during which the solution became very pale yellow. (10 g, 72 mmoles) NaClO$_4$·H$_2$O were added and the solution was neutralized with dilute HClO$_4$. Excess acid caused dissolution of the product, and therefore was avoided. The pale yellow precipitate (610 mg, 67%) was
washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for $[\text{Rh(C}_{10}\text{H}_{24}\text{N}_{4})(\text{OH})(\text{H}_{2}\text{O})](\text{ClO}_{4})_{2}$: C, 22.32; H, 5.24; N, 10.41; Cl, 13.18. Found: C, 22.09; H, 5.19; N, 10.21; Cl, 13.10.

**Trans-[Rh(cyclam)ClBr]ClO₄**

(218 mg, .531 mmoles) trans-[Rh(cyclam)Cl₂]Cl and (1 pellet, ~2.5 mmoles) NaOH were dissolved in 25 ml water and heated under reflux for 5 minutes, during which the solution turned paler yellow. (10 ml, 87 mmoles) conc. HBr and 10 ml 70% HClO₄ were added and the solution was heated at 55° for 20 hours during which a yellow precipitate formed. The product (118 mg, 43%) was recrystallized from water, washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for $[\text{Rh(C}_{10}\text{H}_{24}\text{N}_{4})\text{Br}]\text{ClO}_{4}$: C, 23.19; H, 4.67; Br, 15.42; Cl, 13.69. Found: C, 23.36; H, 4.70; Br, 15.35; Cl, 13.76.

**Trans-[Rh(cyclam)ClI]ClO₄**

(200 mg, .292 mmoles) trans-[Rh(cyclam)I₂]I was dissolved in 400 ml 0.1 M NaCl and heated at 60° in a constant temperature bath for 2 days. 25 ml 70% HClO₄ were added to precipitate the complex, which was purified by repeating the procedure. The orange product (130 mg, 79%) was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for $[\text{Rh(C}_{10}\text{H}_{24}\text{N}_{4})\text{I}]\text{ClO}_{4}$: C, 21.26; H, 4.28; I, 22.46; Cl, 12.55. Found: C, 21.55; H, 4.60; I, 22.39; Cl, 12.84.
Trans-[Rh(cyclam)Cl(N₃)]ClO₄

(232 mg, 0.476 mmoles) trans-[Rh(cyclam)(N₃)₂]ClO₄ was added to 50 ml 1.0 M HCl and heated at 85° for 6 hours. 5 ml 70% HClO₄ were added to precipitate the complex, which was recrystallized from 40 ml water and 2 ml 70% HClO₄. The yellow product (140 mg, 61%) was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)Cl(N₃)ClO₄]: C, 25.10; H, 5.16; N, 20.42; Cl, 14.76. Found: C, 25.15; H, 4.95; N, 20.29; Cl, 14.81.

Trans-[Rh(cyclam)Cl(NCS)]ClO₄

(134 mg, 0.242 mmoles) trans-[Rh(cyclam)Cl(H₂O)](ClO₄)₂ and (1.0 g, 12 mmoles) NaSCN were dissolved in 15 ml water and heated under reflux for 15 minutes. (5.0 g, 36 mmoles) NaClO₄·H₂O was added to precipitate the yellow complex (73 mg, 61%), which was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)Cl(NCS)]ClO₄: C, 26.62; H, 4.88; N, 14.11; Cl, 14.29; S, 6.46. Found: C, 26.56; H, 4.81; N, 13.84; Cl, 14.33; S, 6.46.

Trans-[Rh(cyclam)BrI]ClO₄

(280 mg, 0.410 mmoles) trans-[Rh(cyclam)I₂]Br and (1 pellet, ~2.5 mmoles) NaOH were added to 50 ml water and heated under reflux for 15 minutes. The yellow solution was filtered, (4.0 ml, 35 mmoles) conc. HBr were added, and the solution was heated at 70° for 5 minutes. The volume was increased to 500 ml to dissolve the bromide salt. 50 ml 70% HClO₄ were added to precipitate the product. The orange crystals
mg, 63%) were washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C_{10}H_{24}N_{4})Br]ClO_4: C, 19.71; H, 3.97; N, 9.19; Br, 13.11; I, 20.82. Found: C, 19.70; H, 3.80; N, 9.01; Br, 12.90; I, 20.92.

Trans-[Rh(cyclam)Br(N\textsubscript{3})]ClO\textsubscript{4}

(149 mg, 0.306 mmoles) trans-[Rh(cyclam)(N\textsubscript{3})\textsubscript{2}]ClO\textsubscript{4} were added to 25 ml 1.0 M HClO\textsubscript{4} and heated under reflux for 5 hours. (2.6 g, 25 mmoles) NaBr was added and the yellow solution was heated at 70° for 1 hour. 5 ml 70% HClO\textsubscript{4} were added to precipitate the product, which was recrystallized from 25 ml water and 2 ml 70% HClO\textsubscript{4}. The orange crystals (110 mg, 69%) were washed with ethanol and ether, dried under vacuum, and protected from light.

Anal. Calculated for [Rh(C_{10}H_{24}N_{4})Br(N\textsubscript{3})]ClO_4: C, 22.90; H, 4.61; N, 18.69; Br, 15.23; Cl, 6.76. Found: C, 22.76; H, 4.74; N, 18.55; Br, 15.08; Cl, 6.78.

Trans-[Rh(cyclam)Br(NCS)]ClO\textsubscript{4}

(214 mg, 0.340 mmoles) trans-[Rh(cyclam)Br(H\textsubscript{2}O)](ClO\textsubscript{4})\textsubscript{2} and (1.0 g, 12 mmoles) NaSCN were dissolved in 15 ml water and heated under reflux for 10 minutes which made the solution turn from orange to yellow. (10 g, 72 mmoles) NaClO\textsubscript{4}·H\textsubscript{2}O was added to precipitate the yellow complex (14A mg, 78%), which was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C_{10}H_{24}N_{4})Br(NCS)]ClO_4: C, 24.64; H, 4.47; N, 12.95; Br, 14.78; Cl, 6.56. Found: C, 24.82; H, 4.39; N, 12.97; Br, 14.59; Cl, 6.70.
Trans-[Rh(cyclam)I(N_{3})]ClO_{4}

(306 mg, 0.447 mmole) trans-[Rh(cyclam)I_{2}]I and (1 pellet, ~2.5 mmole) NaOH were added to 200 ml water and heated under reflux for 5 minutes. The yellow solution was filtered and (20 g, 310 mmole) NaN_{3} was added. Then the solution was neutralized with dilute HClO_{4} during which it turned orange. 50 ml 70% HClO_{4} were added to precipitate the orange product (81 mg, 32%), which was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C_{10}H_{24}N_{4})I(N_{3})]ClO_{4}: C, 21.01; H, 4.23; N, 17.15; I, 22.20. Found: C, 21.26; H, 4.21; N, 17.09; I, 22.31.

Trans-[Rh(cyclam)I(NCS)]ClO_{4}

(289 mg, 0.466 mmole) trans-[Rh(cyclam)I(H_{2}O)](ClO_{4})_{2} and (1.0 g, 12 mmole) NaSCN were dissolved in 25 ml water and heated under reflux for 15 minutes, which made the solution turn from red to orange. (10 g, 72 mmole) NaClO_{4}·H_{2}O was added to precipitate the pale orange complex (227 mg, 87%), which was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C_{10}H_{24}N_{4})I(NCS)]ClO_{4}: C, 22.48; H, 4.12; N, 11.92; I, 21.59; Cl, 6.03. Found: C, 22.60; H, 4.03; N, 11.95; I, 21.74; Cl, 5.94.

Trans-[Rh(cyclam)(N_{3})(NCS)]ClO_{4}

(243 mg, 0.432 mmole) trans-[Rh(cyclam)(N_{3})(H_{2}O)](ClO_{4})_{2} and (1.0 g, 12 mmole) NaSCN were dissolved in 20 ml water and heated at 70° for 75 minutes, during which the solution remained yellow. (10 g, 72 mmole)
NaClO₄·H₂O was added to precipitate the yellow complex (142 mg, 64%), which was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₀N₄)(N₃)(NCS)]ClO₄: C, 25.77; H, 4.72; N, 21.85; S, 6.25. Found: C, 25.97; H, 4.72; N, 21.97; S, 6.27.

Resolution of Racemic cis-[Rh(cyclam)Cl₂]Cl

(500 mg, 1.22 mmoles) cis-[Rh(cyclam)Cl₂]Cl and (90 g, 2.7 mmoles) d-ammonium α-bromocamphor-κ-sulfonate were dissolved in 15 ml water and frozen for one week. The mixture was melted and filtered. The pale yellow precipitate was washed with a few drops of ice cold water and ground thoroughly with 2 ml of 1:1:1 ethanol, conc. HCl, and ether. The 1-cis-[Rh(cyclam)Cl₂]Cl was filtered (149 mg, 60%).

Using a mercury and a sodium lamp, the rotation of a .58% solution was too small to measure an a Rudolph polarimeter.

The ORD spectrum of a 1.13% solution was recorded with a Cary 60 spectrometer. The spectrum exhibited zero rotation at 353 and 300 μm, which corresponds to the absorption maxima of the cis isomer. There was a positive rotation (.0007°) at 325 μm and a negative rotation (.0007°) at 370 μm using a 1mm cell.

\[
\begin{align*}
\lambda \nu &= 325 \mu m = +6^\circ \\
\lambda \nu &= 370 \mu m = -6^\circ 
\end{align*}
\]

3. Revised Preparations

The use of the base hydrolysis pathway for the preparation of the mixed trans-Rh(cyclam)XY⁺ complexes was so successful in terms of product purity and reduction of preparation time, that it was applied
to reactions which were originally successful by direct substitution, but with more difficulty and time-consuming procedures. This was true even for trans-Rh(cyclam)X$_2$\(^+\) preparations. The experimental detail of five of the revised preparations are given, but it is apparent that this method combined with control of pH is the key to almost any conceivable complex involving unidentate ligands with reasonable donor properties, starting with the trans-Rh(cyclam)Cl$_2$\(^+\) complex. It could also be applied to cis-Rh(cyclam)X$_2$\(^+\) complexes, but, as yet, not to mixed cis complexes, since the cis base hydrolysis cannot be stopped after the substitution of only one unidentate ligand. This is because the rates for base hydrolysis of the two cis unidentate ligands is nearly equal, involving a strong trans amido group for both, and relatively weaker differential cis effects.

The preparation of the trans-dinitro complex from the trans-chloroaquo or trans-azidoaquo is especially interesting, since it shows the very large trans effect of nitro. After the rapid anation to the trans-acidonitro, the acido group is subject to rapid acid hydrolysis even at room temperature. This is convincing evidence that the difficult preparation by direct substitution of the trans-dichloro complex is due to interference by another reaction, most likely base hydrolysis, in a solution made more basic by the strongly basic nitrite anion. At room temperature, the base hydrolysis rate is very slow, and does not interfere with the trans-dinitro formation from trans-chloroaquo, which is complete in less than one minute.

The preparations were carried out at least twice in each case to test the reproducibility of the methods. Each experiment gave products which were as pure or purer than those analyzed from the original.
procedures, as indicated by the electronic maximum to minimum absorption ratios and the values of the extinction coefficients.

Trans-[Rh(cyclam)ClI]ClO₄

(204 mg, 0.301 mmoles) trans-[Rh(cyclam)I₂]I and (1 pellet, ~2.5 mmole) NaOH were added to 25 ml water and heated under reflux for 10 minutes. (1.0 g, 17 mmoles) NaCl were added, followed by 3 ml 70% HClO₄ while the solution was still hot. The product was filtered, and the procedure was repeated with a 2 minute reflux period. The orange crystals (91 mg, 54%) were washed with ethanol and ether, and dried under vacuum.

The electronic spectrum indicated a product at least as pure as that analyzed from the original procedure.

Trans-[Rh(cyclam)IBr]ClO₄

(223 mg, 0.326 mmoles) trans-[Rh(cyclam)I₂]I and (1 pellet, ~2.5 mmole) NaOH were added to 25 ml water and heated under reflux for 10 minutes. (1.0 g, 9.7 mmoles) NaBr was added with stirring, followed by 5 ml 70% HClO₄. The procedure was repeated on the crude product with a 2 minutes reflux period and filtration before precipitation. The orange product (116 mg, 58%) was washed with ethanol and ether, and dried under vacuum.

The electronic spectrum indicated at least as pure a product as that analyzed from the original procedure.

Trans-[Rh(cyclam)Br₂]Br

(1.0 g, 2.4 mmoles) trans-[Rh(cyclam)Cl₂]Cl was treated repeatedly
with NaOH and HBr at reflux temperature in 25 ml water. The acid solution was filtered and the orange product (781 mg, 61%) was washed with ethanol and ether, and dried under vacuum.

The electronic spectrum indicated a better product than that produced by the original procedure, for which an acceptable analysis was obtained.

Trans-[Rh(cyclam)I₂]I

The preparation of the diiodo complex was improved and shortened by heating either the cis or trans-dichloro complex in 3 liters of slightly basic NaI solution. Acidification of the solution with HCl before precipitation gave an excellent yield (90%). The procedure was repeated until the trans diiodo spectrum was obtained. The cis dichloro complex could be used since the cis diiodo complex isomerized to the trans complex at reflux temperature.

The electronic spectrum indicated a better product than that produced by the original procedure.

Trans-[Rh(cyclam)(NO₂)₂]ClO₄

(298 mg, 612 mmoles) trans-[Rh(cyclam)(N₂)₂]ClO₄ was added to 25 ml 1.0 M HClO₄ and heated under reflux for 15 hours to give the azido-aquo complex, or more conveniently the base hydrolysis reaction was used with protonation of the azidohydroxo complex. (2.0 g, 29 mmoles) NaN₂O₂ was added, which caused the formation of a white precipitate at room temperature. The white product (170 mg, 40%) was washed with ethanol and ether, and dried under vacuum. The electronic spectrum and the
analysis indicated the dinitro product.


The same results were obtained for the anation of the trans-chloroaquo complex with nitrite.

2. Attempted Preparations

The direct reaction of $\text{RhCl}_{3}\cdot3\text{H}_{2}\text{O}$ and cyclam in aqueous solution of an anion ($\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$, and $\text{N}_3^-$) gave the $\text{Rh}($cyclam)$\text{X}_2^+$ complex

\[
\text{e.g. } \text{RhCl}_{3}\cdot3\text{H}_{2}\text{O} + \text{cyclam} \xrightarrow{1\text{ M Br}^-} \text{cis and trans-Rh(cyclam)Br}_2^+
\]

of the particular anion used. In no case was complete separation of the isomers successful. The trans isomer was present as a small percentage ranging from approximately 5% for the dichloro to 20% for the diiodo preparation. The cis isomer was less soluble than the trans. Further work was not necessary after the separation of the dichloro isomers was very readily executed in methanol, because of much greater solubility differences in that solvent.

The preparation of the more symmetric cyclam analog, 1,5,9,13-tetraazacyclododecane was tried, but was abandoned after its instability in air was observed.

The attempted substitutions at reflux temperature of the trans-dichloro complex by strongly basic anions such as fluoride and cyanide were unsuccessful, because of the increased interference of the base hydrolysis reaction, compared to the interference in neutral solutions of the less basic anions. As mentioned, even the dinitro preparation was made difficult because of base hydrolysis. The electronic spectrum
of the products produced confirmed the presence of the dihydroxo complex. The use of an aprotic solvent such as DMSO eliminated the interference by base hydrolysis, and a red product, believed to be the trans-dicyano complex, was observed from the substitution of cyanide on the trans-dichloro complex. However, the red product could not be precipitated with perchlorate of chloride. The isolation of the cyano and fluoro complexes would be of interest because of the expected extremes of the trans effect involved; large for cyano and small for fluoro.

The mixed nitro complexes could not be prepared from the acido-aquo complexes, since after the first anation by nitrite, the very large nitro trans effect gave the dinitro product very rapidly at room temperature. For this reason, attempts were made to isolate the trans-nitrohydroxo complex, which is expected to be readily anated after protonation of the hydroxo ligand to the aquo. Although a product considered to be the nitrohydroxo complex was prepared, it was too soluble to be precipitated in appreciable yields by perchlorate.

The trans-Rh(cyclam)(SO₃)₂⁻ complex was readily prepared by direct substitution of the trans-dichloro complex by SO₃²⁻, but the product was too soluble to be precipitated with sodium cation.

The cis and trans diaquo and dihydroxo complexes were all successfully prepared, but were too soluble to be precipitated with perchlorate.

The cis-chlorohydroxo complex could not be prepared, because the base hydrolysis could not be stopped after the first substitution on the dichloro complex, which has already been discussed.

The attempted preparation of the cis-chloroisothiocyanato complex showed the greater cis effect of isothiocyanato relative to its trans
effect. The substitution reaction produced the diisothiocyanato complex, as indicated by the analysis, under reaction conditions which did not give the trans-diisothiocyanato complex for the substitution of the trans-dichloro complex by SCN⁻.

The experimental details of these attempted preparations are given, in the order they were discussed, and should be useful for further work at the isolation of the complexes, which are of interest for mechanistic and trans effect studies.

1,5,9,13-tetraazacycloclohexadecane

(47 g, 0.25 moles, 49 ml) 1,11-diamino-diazaundecane and (50 g, 0.25 moles, 26 ml) 1,3-dibromopropane were treated in high dilution ethanol similarly to the cyclam preparation. A white waxy precipitate was obtained. It could not be dried properly and was observed to be unstable in air.

Trans-[Rh(cyclam)F₂]ClO₄

(233 mg, 0.568 mmole) trans-[Rh(cyclam)Cl₂]Cl and (2.0 g, 48 mmoles) NaF were added to 50 ml water in a teflon beaker and heated under reflux for 1 hour. (5.0 g, 36 mmole) NaClO₄·H₂O was added to precipitate the pale yellow product (45 mg, 19%), which was washed with ethanol and ether, and dried under vacuum.

Anal. Calculated for [Rh(C₁₀H₂₄N₄)F₂]ClO₄: C, 27.2; H, 5.5; N, 12.7; Cl, 8.0; F, 8.6. Found: C, 19.5; H, 3.8; N, 8.9; Cl, 11.5; F, 16.4.

Spectrum: Shoulder (290 μm) and maximum (394 μm).
Trans-[Rh(cyclam)(CN)₂]ClO₄

(219 mg, 0.535 mmoles) trans-[Rh(cyclam)Cl₂]Cl and (1.0 g, 20 mmoles) NaCN were dissolved in 25 ml water and evaporated to dryness. The residue was heated, which caused it to change from yellow to green to red. The reaction was difficult to reproduce, and a well-defined product was not isolated.

(217 mg, 0.505 mmoles) trans-[Rh(cyclam)Cl₂]Cl and (1.0 g, 20 mmoles) NaCN were added to 50 ml DMF and heated at 150°C. The solution turned from yellow to very dark red. The product could not be isolated with an aqueous NaClO₄ solution.

Trans-[Rh(cyclam)(NO₂)(OH)]ClO₄

(400 mg, 0.809 mmoles) trans-[Rh(cyclam)(NO₂)₂]ClO₄ and (1 pellet, ~2.5 mmoles) NaOH were added to 25 ml water and heated under reflux for 60 minutes. (20 g, 140 mmoles) NaClO₄·H₂O was added to precipitate the product in very low yield. The reaction solution spectrum had a maximum at 283 mp.

Trans-Na[Rh(cyclam)(SO₃)₂]

(242 mg, 0.591 mmoles) trans-[Rh(cyclam)Cl₂]Cl and (2.0 g, 16 mmoles) Na₂SO₃ were dissolved in 25 ml water and heated under reflux for 20 minutes. The solution turned from yellow to colorless. The product could not be precipitated with perchlorate.

Cis-[Rh(cyclam)(OH)₂]ClO₄

Cis-[Rh(cyclam)Cl₂]Cl and (1 pellet, ~2.5 mmoles) NaOH were
dissolved in 25 ml water and heated under reflux for 5 minutes. The product could not be precipitated with perchlorate.

An accurately weighed amount of the cis-hydroxoaquo complex was dissolved in 25 ml 0.1 M NaOH and heated at 85° C for 1 hour to give the dihydroxo complex. The electronic spectrum of the solution was recorded.

Cis-\([\text{Rh}(\text{cyclam})(\text{H}_2\text{O})_2](\text{ClO}_4)_2\]

This complex was prepared by acidifying a cis-dihydroxo solution, but it could not be precipitated with perchlorate.

Acidification of a cis-hydroxoaquo solution gave an equilibrium mixture, and heating at 85° C for 20 hours gave the diaquo complex completely. The electronic spectrum of a solution of predetermined concentration was recorded.

Trans-\([\text{Rh}(\text{cyclam})(\text{OH})_2]\text{ClO}_4\]

Trans- \(\text{Rh}(\text{cyclam})\text{Cl}_2\) Cl and (1 pellet, ~2.5 mmoles) NaOH were dissolved in 25 ml water and heated under reflux for 1 hour. The product could not be precipitated with perchlorate.

(43.85 mg, .08147 mmoles) trans-\([\text{Rh}(\text{cyclam})(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2\] was dissolved in 25.00 ml 0.1 M NaOH and heated at 85° C for 25 hours. The electronic spectrum of the solution was recorded.

Trans-\([\text{Rh}(\text{cyclam})(\text{H}_2\text{O})_2](\text{ClO}_4)_3\]

This complex was prepared by acidifying a trans-dihydroxo solution, but it could not be precipitated with perchlorate.
trans-[Rh(cyclam)(OH)(H$_2$O)](ClO$_4$)$_2$ was

dissolved in 25.00 ml 0.1 M HClO$_4$ and heated at 85° C for 24 hours.

This did not give complete solution, but the electronic spectrum was

recorded and approximate extinction coefficients were calculated.

Cis-[Rh(cyclam)Cl(OH)]ClO$_4$

(529 mg, 1.29 mmoles) cis-[Rh(cyclam)Cl$_2$]Cl and (2 pellets, ~5

mmoles) NaOH were heated under reflux for 10 minutes. The product could

not be precipitated with perchlorate. The electronic spectrum did not

change after an additional 60 minutes of reflux time, indicating that

the product was actually the dihydroxo complex. Limiting the reflux

period always resulted in the rapid formation of the dihydroxo product,

which made it impossible to isolate the monohydroxo complex by this

procedure.

Cis-[Rh(cyclam)(NCS)Cl](SCN)

(544 mg, 1.12 mmoles) cis-[Rh(cyclam)Cl$_2$]ClO$_4$ and (1.0 g, 22

mmoles) NaSCN were added to 50 ml water and heated under reflux for

7 hours. (5.0 g, 62 mmoles) NaSCN was added to precipitate the product

(152 mg, 30%), which was recrystallized from 0.5 M NaSCN, washed with

ethanol and ether, and dried under vacuum.

The analysis indicated the disubstituted product. Anal. Calculated

for [Rh(C$_{10}$H$_{24}$N$_4$)(NCS)$_2$](SCN): C, 32.7; H, 5.05; N, 20.6. Found; C,

33.4; H, 5.22; N, 20.8.
III. CHARACTERIZATION OF SOME DIACIDOCYCLAMRHODIUM(III) COMPLEXES

1. Stereoisomers

The cis and trans isomers of the diacidocyclamrhodium(III) series prepared in this work were assigned on the basis of a comparison of the wavelengths and extinction coefficients of the absorption maxima of their electronic spectra (Tables I and II) with the values for the known isomers of the diacidobis(ethylenediamine)rhodium(III) series. It is readily apparent that the trans isomers exhibit d-d transitions of lesser energy and lesser intensity (see also Fig. 3). This observation was used to confirm the assignment of cyclam complexes for which there are no bis(ethylenediamine) analogs. These cyclam complexes were assigned more clearly on the basis of the infrared spectra.

### TABLE I

The Electronic Spectra of Rh(cyclam)XY^3^+ (Maxima)

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ(mu)</th>
<th>ε(1. cm(^{-1}) mole(^{-1}))^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Cl(_2^+)</td>
<td>354, 299, 207</td>
<td>223, 308, 33900</td>
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<tr>
<td>trans-Cl(_2^+)</td>
<td>406, 310sh, 242sh, 206</td>
<td>78, 80, 3300, 37100</td>
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<tr>
<td>cis-Br(_2^+)</td>
<td>367, 309</td>
<td>243, 871</td>
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<tr>
<td>trans-Br(_2^+)</td>
<td>429, 285, 235</td>
<td>97.3, 2520, 34600</td>
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<tr>
<td>cis-I(_2^+)</td>
<td>407, 295sh, 260sh, 228</td>
<td>1210, 5300, 17500, 38400</td>
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<tr>
<td>trans-I(_2^+)</td>
<td>515sh, 466, 353, 275, 226</td>
<td>64, 204, 13100, 34500, 22800</td>
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<tr>
<td>cis-(N(_3))(_2^+)</td>
<td>339sh, 262</td>
<td>1250, 11800</td>
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<table>
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<th>Complex</th>
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<th>( \epsilon(1. \text{ cm}^{-1} \text{ mole}^{-1}) )</th>
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<tbody>
<tr>
<td>( \text{trans-(N}_3\text{)}_2^+ )</td>
<td>377, 286, 208</td>
<td>892, 12700, 27100</td>
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<tr>
<td>( \text{cis-(NO}_2\text{)}_2^+ )</td>
<td>293sh</td>
<td>1030</td>
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<td>( \text{trans-(NO}_2\text{)}_2^+ )</td>
<td>320sh, 260sh, 213</td>
<td>535, 2100, 30800</td>
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<tr>
<td>( \text{cis-(NCS)}_2^+ )</td>
<td>322, 244</td>
<td>1110, 3630</td>
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<tr>
<td>( \text{trans-(NCS)}_2^+ )</td>
<td>377, 258</td>
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<tr>
<td>( \text{trans-Cl(OH)}^+ )</td>
<td>363, 276</td>
<td>101, 180</td>
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<td>( \text{trans-Cl(H}_2\text{O)}^2+ )</td>
<td>385, 296sh, 224sh</td>
<td>55, 101, 4420</td>
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<tr>
<td>( \text{trans-Br(OH)}^+ )</td>
<td>373, 277sh</td>
<td>113, 384</td>
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<td>( \text{trans-Br(H}_2\text{O)}^2+ )</td>
<td>468, 403, 310sh, 204</td>
<td>37, 63, 106, 25600</td>
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<td>( \text{trans-I(OH)}^+ )</td>
<td>443, 393, 275, 230</td>
<td>153, 158, 5330, 26300</td>
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<td>( \text{trans-I(H}_2\text{O)}^2+ )</td>
<td>494, 341sh, 301sh,</td>
<td>222, 763, 1290, 2240, 24400</td>
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<td>271, 230</td>
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<td>( \text{trans-N}_3\text{(OH)}^+ )</td>
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<td>( \text{cis-(OH)}\text{(H}_2\text{O)}^2+ )</td>
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<tr>
<td>( \text{cis-(OH)}_2^+ )</td>
<td>331, 278</td>
<td>226, 202</td>
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<tr>
<td>( \text{cis-(H}_2\text{O)}_2^3+ )</td>
<td>296, 251</td>
<td>249, 230</td>
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<td>( \text{trans-(OH)}_2^+ )</td>
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<td>101, 163</td>
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<tr>
<td>( \text{trans-(H}_2\text{O)}_2^3+ )</td>
<td>352</td>
<td>65</td>
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<tr>
<td>( \text{trans-ClBr}^+ )</td>
<td>418, 312sh, 260sh, 221</td>
<td>89, 95, 1950, 32700</td>
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<tr>
<td>( \text{trans-ClI}^+ )</td>
<td>493, 445sh, 308, 245</td>
<td>230, 138, 3620, 31300</td>
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TABLE I (concluded)

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<th>Complex</th>
<th>λ(μm)</th>
<th>ε(1. cm⁻¹ mole⁻¹)</th>
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<tr>
<td>trans-Cl(N₃)⁺</td>
<td>382, 270, 207</td>
<td>697, 9390, 23000</td>
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<td>trans-Cl(NCS)⁺</td>
<td>368, 252</td>
<td>340, 8080</td>
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<td>trans-BrI⁺</td>
<td>497, 459, 321, 256</td>
<td>151, 152, 6200, 33900</td>
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<td>trans-Br(N₃)⁺</td>
<td>393, 281, 214</td>
<td>698, 11900, 21400</td>
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<td>trans-Br(NCS)⁺</td>
<td>368, 262</td>
<td>355, 8980</td>
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<tr>
<td>trans-I(N₃)⁺</td>
<td>465sh, 417, 300, 225</td>
<td>283, 654, 10100, 8970, 20900</td>
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<tr>
<td>trans-I(NCS)⁺</td>
<td>434, 412, 296, 274, 224</td>
<td>393, 413, 4220, 5660, 30600</td>
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<tr>
<td>trans-(N₂)(NCS)⁺</td>
<td>352, 270</td>
<td>861, 7330</td>
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*based on analyzed samples

TABLE II

The Electronic Spectra of Rh(en)₂XY⁺ (Maxima)

<table>
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<tr>
<th>Complex</th>
<th>λ(μm)</th>
<th>ε(1. cm⁻¹ mole⁻¹)</th>
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<td>155, 180</td>
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<tr>
<td>trans-Cl₂</td>
<td>406, 286</td>
<td>75, 130</td>
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<td>cis-Br₂</td>
<td>362, 276</td>
<td>210, 900</td>
<td>70</td>
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<tr>
<td>trans-Br₂</td>
<td>425, 276, 231</td>
<td>100, 2300, 30800</td>
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<tr>
<td>cis-I₂</td>
<td>375</td>
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<td>70</td>
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<td>trans-I₂</td>
<td>462, 340, 259, 222</td>
<td>260, 14300, 31000, 20000</td>
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<tr>
<td>trans-(N₃)₂</td>
<td>375, 282</td>
<td>740, 13000</td>
<td>71</td>
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<tr>
<td>cis-(NO₂)₂</td>
<td>290, 245sh</td>
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<td>trans-(NO₂)₂</td>
<td>300sh, 255sh</td>
<td>590, 2400</td>
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The cis-Rh(cyclam)Cl₂⁺ isomer was confirmed by the resolution of the racemic mixture with ammonium d-α-bromocamphor-β-sulfonate. An ORD spectrum showed a very small specific rotation (see p. 55). Racemic cis-[Rh(en)₂Cl₂]Cl has also been successfully resolved, and the optical rotation of the 1-cis isomer was measured \((\beta)_\text{535 nm} = -58°\) \(^{48}\). The relatively small rotation of the cyclam optical isomer could have been the result of poor separation of the diastereoisomers or the increased symmetry of the cyclam cis isomer over the corresponding bis(ethylene-diamine) cis isomer.

The charge transfer absorption peaks for a series of trans complexes clearly shows the shift along the spectrochemical series (Fig. 4). The peak shifts to higher energies along the series trans-I₂, IBr, ICl, and Cl₂. The spectrochemical series lists ligands according to their capacity to cause d orbital splittings \((I < Br < Cl)\). \(^{72}\)

The relative extinction coefficients of the stereoisomers provide evidence for the assignments. Distortion of the octahedral field around the central metal ion tends to remove the center of symmetry with respect to vibrations, and the \(d^6\) states lose some of their g character through vibronic coupling. \(^{73}\). This provides a mechanism for
Figure 3. The Electronic Spectra of Rh(cyclam)XY⁺ Complexes. (A) trans-Cl₂, (B) cis-Cl₂ (C) trans-ClI, and (D) trans-BrI.
Figure 4. The Charge Transfer Spectra of some Rh(cyclam)XY\textsuperscript{+} Complexes.

(A) trans-Cl\textsubscript{2}, (B) trans-ClI, (C) trans-BrI, and (D) trans-I\textsubscript{2}.

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increasing the intensity of the d-d transitions. The two spin allowed bands (\( ^3T_{1g} \rightarrow ^1A_{1g} \) and \( ^3T_{2g} \rightarrow ^1A_{1g} \)) are easily observed, and are obscured by charge transfer bands only for nitro complexes with their large ligand field strengths. An increase in steric constraint is expected to cause greater distortions, and thereby, greater intensities in the visible absorption of the complexes. Collman and Schneider\(^7\) discuss this principle with respect to a cis-Rh(amine)\(X_2^+\) series. The center of symmetry is removed in a cis isomer relative to a trans, considering the primary effects of the N donors and ignoring the secondary effects of the ethylene and propylene linkages. As a result, larger extinction coefficients for the d-d transitions are predicted for the cis isomers. Table III, which is a comparison of some of the Rh(amine)Cl\(_2^+\) complexes shows this trend very clearly, and Table I

**TABLE III**

The Electronic Spectra of some Rh(amine)Cl\(_2^+\) Complexes (Maxima)

<table>
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<tr>
<th>Complex</th>
<th>(\lambda) (mu)</th>
<th>(\epsilon) (1. cm(^{-1}) mole(^{-1}))</th>
<th>Ref.</th>
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<tr>
<td>trans-Rh(cyclam)Cl(_2^+)</td>
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shows that this trend is consistent with the assignment of stereoisomers for the cyclam complexes. It is especially clear in the case of cis-[Rh(cyclam)I₂]I, which has the additional distortion resulting from the size of the iodo ligands. The lower energy d-d transition is about 20 times as intense for the cis isomer. In addition, as noted, the steric effect of the iodo ligands make this the only complex in the series which undergoes stereoisomerization at reflux temperature.

Moreover the effect is more pronounced in the cis series than in the trans. Table III also shows that the larger size and greater flexibility of the cyclam ring relative to the cyclen ring results in less distortion of the octahedral field. The d-d transition intensity is less than that of complexes with only ethylene linkages. Therefore, the presence of the two propylene bridges in cyclam removes some of the steric constraint found in the cis series.

The infrared spectra (cm⁻¹) also provide evidence for the increased distortion of the octahedral field in the cis series (Tables IV, V, and VI; Figures 5 and 6). The decrease in the symmetry of the cis

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<th>v₂(CH)</th>
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Figure 5. The Infrared Spectrum of cis-[Rh(cyclam)Cl2]Cl
Figure 6. The Infrared Spectrum of trans-[Rh(cyclam)Cl₂]Cl₂.
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### TABLE V

The Infrared Spectra of other Ligands and Perchlorate$^{70, 75}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Characteristic Absorption Frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-(N$_3$)$_2$</td>
<td>2020 S, 660 W (N$_3^-$); 617 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-(N$_3$)$_2$</td>
<td>2010 S, 660 W (N$_3^-$); 615 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>cis-(NO$_2$)$_2$</td>
<td>1399 S, 815 M, 830 M (NO$_2^-$); 617 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-(NO$_2$)$_2$</td>
<td>1390 S, 825 M (NO$_2^-$); 617 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>cis-(NCS)$_2$</td>
<td>2100 S, 2080 S, 835 M, 820 M (NCS$^-$); 618 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-(NCS)$_2$</td>
<td>2090 S, 830 M (NCS$^-$); 611 (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-Cl(OH)</td>
<td>3610 M (OH$^-$), 614 (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-Cl(H$_2$O)</td>
<td>1610 M (H$_2$O), 617 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-Br(OH)</td>
<td>3600 M (OH$^-$), 614 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-Br(H$_2$O)</td>
<td>1610 M (H$_2$O), 614 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-I(OH)</td>
<td>3605 M (OH$^-$), 617 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-I(H$_2$O)</td>
<td>1610 M (H$_2$O), 612 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-(N$_3$)(OH)</td>
<td>3495 S (OH$^-$); 2025 S, 660 W (N$_3^-$); 611 S (ClO$_4^-$)</td>
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<tr>
<td>trans-(N$_3$)(H$_2$O)</td>
<td>1610 M (H$_2$O); 2020 S, 670 W (N$_3^-$); 615 S (ClO$_4^-$)</td>
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<tr>
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<td>3540 M (OH$^-$), 1615 M (H$_2$O), 618 S (ClO$_4^-$)</td>
</tr>
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<td>cis-(OH)(H$_2$O)</td>
<td>3440 S, broad (OH$^-$); 1625 M (H$_2$O); 622 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-ClBr</td>
<td>614 S (ClO$_4^-$)</td>
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TABLE V (concluded)

<table>
<thead>
<tr>
<th>Complex</th>
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<tr>
<td>trans-ClI</td>
<td>618 (ClO$_4^-$)</td>
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<tr>
<td>trans-Cl(N$_3$)</td>
<td>2010 S, 660 W (N$_3^-$); 614 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-Cl(NCS)</td>
<td>2090 S, 835 M (NCS$^-$); 611 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-BrI</td>
<td>613 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-Br(N$_3$)</td>
<td>2005 S, 660 W (N$_3^-$); 613 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-Br(NCS)</td>
<td>2090 S, 835 M (NCS$^-$); 611 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-I(N$_3$)</td>
<td>2005 S, 650 W (N$_3^-$); 612 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-I(NCS)</td>
<td>2090 S, 835 M (NCS$^-$); 610 S (ClO$_4^-$)</td>
</tr>
<tr>
<td>trans-(N$_3$)(NCS)</td>
<td>2020 S, 660 W (N$_3^-$); 2100 S, 833 M (NCS$^-$); 610 S (ClO$_4^-$)</td>
</tr>
</tbody>
</table>

S, strong; M, medium; W, weak

TABLE VI

The Rh-L Stretching Frequencies

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<thead>
<tr>
<th>Complex</th>
<th>Rh-N</th>
<th>Rh-N</th>
<th>Rh-N$_3$</th>
<th>Rh-OH</th>
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<td>cis-Cl$_2$</td>
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<td></td>
<td>459</td>
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<tr>
<td>trans-Cl$_2$</td>
<td>493</td>
<td>432</td>
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<td>289</td>
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<td>cis-Br$_2$</td>
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<tr>
<td></td>
<td>450</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-Br$_2$</td>
<td>487</td>
<td>433</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>cis-I$_2$</td>
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<td></td>
<td>423</td>
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<td></td>
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<td>trans-I$_2$</td>
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<td>425</td>
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<tr>
<td>cis-(N$_3$)$_2$</td>
<td>490</td>
<td>437</td>
<td>351</td>
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<td></td>
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<td></td>
<td>459</td>
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<th>Complex</th>
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<tr>
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<td>427</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>trans-I(OH)</td>
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<tr>
<td>trans-I(H₂O)</td>
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<td>trans-(N₃)(H₂O)</td>
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<td>370</td>
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<td>trans-(OH)(H₂O)</td>
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<td>431</td>
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<tr>
<td>cis-(OH)(H₂O)</td>
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<td>546</td>
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<td>trans-Cl(NCS)</td>
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<td></td>
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</table>
TABLE VI (concluded)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Rh-N</th>
<th>Rh-N</th>
<th>Rh-N&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Rh-Cl</th>
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</thead>
<tbody>
<tr>
<td>trans-BrI</td>
<td>490</td>
<td>429</td>
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<td></td>
</tr>
<tr>
<td>trans-Br(N&lt;sub&gt;3&lt;/sub&gt;)</td>
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<td>430</td>
<td>352</td>
<td></td>
</tr>
<tr>
<td>trans-Br(NCS)</td>
<td>498</td>
<td>428</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-I(N&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>491</td>
<td>428</td>
<td>347</td>
<td></td>
</tr>
<tr>
<td>trans-I(NCS)</td>
<td>493</td>
<td>428</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-(N&lt;sub&gt;3&lt;/sub&gt;)(NCS)</td>
<td>499</td>
<td>428</td>
<td>360</td>
<td></td>
</tr>
</tbody>
</table>

complexes results in greater detail in the spectrum. The NH and RhN stretching frequencies, and the CH<sub>2</sub> rocking frequency are single peaks in the trans and double peaks in the cis series. There is greater detail in the cis spectra from 1000 to 1250 cm<sup>-1</sup>, which includes the CN and CC stretching frequencies. In addition, the nitro and isothiocyanato stretching frequencies are split in the cis complexes.

2. Linkage Isomers

The thiocyanate ion is bonded in the isothiocyanato form (N-bonded) as determined from its spectra. A medium band near 835 cm<sup>-1</sup> was observed for each thiocyanate complex (Table V). Turco and Pecile<sup>76</sup> reported the range 780-860 cm<sup>-1</sup> for the C-S stretching frequency in isothiocyanato complexes as opposed to 690-720 cm<sup>-1</sup> in thiocyanato complexes. In this work, no i.r. bands were observed in the 690-720 cm<sup>-1</sup> range. A more reliable assignment can be made on the basis of the ξ(NCS) fundamental mode, which occurs in the 460-490 cm<sup>-1</sup> range for M-NCS, while the corresponding band for M-SCN occurs from 410 to 440 cm<sup>-1</sup>.
In this work, a single weak band was present near 460 cm\(^{-1}\), which supports the isothiocyanato assignment. This is a necessary confirmation, since the first overtone of the \(\delta(\text{NCS})\) fundamental, which would occur for both M-SCN and M-NCS, is a band between 800 and 880 cm\(^{-1}\) with an intensity comparable to the \(\nu(\text{C-S})\) mode, and therefore, may be mistaken as diagnostic of isothiocyanato. The most reliable criterion for M-NCS bonding is a broad band in the vicinity of 2000 cm\(^{-1}\), while M-SCN gives a very sharp band in the same region in the spectrum of the solid\(^{77}\). Again the isothiocyanato assignment for all the complexes prepared, involving the thiocyanate ion, was indicated by a characteristically broad band in the range 2080-2100 cm\(^{-1}\).

The electronic spectra were in agreement with this assignment. According to Schaffer\(^{78}\) and Jorgensen\(^{79}\), thiocyanato should fit close to chloro and bromo in the spectrochemical series, while isothiocyanato would fit along with stronger ligands such as azido, at lower wavelengths. Comparing the lower energy d-d transition of the thiocyanato, azido, and halo complexes (Table I), it is evident that thiocyanato has a ligand field strength very close to that of azido.

The ultraviolet spectra of the dinitro complexes show that the linkage isomers contain nitro rather than nitrito ligands. Nitrito has a ligand field strength near that of hydroxo, whereas nitro is close to the strongest ligands in the spectrochemical series. The absorption maxima for the nitro complexes are the farthest in the UV, and are observed as shoulders due to the proximity of the charge transfer peaks. All the comparable hydroxo maxima are farther in the visible region.

The sharp infrared band near 820 cm\(^{-1}\) is diagnostic of a
isomer. It should not be confused with a broad peak near 860 cm⁻¹ found in both nitro and nitrito isomers.

The greater stability of the isothiocyanato and the nitro isomers over the thiocyanato and nitrito isomers tends to indicate the hardness or class (a) character of the Rh(cyclam) substrate. This principle is clearly illustrated by the triad Zn(II), Cd(II), and Hg(II). Class (a) Zn(II) bonds with N, borderline Cd(II) bonds with N or S, and class (b) Hg(II) bonds with S.

3. Thermodynamic Trans Effect

The σ-inductive theory of the trans effect accounts for trans activation through competition for the σₓ M.O. or repulsion of electrons in the metal pₓ orbital. Therefore, the theory predicts that trans destabilization is related to trans labilization, provided π-effects are not important. The assumption that the changes in ν(Rh-X) can be correlated with changes in bond strength is probably safe for a series of related compounds. Although there is no necessity that this assumption be so, due to the more complex bond strength relationships of coupled modes, the decrease in ν(Pt-X) in trans-Pt(PEt₃)₂LCl was found to be related to the increasing trans effect of L, provided that π-bonding is not a complicating factor. In addition, a similar correlation has been found for ν(Pt-N) in cis-PtX₂(NH₃)₂, and in trans-Pt(NH₂)LCl₂; and for ν(Pt-H) in trans-PtA₂LH, where A is As(Et)₃ and a series of substituted phosphines. Similarly, the trans destabilization effect can be inferred from the shifts in the ν(Rh-X) frequencies. In each of the cis complexes a different group is trans to a cyclam nitrogen. Therefore, shifts in the ν(Rh-N) frequencies...
provide a basis for ordering the trans ligands according to their bond weakening influence. From the data in Table VI, it is clear that the order of trans bond weakening ability is \( \text{NO}_2^- > I^- > \text{Br}^- > \text{Cl}^- \sim N_3^- \) > \( \text{N(cyclam)} > \text{NCS}^- \). \( \text{N(cyclam)} \) was positioned on the basis of the trans complexes in which \( \text{N(cyclam)} \) is trans to each Rh-N bond. The order is expected on comparison with the trans effect orders of other octahedral systems, except for azido. However, azido is a good \( \kappa \)-donor, and as such, has an additional mechanism for trans activation, which is related more to the transition state than the ground state. The same relative order of trans bond weakening is observed for \( \nu(\text{Rh-N}_3) \) in trans-Rh(cyclam)L(N\(_3\))\(^+\) and for \( \nu(\text{Rh-OH}) \) in trans-Rh(cyclam)L(OH)\(^+\), where \( L \) is a halo or azido ligand. The tentative Rh-Cl stretching mode exhibits the same trans dependence on \( L \) in trans-Rh(cyclam)LCl\(^+\).

The thermodynamic trans effect order can also be inferred from the acid strengths of the trans-acidoaquo complexes. This can be done because a weaker O-H bond is expected to mean a stronger Rh-O bond. Therefore, the larger the value of \( pK_a \), the greater the trans effect of the ligand trans to the Rh-O bond. Of course, such a comparison is meaningful only for complexes of the same charge and those with little \( \kappa \)-bonding. The following results were obtained for trans-Rh(cyclam)\(-L(H_2O)2^+\) using a Radiometer pH 4 (22 °C, \( \mu = 3.6 \times 10^{-3} \) M).

<table>
<thead>
<tr>
<th>( L )</th>
<th>( pK_a )</th>
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<tbody>
<tr>
<td>( N_3^- )</td>
<td>5.76</td>
</tr>
<tr>
<td>( I^- )</td>
<td>5.50</td>
</tr>
<tr>
<td>( \text{Br}^- )</td>
<td>5.30</td>
</tr>
<tr>
<td>( \text{Cl}^- )</td>
<td>5.24 ± .05</td>
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The value for azido is not comparable to the halo values because of the azido π-donor property. In addition, the strong basicity of N$_3^-$ could contribute to the high values for the pH measurement of the azidoaquo complex.
IV. KINETIC STUDIES

1. Kinetic Results

The kinetic results of the substitutions of the dihalocyclam-rhodium(III) complexes were obtained by monitoring the reaction spectrometrically at a wavelength for which the difference between the absorbance intensities of the reactant and product is large. Secondly, the wavelength was chosen such that the absorbance intensity of the reactant or product was large enough to allow the use of very low complex concentrations (~2 \times 10^{-5} M), that is, low enough to avoid precipitation in the particular reaction medium and to permit solution of the reactant complex. This was especially important for diiodo complex formation in an iodide medium due to the limited solubility of the diiodo complex in iodide solution. The most suitable wavelength was usually that of a charge transfer peak with an extinction coefficient over 30,000 \text{ l. cm}^{-1} \text{ mole}^{-1}.

An accurately weighed sample was dissolved in the appropriate reaction medium using a 50 or 100 ml volumetric flask as the reaction vessel. The reaction flask was heated in a thermostated oil bath (Sargent), which could be regulated to ±0.01°C. A volumetric flask was convenient since it could be easily clamped in the oil bath, and could be kept airtight to prevent evaporation of the reaction solution between samples with a tightly fitting stopper. The flask was not wrapped in aluminum foil, since significant differences due to photocatalysis were not observed in wrapped and unwrapped flasks, even for reaction in iodide media.

The reactions were studied at 3 temperatures over a 20 to 30
degree range to permit calculation of the activation parameters. The temperatures were chosen high enough to observe at least one half-life in a reasonable length of time, but were subject to an upper limit, the boiling point of the reaction medium. The highest temperature used was 95° C. At least 9 runs were monitored at the upper and at the lower temperatures to increase the accuracy of the activation parameter calculations. The runs at the middle temperature were monitored mainly to check the linearity of the activation enthalpy plot.

Samples were withdrawn at suitable intervals with a 3 ml pipet and were quenched in 50 ml beakers by cooling in a water bath at room temperature. At least 15 minutes were required for the reaction solutions to reach the temperature of the oil bath, after which the initial sample was taken corresponding to time, zero. This could be done, even though the reaction was already in progress, since the reactions were pseudo-first order, with a linear rate plot passing through the origin.

For the first run in a series, the ultraviolet spectrum was scanned to observe the isosbestic points, and to determine a wavelength at which there was a large difference between the reactant and product absorbances (see Fig. 7). Subsequent runs were generally monitored at the predetermined wavelength.

The pseudo-first order rate constants for the substitution reactions were determined graphically (Fig. 8) from the relationships:

(1) for spectral decrease, \( k = \frac{2.303 \log A_\infty - A_t}{t} \), and

(2) for spectral increase, \( k = \frac{2.303 \log A_t - A_\infty}{t} \).
Figure 7. Spectral changes during the trans-\(\text{Rh(cyclam)}\text{I}_2^+ + \text{Cl}^-\) reaction.
Figure 8. Graphical determination of $k_{85}$ for trans-Rh(cyclam)ICl$^+$ + I$^-$ reaction.
where $A_0$ is the absorbance of the initial reading and $A_{\infty}$ is the absorbance calculated from the known extinction coefficient of the product being formed. The expressions are adaptations of the general expressions derived\textsuperscript{87} for the correlation of physical properties with concentrations for the determination of rate constants. At the low concentrations of complex used in these studies, a linear relationship between absorbance and concentration is expected.

The calculated value of $A_{\infty}$ could be used, since the reaction media were chosen with the concentrations of the substituting anion high enough to give complete reaction. In several of the runs which were allowed to react for 8 half-lives (99.6% completion) or more, there was excellent agreement of the experimental and calculated values of $A_{\infty}$. In the slowest runs, for which base hydrolysis was a relatively larger error, the experimental and calculated values of $A_{\infty}$ did not agree as well, but the use of the calculated value gave excellent linearity of the rate plot for at least one half-life, and as such, were considered accurate determinations of the substitution rate constants for complete reaction.

The activation parameters were calculated from the transition state theory expression for the "thermodynamic" treatment of reaction rates\textsuperscript{88}.

$$k = \frac{k_B e^{\Delta S^+/R} e^{-\Delta H^+/RT}}{h}$$

where $R$ (gas constant) is 1.987 cal mole\textsupers-1 deg\textsupers{-1}, $k_B$ (Boltzmann) is 1.381 x 10\textsupers{-16} erg deg\textsupers{-1}, and $h$ (Planck) is 6.624 x 10\textsupers{-27} erg sec.

For a reaction in solution in the liquid state the activation
enthalpy is less than the Arrhenius activation energy by RT or \( \sim 600 \) cal mole\(^{-1}\) at room temperature.

\[
\Delta H^\ddagger = E_a - RT
\]

The rate data were evaluated statistically using the method of pooled variances\(^{89}\) for populations of different means but with a common variance. It was assumed that the variance of the rate constants did not depend on the temperature. Therefore, the percent standard deviation for the 3 temperatures is:

\[
\%\sigma = \sqrt{\frac{\sum_{i} S_{T_i}}{N - 3}}
\]

where \( N \) is the total number of runs at all 3 temperatures, and

\[
S_{T_i} = \sum_{1} \frac{(k_i - \bar{k})^2}{k}
\]

where \( k_i \) is a rate constant at temperature, \( T \), and \( \bar{k} \) is the average rate constant at \( T \).

The percentage standard deviation for the rate constant at a given temperature is given by

\[
\%\sigma_{k_T} = \%\sigma / \sqrt{n}
\]

where \( \%\sigma \) is that for the 3 temperatures and \( n \) is the number of runs at the particular temperature being considered. Since the values of \( \bar{k} \) are different at different temperatures, the pooled variance technique requires the use of percentages.

Using the transition state theory expression for reaction rates,
and assuming that the activation enthalpy is constant for the small temperature range used, the consideration of the rate constants in pairs gives the expression:

\[ \Delta H_{12}^{\dagger} = 4.576 \frac{T_1 T_2}{T_1 - T_2} \log \frac{k_1 T_2}{k_2 T_1} \]

where \( \Delta H_{12}^{\dagger} \) is the activation enthalpy determined on the basis of the two temperatures \( T_1 \) and \( T_2 \), and \( k_1 \) and \( k_2 \) are the respective rate constants at these temperatures. Therefore, 3 temperatures give the 3 values \( \Delta H_{12}^{\dagger}, \Delta H_{23}^{\dagger}, \) and \( \Delta H_{13}^{\dagger} \).

The standard deviation on \( \Delta H_{12}^{\dagger} \) was calculated assuming exact values for the temperature. This could be done since the temperatures were regulated to \( \pm 0.01^\circ \text{C} \). The standard deviation of \( \Delta H_{12}^{\dagger} \) is accordingly:

\[ \sigma(\Delta H_{12}^{\dagger}) = \pm 4.576 \frac{T_1 T_2}{T_1 - T_2} \sqrt{\frac{\sigma_{\log k_1}^2 + \sigma_{\log k_2}^2}{3}} \]

where \( \sigma_{\log k} \) is approximately \( \log (1 - \sigma_k/100) \) and \( \sigma_k \) is expressed as a percentage.

The enthalpy of activation is found using a weighted average of the enthalpies found by pairing the temperatures:

\[ \Delta H^{\dagger} = \frac{w_{12} H_{12}^{\dagger} + w_{23} H_{23}^{\dagger} + w_{13} H_{13}^{\dagger}}{w_{12} + w_{23} + w_{13}} \]

and

\[ \sigma(\Delta H^{\dagger}) = 1/(w_{12} + w_{23} + w_{13})^{1/2}, \]

where \( w_{12} = 1/\sigma^2(\Delta H_{12}^{\dagger}) \).

The entropy of activation is found by substituting the determined
value of the enthalpy of activation in the original transition state expression:

\[
\Delta S^\ddagger = 4.576 \log \frac{k}{T} + \Delta H^\ddagger - 47.23 \text{ (cal deg}^{-1} \text{ mole}^{-1}), \text{ and}
\]

\[
\sigma(\Delta S^\ddagger) = \pm (4.576 \sigma^2 \log \frac{k}{T} + \sigma(\Delta H^\ddagger)^2)^{1/2}
\]

\[
\pm \frac{\sigma(\Delta H^\ddagger)}{T}
\]

The agreement of \(\Delta H_{12}^\ddagger, \Delta H_{23}^\ddagger, \text{ and } \Delta H_{13}^\ddagger\) are an indication of the linearity of the activation enthalpy plot. The most linear plot was obtained for the acid hydrolysis of the trans-diido complex, and the least linear, for the acid hydrolysis of the trans-chlorobromo complex. The poorest \(-\log k \text{ vs. } 1/T\) plot is shown in Fig. 6.

The temperature dependent studies were carried out, since the use of rates alone for the kinetic comparison of a reaction series is meaningless, when both activation parameters vary in the series. An analysis of the transition state theory rate expression shows that a \(\ln k/T \text{ vs. } 1/T\) plot is characterized by the slope dependence on \(\Delta H^\ddagger\) and the \(y\)-intercept dependence on \(\Delta S^\ddagger\). Therefore, if \(\Delta S^\ddagger\) or \(\Delta H^\ddagger\) is constant for a reaction series, the plots do not cross, and \(\log k\) is an unambiguous indication of reactivity order. However, if both \(\Delta S^\ddagger\) and \(\Delta H^\ddagger\) vary, the plots can cross and give contradictory results depending on the temperature of the rate study. This is made very clear by these studies, because the intersections were observed in the temperature range which was convenient for reasonable reaction times. For example, the acid hydrolysis of trans-diido \((2.92 \times 10^{-4} \text{ sec}^{-1})\) is faster than that of trans-chloroiodo \((2.10 \times 10^{-4} \text{ sec}^{-1})\) at
Figure 6. Activation enthalpy plot for the acid hydrolysis of trans-Rh(cyclam)ClBr⁺.

85°C, and slower (7.55 x 10⁻⁶ sec⁻¹) than that of trans-chloroiodo (8.36 x 10⁻⁶ sec⁻¹) at 55°C. This is the expected result, assuming that the diodo reaction has the larger value for its entropy of activation, which was found to be the case experimentally.
The substitution reactions were used to study the acid hydrolysis rates, since the acid hydrolysis reaction does not go to completion. For example, the trans-chloroiodo acid hydrolysis reaction, in a direct study, ended at 69% reaction completion. The rate constants for the first order approach to equilibrium (Table VIII) were larger than the acid hydrolysis rate constant, since they are the sum of the acid hydrolysis rate constant and the anation rate constant. The substitution rate is limited by the acid hydrolysis rate, and the reaction can be driven to completion by increasing the substituting anion concentration. (See also p. 98)

At first the substitutions of some trans-dihalo complexes were studied in aqueous media (distilled, ion-exchanged water) without any attempt to adjust the pH of the reaction solution to obtain the acid hydrolysis rates. Although the iodide reaction media (0.1 M) gave a pH as high as 6.4, when heated at 85°C, it was assumed that base hydrolysis would present only a very small error, if any, in the pH range from 5.6 to 6.4 on comparison with the bis(ethylenediamine) results. The error was not evident for the more rapid trans-diodo acid hydrolysis in chloride and bromide solutions, as indicated by excellent isosbestic points, and linearity of the kinetic plots, although there was some fall-off from linearity after two half-lives. However, the reactions in iodide media, in which the trans-diodo complex was being formed, exhibited marked deviation from linearity. At first this was attributed to solubility problems, since the iodide salt of the trans-diodo complex is only sparingly soluble in an iodide solution. This assumption was proved erroneous by studies involving pH control, using more acidic solutions, in which excellent linearity of the kinetic
plots was observed for more than four half-lives. In addition, changing the iodide concentration over a ten-fold range gave nearly the same times for the beginning of nonlinear plots, indicating that precipitation was not the problem.

An attempted direct study of the acid hydrolysis of the trans-iiodoaquo complex at 85° C provided evidence for the base hydrolysis reaction in neutral solution (pH ~ 5.6), since there was a reaction with an appreciable rate giving a spectrum similar to the trans-hydroxo-aquo complex. Isosbestic points were not maintained, indicating some trans-diaquo formation, probably as the result of trans-hydroxoaque protonation. Acidification of the solution caused flattening of the hydroxoaque electronic absorbance maxima, and gave a spectrum more similar to the trans diaquo complex. In approximately 0.1 M HClO₄ at 85° C, there was no apparent reaction after four days, which is the expected result of an acid hydrolysis, since the trans effect of H₂O is very much less than that of iodo. It was evident that base hydrolysis occurred with an appreciable rate in neutral solution and could contribute a large error to the slower reactions, and even to the faster reactions in a 0.1 M NaI reaction medium, which becomes almost ten times as basic when heated at 85° C. Since the base hydrolysis reaction is usually first order in hydroxide, the base hydrolysis rate would be increased tenfold. This accounts for the marked fall-off from linearity of the kinetic plots for the substitution rates in iodide, since a spectral increase was monitored for the trans-diiodo formation, and base hydrolysis results in a spectral decrease at the wavelength studied due to the much lower extinction coefficient of the hydroxo products.
On the other hand, the acidification of iodide reaction solutions resulted in triiodide formation, as determined by its electronic spectrum, and its yellow color for more concentrated solutions. The triiodide spectrum has absorbance maxima (285 and 353 μm) at almost the same wavelengths as the trans-diodo complex (275 and 353 μm) with similar extinction coefficients (39000 vs. 34500 and 26400 vs. 13100 respectively), and therefore, its formation gives apparently greater values for the rate constants determined by diodo formation. Even for concentrations of acid and iodide low enough to make iodine formation a negligible error, as determined by heating the reaction solution at 85°C and making a spectral comparison with the same solution at room temperature, there was an apparent catalytic effect by triiodide.

These observations necessitated the determination of the lowest iodide concentration to give reaction completion, that is, complete anation of the trans-iodoaquo intermediate to the trans-diodo product, and the lowest acid concentration to eliminate base hydrolysis. The lowest iodide concentration was found by an equilibrium study on the anation of trans-Rh(cyclam)I(H2O)2+ by I- at 85°C in 10^-5 M HClO4:

<table>
<thead>
<tr>
<th>[NaI], M</th>
<th>% reaction</th>
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<tr>
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<tr>
<td>.002</td>
<td>81</td>
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</tr>
<tr>
<td>.01</td>
<td>96</td>
</tr>
</tbody>
</table>

10^-5 HClO4 was used since lower concentrations caused fall-off from linearity of the kinetic plots of the acid hydrolysis of trans-ClI and trans-BrI, indicating interference by base hydrolysis.
The reaction of trans-iodochloro and iodide (.01 and .02 M) in
$10^{-5}$ M HClO$_4$ gave linear kinetic plots for as much as 4 half-lives,
and the experimental value of $A_{\infty}$ corresponded to the calculated value
indicating that both problems were overcome. In addition, the values
for $k_{85}$ were approximately equal at both concentrations of $I^-$ (Table
VIII), and the isosbestic points were sharp and equal to those ob-
tained for the reverse reactions, for example, trans-diodo and chloride.

Unfortunately, the slower reactions of trans-dichloro and trans-
dibromo in iodide gave linear rate plots for only one half-life, and
reached only approximately 95% reaction completion. The linear part of
the rate plot based on the calculated value of $A_{\infty}$ was used to deter-
mine the rate constant, since the previous work had shown that .02 M
$I^-$ in $10^{-5}$ M HClO$_4$ were the highest concentrations of acid and iodide
which could be used without interference by iodine.

The acid hydrolysis of the trans-dichloro complex in a bromide
medium showed a marked degree of interference by base hydrolysis even
in $10^{-5}$ M HClO$_4$. The five-fold increase in bromide concentration gave
identical rate results with the same degree of fall-off from linearity.
Therefore, the acidity was increased to $10^{-3}$ M HClO$_4$, and excellent
linearity was obtained. However, the rate was slower than that in an
iodide medium. This would be expected if the second stage of the re-
action, the acid hydrolysis of trans-chlorobromo had a rate comparable
to the first. The second chloro substitution ($k_{85} = 1.42 \times 10^{-6}$ sec$^{-1}$)
was found to be even slower than the first ($k_{85} = 2.35 \times 10^{-6}$ sec$^{-1}$)
in a bromide reaction medium at the temperatures studied due to a more
negative entropy of activation for the second step. This problem is
not encountered in iodide media since the second step is about ninety
times faster than the first at \(85^\circ C\).

Some preliminary results were obtained for the acid hydrolysis of the trans-I(N\(_3\)) and I(NCS) complexes, in neutral media. Even though the results are subject to large base hydrolysis errors, the inertness of the azido \((7.1 \times 10^{-6} \text{ sec}^{-1})\) and isothiocyanato \((3.1 \times 10^{-6} \text{ sec}^{-1})\) complexes at \(85^\circ C\) indicates that they are poor leaving groups, since iodo is expected to have a large trans effect relative to both.

The kinetic results of the substitutions of the halo complexes are given in Tables VII to XII (conc., M; \(k, \text{ sec}^{-1}\)). The rate data from which the average values in the tables were calculated is given in the appendix. The rates in neutral media are included to show the degree of interference by base hydrolysis. Of course, the nonlinearity of the neutral runs made it necessary to calculate the rate constants on the basis of the initial rates for a segment of the reaction less than one half-life. Since the hydroxo complexes generally had lower absorbances at the wavelengths monitored, the base hydrolysis contributed a positive or negative error depending on the measurement of a spectral decrease or increase respectively.

**TABLE VII**

| Substitution Rates of trans-Rh(cyclam)I\(_2^+\) + X\(^-\) |
|-------------------|---------|-----------------|-----------------|------|-----|
| \(T, ^\circ C\)   | \(X^-\) | \([X^-]\) | \([\text{HClO}_4]\) | \(10^6k, \text{ sec}^{-1}\) |
| 55                | Cl\(^-\) | .02    | \(10^{-5}\)     | 7.55       | .03  |
|                   | Cl\(^-\) | .1     | 0               | 8.40       | .03  |
|                   | Cl\(^-\) | .2     | 0               | 7.62       |      |
|                   | Br\(^-\) | .02    | \(10^{-5}\)     | 7.67       | .05  |
|                   | Br\(^-\) | .1     | 0               | 8.42       | .05  |
TABLE VII (concluded)

<table>
<thead>
<tr>
<th>T, °C</th>
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<th>[X⁻]</th>
<th>[HClO₄]</th>
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TABLE VIII

Substitution Rates of trans-Rh(cyclam)ICl⁺ + I⁻

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<th>[HClO₄]</th>
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<th>σ</th>
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*first order approach to equilibrium
### TABLE IX

Substitution Rates of trans-kh(cyclam)IBr⁺ + I⁻

<table>
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<th>T, °C</th>
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<th>[HClO₄] 10⁶ k</th>
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### TABLE X

Substitution Rates of trans-kh(cyclam)Cl₂⁺ + X⁻

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<th>T, °C</th>
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<th>[X⁻]</th>
<th>[HClO₄] 10⁶ k</th>
<th>σ</th>
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TABLE XI
Substitution Rates of trans-Rh(cyclam)Br₂⁺ + I⁻

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TABLE XII
Substitution Rates of trans-Rh(cyclam)BrCl⁺ + Br⁻

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<th>T, °C</th>
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</tr>
</tbody>
</table>

2. Kinetic Trans Effect

The kinetic data for the acid hydrolysis reactions of the trans-dihalo complexes can be used to compare the trans effects of the halo ligands quantitatively. The substitution rates obtained in this work are the acid hydrolysis rates. The rate constants by themselves are a poor indication, and can give contradictory results, as discussed. For this reason, the thermal data for the reactions was compiled (Table XIII), and was used as the basis for the trans effect comparisons.
### TABLE XIII

Thermal Parameters for the Acid Hydrolysis of trans-Rh(cyclam)LX*  

<table>
<thead>
<tr>
<th>L</th>
<th>X</th>
<th>ΔH$^+$ kcal mole$^{-1}$</th>
<th>ΔS$^+$ cal deg$^{-1}$ mole$^{-1}$</th>
<th>10$^6$ k</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>27.7 ± .1</td>
<td>+2.29 ± .13</td>
<td>292</td>
</tr>
<tr>
<td>I</td>
<td>Br</td>
<td>25.6 ± .1</td>
<td>-4.02 ± .21</td>
<td>232</td>
</tr>
<tr>
<td>I</td>
<td>Cl</td>
<td>24.5 ± .1</td>
<td>-7.34 ± .13</td>
<td>212</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>27.6 ± .1</td>
<td>-7.61 ± .36</td>
<td>2.35</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>28.7 ± .2</td>
<td>-4.41 ± .46</td>
<td>2.40</td>
</tr>
<tr>
<td>Br</td>
<td>Cl</td>
<td>26.6 ± .1</td>
<td>-11.4 ± .3</td>
<td>1.42</td>
</tr>
</tbody>
</table>

### TABLE XIV

Linearity of ΔH$^+$ Plots for the Acid Hydrolysis of trans-Rh(cyclam)LX*  

<table>
<thead>
<tr>
<th>L</th>
<th>X</th>
<th>ΔH$_{12}$$^+$</th>
<th>ΔH$_{23}$$^+$</th>
<th>ΔH$_{13}$$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>27.6</td>
<td>27.7</td>
<td>27.7</td>
</tr>
<tr>
<td>I</td>
<td>Br</td>
<td>25.8</td>
<td>25.4</td>
<td>25.6</td>
</tr>
<tr>
<td>I</td>
<td>Cl</td>
<td>24.6</td>
<td>24.3</td>
<td>24.5</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>27.4</td>
<td>27.7</td>
<td>27.6</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>28.6</td>
<td>28.9</td>
<td>28.7</td>
</tr>
<tr>
<td>Br</td>
<td>Cl</td>
<td>26.2</td>
<td>27.1</td>
<td>26.6</td>
</tr>
</tbody>
</table>

Comparing the same data for the bis(ethylenediamine) analogs (Table XV), the ΔH$^+$ differences are more or less the same for the two systems. The ordering of the ligands is the same in terms of the trans effect and the leaving group effect, as expected. The kinetic trans effect order...
TABLE XV

Thermal Parameters for the Acid Hydrolysis of trans-Rh(en)$_2$LX$_56$

<table>
<thead>
<tr>
<th>L</th>
<th>X</th>
<th>$\Delta H^\dagger$ kcal mole$^{-1}$</th>
<th>$\Delta S^\dagger$ cal deg$^{-1}$ mole$^{-1}$</th>
<th>$10^6 k_{50},$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>25.1 ± .2</td>
<td>+1 ± 1</td>
<td>124</td>
</tr>
<tr>
<td>I</td>
<td>Br</td>
<td>23.1 ± .1</td>
<td>-3 ± 1</td>
<td>474</td>
</tr>
<tr>
<td>I</td>
<td>Cl</td>
<td>21.1 ± .3</td>
<td>-7 ± 2</td>
<td>825</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>24.7 ± .3</td>
<td>-9 ± 1</td>
<td>1.49</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>25.2 ± .3</td>
<td>-5 ± 1</td>
<td>5.3</td>
</tr>
<tr>
<td>Br</td>
<td>Cl</td>
<td>23.2 ± .5</td>
<td>-12 ± 2</td>
<td>3.94</td>
</tr>
</tbody>
</table>

(I > Br > Cl) is the same as the thermodynamic order indicated by the infrared studies, and the leaving group order (Cl > Br > I) indicates class (b) behavior. The large trans effect differences are consistent with class (b) behavior, and the correlation between the kinetic and thermodynamic trans effects is consistent with the $\sigma$-donor theory for weak $\pi$-bonders.

From the preparative work, it was evident that nitro had a much greater trans effect than iodo, since the anation of a trans-haloaquo complex gave the trans-dinitro product at room temperature. The trans-haloisothiocyanato complexes were refluxed for days and could not be substituted to the diisothiocyanato product, indicating the relatively weak trans effect of isothiocyanato.

The substitutions of the stronger trans halo activator were too slow for practical temperature dependent studies below the b.p. of the reaction medium. The substitution of iodo by chloro in the trans-chloroiodo complex showed no apparent reaction after 63 hours at 95° C.
The substitutions of bromo by chloro in the trans-chlorobromo complex \((k_{95} = 3.0 \times 10^{-7} \text{ sec}^{-1})\) and of iodo by bromo in trans-bromoiodo \((k_{95} = 1.6 \times 10^{-6} \text{ sec}^{-1})\) were very slow. These results are expected due to a combination of weak trans effects and poor leaving groups. Moreover, the catalytic behavior found for the bis(ethylenediamine) analogs was not observed. Each of the three reactions was carried out in \(10^{-2} \text{ M HClO}_4\) to prevent interference by base hydrolysis.

An unexpected result of this work was the leaving group effect on the relative iodo and bromo trans effects. As mentioned in the introduction, it is expected that the trans effect differences should be greater for the leaving group with the stronger bond. In these studies, the difference between the iodo and bromo trans effects is \(2.1 \text{ kcal mol}^{-1}\) when chloro is the leaving group, and \(3.1 \text{ kcal mol}^{-1}\) when bromo is the leaving group. This contradicts the generalization that trans destabilization is less effective for softer leaving groups. The data in Table XV for the bis(ethylenediamine) complexes also disagree, and give equal trans effects irrespective of the leaving group.

3. Mechanism of Rhodium(III) Substitution

For all the substitution reactions of the trans-dihalo complexes, the rates were found to be independent of the nature and concentration of the nucleophile, and no change of rate was found over a five-fold increase in ionic strength. This is evidence for the two step reaction of acid hydrolysis followed by anation, for which the anion concentration was large enough \((.01 - .1 \text{ M, 400 - 4000-fold excess})\) to insure that the first step was rate determining, and that the reaction went to completion.
\[(1) \text{trans-Rh(cyclam)}LX^+ + H_2O \rightarrow \text{trans-Rh(cyclam)}(H_2O)^{2+} + X^-(\text{slow})
\]
\[(2) \text{trans-Rh(cyclam)}L(H_2O)^{2+} + Y^- \rightarrow \text{trans-Rh(cyclam)}LY^+ + H_2O \text{ (fast)}
\]

The anation reaction which follows the acid hydrolysis is fast relative to the latter, and therefore, the substitution rate is a measure of the acid hydrolysis rate. For example, the anation of trans-iodoacqo in .02 M I\(^-\) at 85\(^\circ\) C is more than fifty times faster than the acid hydrolysis of the trans-haloiodo complexes comparing \(k\) (acid hydrolysis) to \(k\) (anation)[I\(^-\)]. The latter term contains [I\(^-\)] since anation is a second order reaction in the concentration range studied.

These experiments were not intended to distinguish between dissociation and displacement mechanisms for the rate determining step. Both a pyramidal dissociative activated complex and an octahedral wedge, formed by assistance through cis attack, are consistent with the total retention of configuration found in the acid hydrolysis reactions studied in this work, but a trigonal bipyramid is not. The bipyramid is not since it is expected to give some stereochemical change. It is most likely that the degree of solvent assistance in the octahedral wedge varies from reaction to reaction, and that the extremes shown in the diagrams are special cases.
Two major differences between the cyclam and bis(ethylenediamine) systems were observed. First the cyclam complexes are more inert with $\Delta H^\ddagger$ ranging from 2.5 to 3.5 kcal mole$^{-1}$ higher for the cyclam complex reactions. The larger enthalpies of activation for the cyclam complexes are expected because of the destabilization of the transition state due to less efficient solvation with increasing chelation$^{92}$. In addition, the increased rigidity of the cyclam chelate resists rearrangement in the transition state.

Secondly, the sensitivity of the cyclam complexes to base hydrolysis was not found in the bis(ethylenediamine) system. It is evident that a secondary amine, such as cyclam facilitates base hydrolysis greatly relative to a primary amine, such as bis(ethylenediamine). This is evidence for the conjugate base mechanism (SN1 or SN2), since both amines are expected to be poor activators, and cannot account for the large difference in behavior. However, the $N^-$ and $NH^+$ conjugate bases are excellent activators. For Co(III), they are considered good $\pi$-donor activators. This does not seem to be the case for Rh(III), for which $\pi$-bonding is less important. The cis complexes ($N^-$ trans to $X^-$) were more reactive than the trans ($N^-$ cis to $X^-$), which shows that the activation is a $\sigma$-donor effect with greater activation in the trans direction. The relatively greater importance of the trans effect for Rh(III) is also shown by the two step base hydrolysis of the trans complexes. The base hydrolysis of trans-Rh(cyclam)Cl(OH)$^+$ is slower than that of trans-Rh(cyclam)Cl$_2^+$. Therefore the cis effect can be attributed to overall activation, which is further influenced by the greater importance of the trans effect. This is supported by the observation that the base hydrolysis of cis-Rh(cyclam)Cl$_2^+$ gave only
the dihydroxo product. The trans-\(N^-\) group causes almost the same degree of activation of the leaving chloro groups, and is not influenced by differential cis effects in the way that the cis effect is influenced by the much greater differential trans effects.
V. CONCLUSION

The kinetic studies made possible by the number of complexes prepared, have been only begun because of the length of time involved in the acid hydrolysis studies of the trans-dihalo complexes. These studies could be extended to include the other diacido complexes and the cis isomers for a direct comparison of the cis effect for Rh(III). However, it is probable that acid dependence would have to be determined in the case of leaving groups which are the anions of weak acids, since acid catalysis is expected.

The anation kinetics of the trans-acidoaquo complexes and the base hydrolysis kinetics of the diacido complexes could be determined even more conveniently, since the reactions are faster. In addition, the thermodynamic studies of the acid hydrolysis, base hydrolysis, and anation reactions would provide a more comprehensive view of the cyclamrhodium(III) system. The thermodynamic data can also be obtained by means of conventional spectrometric techniques.

The completion of this work will provide an excellent comparison to the more commonly studied Co(III) systems on the basis of the octahedral cis and trans effects, and also the mechanisms of substitution and anation.
## APPENDIX

### TABLE A-I
Substitution Rates of trans-Rh(cyclam)I$_2^+$ + X$^-$

<table>
<thead>
<tr>
<th>T, °C</th>
<th>X$^-$</th>
<th>[X$^-$]</th>
<th>[HClO$_4$]</th>
<th>$10^6$ k, sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>Cl$^-$</td>
<td>.02</td>
<td>$10^{-5}$</td>
<td>7.67, 7.52, 7.39, 7.54, 7.52, 7.47, 7.42, 7.46, 7.47</td>
</tr>
<tr>
<td></td>
<td>Cl$^-$</td>
<td>.1</td>
<td>0</td>
<td>8.34, 8.42, 8.71, 8.35, 8.35, 8.41, 8.23, 8.30, 8.34, 8.40, 8.30, 8.71, 8.34, 8.35, 8.46</td>
</tr>
<tr>
<td></td>
<td>Br$^-$</td>
<td>.02</td>
<td>$10^{-5}$</td>
<td>7.97, 7.81, 7.59, 7.64, 7.44, 7.31, 7.31, 7.59, 7.83</td>
</tr>
<tr>
<td></td>
<td>Br$^-$</td>
<td>.1</td>
<td>0</td>
<td>8.45, 8.28, 8.45, 8.25, 8.45, 8.36, 8.58, 8.50</td>
</tr>
<tr>
<td>70</td>
<td>Cl$^-$</td>
<td>.02</td>
<td>$10^{-5}$</td>
<td>4.95, 5.13, 5.18, 5.13, 5.14, 5.11, 5.16, 5.21, 5.27</td>
</tr>
<tr>
<td></td>
<td>Cl$^-$</td>
<td>.1</td>
<td>0</td>
<td>5.41, 5.36, 5.47, 5.50, 5.50, 5.50, 5.50, 5.55</td>
</tr>
<tr>
<td></td>
<td>Br$^-$</td>
<td>.02</td>
<td>$10^{-5}$</td>
<td>5.09, 5.11, 5.09, 5.09, 5.05, 5.10, 5.11, 5.11, 5.14</td>
</tr>
<tr>
<td></td>
<td>Br$^-$</td>
<td>.1</td>
<td>0</td>
<td>5.42, 5.55, 5.35, 5.27, 5.21, 5.21, 5.40</td>
</tr>
<tr>
<td>85</td>
<td>Cl$^-$</td>
<td>.1</td>
<td>0</td>
<td>2.98, 2.93, 2.92, 2.94, 2.95, 2.95, 2.90, 2.92, 2.94, 2.91, 2.94, 2.91, 2.91, 2.93, 2.92</td>
</tr>
</tbody>
</table>
**TABLE A-I (concluded)**

<table>
<thead>
<tr>
<th>T, °C</th>
<th>X⁻</th>
<th>X⁻</th>
<th>HClO₄</th>
<th>10⁶ k, sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br⁻</td>
<td>.02</td>
<td>10⁻⁵</td>
<td></td>
<td>2.96, 2.90, 2.93, 2.88, 2.89, 2.90, 2.96, 2.94, 2.94</td>
</tr>
<tr>
<td>Br⁻</td>
<td>.1</td>
<td>0</td>
<td></td>
<td>3.02, 3.00, 3.02, 3.10, 3.11, 3.14</td>
</tr>
</tbody>
</table>

**TABLE A-II**

Substitution Rates of trans-Rh(cyclam)ICl⁺ + I⁻

<table>
<thead>
<tr>
<th>T, °C</th>
<th>[I⁻]</th>
<th>[HClO₄]</th>
<th>10⁶ k, sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>.1</td>
<td>0</td>
<td>10.6, 10.6, 10.3, 10.9, 10.7, 10.4, 10.1, 11.1</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td>10⁻⁵</td>
<td>8.17, 8.35, 8.38, 8.37, 8.12, 8.35, 8.46, 8.46, 8.56</td>
</tr>
<tr>
<td>70</td>
<td>.1</td>
<td>0</td>
<td>49.3, 49.3, 51.2, 48.8, 50.3, 49.7, 48.9, 48.2</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td>10⁻⁵</td>
<td>45.6, 46.2, 45.4, 45.8, 45.8, 45.5, 45.3, 45.5, 45.5</td>
</tr>
<tr>
<td>85</td>
<td>.01</td>
<td>0</td>
<td>178, 186, 180, 182, 179, 183, 181, 180</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td>0</td>
<td>181, 182, 178, 179, 181, 187, 186</td>
</tr>
<tr>
<td></td>
<td>.04</td>
<td>0</td>
<td>226, 210, 200, 210, 212, 208, 208, 204, 215, 199, 206, 212</td>
</tr>
</tbody>
</table>
**TABLE A-II** (concluded)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>[I⁻]</th>
<th>[HClO₄]</th>
<th>10⁶ k, sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>.05</td>
<td>0</td>
<td>197, 197, 197, 202, 193, 205, 199, 195, 208, 200</td>
<td></td>
</tr>
<tr>
<td>.07</td>
<td>0</td>
<td>218, 218, 209, 202, 222, 228, 228, 232, 220, 226</td>
<td></td>
</tr>
<tr>
<td>.1</td>
<td>0</td>
<td>233, 243, 234, 236, 227, 231, 233, 234</td>
<td></td>
</tr>
<tr>
<td>.02</td>
<td>10⁻⁵</td>
<td>206, 210, 210, 212, 215, 211, 209, 206, 216, 214, 223, 216</td>
<td></td>
</tr>
<tr>
<td>.04</td>
<td>10⁻⁵</td>
<td>221, 229, 228, 224, 228, 227, 229, 226</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>183, 208, 224, 190, 192, 177, 175, 205, 215</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE A-III**

Substitution Rates of trans-Rh(cyclam)IBr⁺ + I⁻

<table>
<thead>
<tr>
<th>T, °C</th>
<th>[I⁻]</th>
<th>[HClO₄]</th>
<th>10⁶ k, sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>.1</td>
<td>8.81, 9.35, 8.69, 10.9, 9.57, 8.99, 9.10, 8.20</td>
<td></td>
</tr>
<tr>
<td>.02</td>
<td>10⁻⁵</td>
<td>7.86, 7.99, 7.83, 7.86, 8.03, 7.86, 7.91, 7.96, 8.10</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>.1</td>
<td>55.8, 53.7, 51.5, 53.2, 55.4, 55.8, 51.7, 51.8</td>
<td></td>
</tr>
<tr>
<td>.02</td>
<td>10⁻⁵</td>
<td>44.0, 48.6, 48.8, 47.5, 44.8, 49.1, 48.7, 45.7, 44.6</td>
<td></td>
</tr>
</tbody>
</table>

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### TABLE A-III (concluded)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>[I⁻]</th>
<th>[HClO₄⁻]</th>
<th>10⁶ k, sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>.1</td>
<td>0</td>
<td>255, 274, 274, 270, 274, 270, 266, 258</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td>10⁻⁵</td>
<td>233, 231, 233, 230, 233, 234, 230, 233, 234, 230, 233</td>
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</tbody>
</table>

### TABLE A-IV

Substitution Rates of trans-Rh(cyclam)Cl₂⁺ + X⁻

<table>
<thead>
<tr>
<th>T, °C</th>
<th>X⁻</th>
<th>[X⁻]</th>
<th>[HClO₄⁻]</th>
<th>10⁶ k, sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>Br⁻</td>
<td>.1</td>
<td>0</td>
<td>.621, .620, .641, .633, .639, .601, .619, .620</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.02</td>
<td>1.14, 1.08, 1.07, 1.06, 1.03, 1.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>I⁻</td>
<td>.02</td>
<td>10⁻⁵</td>
<td>.760, .756, .753, .760, .760, .755, .750, .756, .753</td>
</tr>
<tr>
<td>85</td>
<td>Br⁻</td>
<td>.1</td>
<td>0</td>
<td>1.68, 1.76, 1.75, 1.74, 1.76, 1.80, 1.79, 1.74, 1.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.68</td>
<td>2.56, 2.82, 2.88, 2.58, 2.61, 2.77, 2.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>I⁻</td>
<td>.02</td>
<td>10⁻⁵</td>
<td>2.38, 2.36, 2.36, 2.35, 2.34, 2.30, 2.33, 2.38, 2.32</td>
</tr>
<tr>
<td>95</td>
<td>Br⁻</td>
<td>.1</td>
<td>0</td>
<td>4.70, 4.63, 4.71, 4.68, 4.79, 4.95, 4.82, 4.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.72</td>
<td>5.72, 5.55, 5.55, 5.72, 5.72, 5.72, 5.72, 5.90, 5.55, 5.55</td>
<td></td>
</tr>
</tbody>
</table>

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**TABLE A-IV (concluded)**

<table>
<thead>
<tr>
<th>T, °C</th>
<th>X^-</th>
<th>CIO4^-</th>
<th>10^6 k, sec^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br^-</td>
<td>0.1</td>
<td>10^-5</td>
<td>5.87, 6.06, 5.95, 6.19, 6.00, 5.88, 5.87, 5.70, 5.61</td>
</tr>
<tr>
<td>Br^-</td>
<td>0.02</td>
<td>10^-3</td>
<td>6.06, 6.10, 6.05, 5.97, 6.04, 5.99, 6.00, 6.06</td>
</tr>
<tr>
<td>I^-</td>
<td>0.1</td>
<td>0</td>
<td>6.60, 6.24, 6.46, 6.24, 6.35, 6.72, 6.79, 6.10</td>
</tr>
<tr>
<td>I^-</td>
<td>0.02</td>
<td>10^-5</td>
<td>6.86, 6.95, 6.98, 6.88, 7.04, 6.93, 6.92, 6.99, 6.95</td>
</tr>
</tbody>
</table>

**TABLE A-V**

**Substitution Rates of trans-Rh(cyclam)Br_2^+ + I^-**

<table>
<thead>
<tr>
<th>T, °C</th>
<th>I^-</th>
<th>CIO4^-</th>
<th>10^6 k, sec^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>.02</td>
<td>10^-5</td>
<td>.735, .734, .735, .739, .747, .740, .737, .736, .730</td>
</tr>
<tr>
<td>80</td>
<td>.1</td>
<td>0</td>
<td>1.01, 1.04, .854, .886, 1.06, .958, .965, .830</td>
</tr>
<tr>
<td>85</td>
<td>.1</td>
<td>0</td>
<td>1.43, 1.50, 1.52, 1.87, 1.52, 1.63, 1.42, 1.62, 1.65, 1.66, 1.49, 1.53, 1.54, 1.43</td>
</tr>
<tr>
<td></td>
<td>.02</td>
<td>10^-5</td>
<td>2.40, 2.42, 2.42, 2.41, 2.42, 2.36, 2.38, 2.40, 2.36</td>
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<td>.1</td>
<td>0</td>
<td>2.35, 2.46, 2.32, 2.64, 2.66, 2.65</td>
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<td>95</td>
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<td>10^-5</td>
<td>7.28, 7.49, 7.33, 7.44, 7.50, 7.45, 7.52, 7.53, 7.40</td>
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<th>T, °C</th>
<th>[Br⁻]</th>
<th>[HClO₄]</th>
<th>10⁶ k, sec⁻¹</th>
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<tr>
<td>75</td>
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<td>10⁻³</td>
<td>4.88, 4.67, 4.82, 4.77, 4.82, 4.58, 4.99, 4.90, 4.86</td>
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<td>10⁻³</td>
<td>4.13, 4.15, 4.08, 4.13, 4.16, 4.07, 4.01, 4.07, 4.07</td>
</tr>
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</table>

TABLE A-VI
Substitution Rates of trans-Rh(cyclam)BrCl⁺ + Br⁻
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VITA AUCTORIS

Born: Tillsonburg, Ontario
Primary School: Middleton S.S. 12
Secondary School: Delhi DHS
University: B.A., University of Western Ontario
Awards: Ontario Fellowship (1967-68)
National Research Council Postgraduate Scholarship (1968-70)
Professional Society: Chemical Institute of Canada
Marital Status: Wife, Marie Lucille
Daughter, Susan Marie