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MILLER, Warren Victor, 1944-

STUDIES IN COORDINATION CHEMISTRY: PART I.

COORDINATION COMPLEXES OF THE TRIVALENT
LANTHANIDE IONS WITH OXYGEN DONOR LIGANDS.

PART II. KINETICS OF THE ACID HYDROLYSIS
OF SOME DISTORTED OCTAHEDRAL COBALT(III)
COMPLEXES WITH β,β' β'' -TRIAMINOTRIETHYLAMINE.

State University of New York at Binghamton,
Ph.D., 1971

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BY
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WARREN V. MILLER

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in State University of New York
at Binghamton
1970

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OCTAHEDRAL COBALT(III) COMPLEXES WITH
 β, β', β'' -TRIAMINOTRIETHYLAMINE

A Dissertation

By

WARREN V. MILLER

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VITA

The author was born in Rochester, New York on October 4, 1944. He attended the Rochester public school system, and graduate from Benjamin Franklin High School in June, 1962. He entered Clarkson College of Technology in September, 1962 and graduated with a B.S. in chemistry in June, 1966.

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1. "Complexes of γ -Butyrolactam with Lanthanide Nitrates", J. Inorg. Nucl. Chem., 30, 2785 (1968).
2. "Some Lanthanide Complexes with Cyclic Amides", J. Inorg. Nucl. Chem., 30, 3287 (1968).
3. "Fluorescent Lanthanide Complexes with 2,2'-Bipyridine 1,1'-Dioxide", J. Inorg. Nucl. Chem., 31, 1427 (1969).
4. "Transition Metal Nitrate Complexes of γ -Butyrolactam", J. Inorg. Nucl. Chem., 32, 0000 (1970).
5. "A Cerium(IV) Complex with 2,2'-Bipyridine 1,1'-Dioxide", J. Inorg. Nucl. Chem., 32, 0000 (1970).
6. "Kinetics of the Aquation of Bromoaquo(triaminotriethylamine)cobalt (III) Ion", Inorg. Chem., 9, 0000 (1970).
7. "Kinetics of the Acid Hydrolysis of Chloroaquo(triaminotriethylamine)cobalt(III) Ion", to be published.

8. "Synthesis and Characterization of Some Octahedral Cobalt(III) Complexes with β, β', β'' -(Triaminotriethylamine)", to be published.

Papers number 1 and 2 were presented before the Inorganic Division at the 156th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1968.

The author and Frances Dello Ioio were married on July 2, 1967, and are the parents of Allison Coleen, now nine months old.

PREFACE

~~Coordination~~ chemistry can be divided into two very general areas, one being the study of very reactive, labile, systems, and the other being the investigation of relatively inert species. With the hope of learning something about both of these areas, and with a desire to make a contribution to each, this thesis is comprised of two separate parts, the first dealing with the very labile complexes of the lanthanide elements, and the second dealing with the relatively inert complexes of Co(III).

In Section A of Part I, a summary of past work in the area of lanthanide complexes with oxygen donor ligands is presented. In Section B, the synthesis and characterization of several lanthanide perchlorate complexes of γ -butyrolactam, and N-methyl- γ -butyrolactam are reported. A similar study of the lanthanide nitrate complexes of γ -butyrolactam is reported in Section C. In Section D of Part I, a study of the fluorescence behavior of the europium and terbium perchlorate complexes of 2,2'-bipyridine 1,1'-dioxide is described. The final section of Part I describes the direction in which the work described in this thesis can be extended.

In Section A of Part II, the present state of knowledge on the acid hydrolysis reactions of Cr(III) and Co(III) halo-amine complexes is reviewed. In Section B a kinetic study of the acid hydrolysis of bromo-aquo(triaminotriethylamine)cobalt(III) ion is reported and the data

compared with that of other Cr(III) and Co(III) systems. A similar study for the corresponding chloroaquo complex is reported in Section C. In the last section of Part II, possible future research problems arising from the author's work are discussed.

PART I

Coordination Complexes of the Trivalent

Lanthanide Ions with Oxygen Donor Ligands

A. General Introduction

Because of the position of the lanthanide elements in the periodic table, the coordination chemistry of these fourteen elements is considerably different from that of the transition metals. Beginning with the first member of the series, lanthanum, there is a successive filling of the 4f orbitals with electrons until for the final member of the series, lutetium, there is a $4f^{14}$ configuration. Quantum mechanical calculations for these orbitals have shown that, unlike the d electrons, the 4f electrons are not available for bonding, but are in fact buried deep inside the atom. One would then expect a considerable decrease in the covalent character of the metal-ligand bond in lanthanide complexes relative to that of similar complexes of the transition elements. The very low degree of covalence in lanthanide complexes has been substantiated by studies of the nephelauxetic effect of various ligands in both the ¹praseodymium and ²neodymium systems. It was found that in both studies all of the complexes were at least 98% ionic. The observed stability of lanthanide coordination complexes can then be best explained by the strong coulombic attraction between the tripositive lanthanide ion and the partial negative charge localized on the donor atom of the ligand. This type of bonding is very similar to that which is present in complexes of the heavier alkaline earth metals.

The ion dipole type of bonding in lanthanide complexes is largely responsible for the observed differences between the chemical and physical behavior of these complexes and that of the transition elements. Since the d orbitals of transition metals are involved in bonding and have a fixed orientation around the metal nucleus, any coordination complex of a transition

metal must have a fixed stereochemistry in order to insure a maximum overlap with the ligand orbitals. Furthermore, since each set of hybridized metal orbitals overlaps with a fixed number of ligand orbitals, the coordination numbers of transition metal complexes are usually well defined. In the case of the lanthanides, however, the metal ion can best be pictured as a sphere with a uniform positive charge distributed on it. The geometry and coordination numbers of lanthanide complexes are then determined primarily by the size of both the metal ion and the ligand, and by the shape and charge of the ligand. Furthermore, while geometrical isomers are common in transition metal complexes, similar behavior is not normally observed in lanthanide compounds because of the increased lability of the metal-ligand bond.

An additional factor contributing to the stability of transition metal complexes is the crystal field stabilization energy. Theory predicts that in an octahedral ligand field, the five degenerate orbitals split into a triply degenerate and a doubly degenerate set of orbitals with respective energies lower and higher than that of the original set of orbitals. Since these orbitals are incompletely filled with electrons, those of lower energy will be filled first and hence a net stabilization energy is gained. In the case of the lanthanides, however, quantum mechanical calculations for the 4f orbitals have been done,³ and it was found that, in an octahedral ligand field, the seven f orbitals split into a low energy nondegenerate orbital and two higher energy sets of triply degenerate orbitals. However, because the 4f orbitals are shielded from the ligand field the maximum value for the crystal field stabilization energy is less than 1 kcal mole⁻¹ as opposed to typical values of 25 or more kcal mole⁻¹ for transition metal complexes.

Because the ligand field stabilization energy is negligible in lanthanide complexes, the factors which are most important in determining the stability

of these compounds are the charge to radius ratio of the metal ion, and the degree of partial negative charge localized on the donor atom of the ligand. Due to the f electrons imperfectly shielding each other from the nucleus, as the atomic number of the lanthanide increases the ionic radius of the ion decreases. This effect is called lanthanide contraction, and is responsible for the decrease in the ionic radii of the tripositive ions from 1.06Å to 0.84Å in proceeding from the first to the last member of the series. Since the charge is constant, the charge to radius ratio for the heavier lanthanides is considerably larger than for the lighter ones, and hence the heavier lanthanides would be expected to interact more strongly with a negatively charged ligand. The effect of the charge to radius ratio on the formation constants of lanthanide complexes is easily seen in the ΔG values for the formation of lanthanide ethylenediaminetetraacetic acid (EDTA) complexes in aqueous solution. The values show a gradual increase from $-20.72 \text{ kcal mole}^{-1}$ for lanthanum to $-26.11 \text{ kcal mole}^{-1}$ for lutetium.⁴

The effect of the negative charge localized on the donor atom of the ligand is equally as important in determining the stability of lanthanide complexes. Clearly, since oxygen has a very high electronegativity, it would be expected to interact much more strongly with a positively charged ion than would a less electronegative element. It is not surprising then that almost all of the lanthanide coordination complexes which have been prepared are with oxygen donors, although a few complexes with nitrogen donors are also known. Good π -bonding ligands such as olefins, carbon monoxide, phosphines, and sulfides do not complex with the lanthanide elements.

A survey of the literature in the area of lanthanide coordination chemistry quickly reveals that the number of lanthanide complexes with oxygen donors is extensive. By far, the vast majority of these compounds are with charged organic anions such as carboxylates. Since these compounds are

generally unrelated to the type of complexes which were characterized in this study, they will not be discussed in any detail. The second group of complexes which has been studied extensively is that of neutral organic compounds with oxygen donor atoms. These complexes are directly related to those in this study, and a brief description of their properties is presented.

All of the neutral oxygen donor ligands can be divided into a few categories depending upon whether the oxygen atom is bonded to a group VI, V, or IV atom in the ligand. In the case of the group VI oxide donors, the only lanthanide complexes reported are those of sulfoxides. In 1966 Krishnamurthy and Soundararajan⁵ reported the syntheses of several lanthanide perchlorate complexes of dimethyl sulfoxide (DMSO). The compounds were prepared by adding DMSO to a solution of the lanthanide perchlorate in methanol, and analyses of the compounds showed that those lanthanides with the larger ionic radii had eight coordinated DMSO molecules, while those of smaller radii had only seven. The infrared spectra of these complexes showed a decrease in the S-O stretching frequency of 50 cm^{-1} relative to that of the free ligand. This was interpreted to indicate coordination of the DMSO through the oxygen atom rather than the sulfur. The infrared spectra as well as conductance measurements in nitrobenzene and N,N'-dimethyl formamide (DMF) indicated that the perchlorate groups were ionic.

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In another study, Ramalingam and Soundararajan reported the preparation of several lanthanide nitrate complexes of DMSO. Analyses of these compounds showed that they were quite different from their perchlorate analogs. The larger lanthanides were found to have only four coordinated DMSO molecules, while the smaller ones had only three. The infrared spectra of all of the complexes showed that the DMSO was coordinated through the oxygen atom, and also that the nitrate groups were coordinated. On the basis of conductance data for the complexes in various organic solvents with different donor

properties, it was concluded that two of the nitrate groups were bonded as monodentate ligands and the third as a bidentate. The respective coordination numbers for the larger and smaller lanthanide ions would then be eight and seven, as in the corresponding perchlorate complexes. The only other sulfoxide complexes which have been reported are the lanthanide perchlorate complexes with diphenyl sulfoxide.⁷ In all of these compounds the number of coordinated sulfoxide groups was found to be six.

The next important group of compounds is that of the group V oxides.⁸ In 1967 Cousins and Hart reported the syntheses of several lanthanide nitrate complexes with triphenylphosphine oxide (Ph_3PO). It was found that a large variety of mixed complexes could be prepared in ethanol or acetone with coordinated solvent molecules. Furthermore, it was found that while some of the complexes contained both ionic and coordinated nitrate groups, others contained only complexed nitrate. At higher temperatures, any coordinated solvent molecules could be removed, and simple compounds of the type $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NO}_3)_3]$ were formed. The infrared spectra of all of the compounds showed a decrease in the P-O stretching frequency of the ligand from 1195 cm^{-1} in Ph_3PO to below 1172 cm^{-1} in the complexes. The decrease in frequency upon coordination was interpreted to indicate coordination of the phosphine oxide through the oxygen atom. The small magnitude of the shift was attributed to the very small degree of π -bond character in the P-O bond, and to the presence of coupling between the metal oxygen and phosphorous oxygen stretching vibrations. The coordinated nitrato groups were believed to be bidentate, and the coordination number of all of the complexes was believed to be nine, regardless of the ionic radius of the lanthanide ion. The europium triphenylphosphine oxide complex was found to exhibit a strong fluorescence when excited by ultraviolet radiation.⁹

In a similar study, a series of lanthanide nitrate complexes with triphenylarsine oxide were also reported.¹⁰ In general, their behavior was similar to that observed for the corresponding triphenylphosphine oxide compounds, and several types of complexes containing coordinated solvent molecules were obtained. Although the ligand was believed to be coordinated through the oxygen atom, the infrared spectra of all of the complexes showed an increase in the As-O stretching frequency upon coordination. The increase was attributed to coupling of the metal oxygen and arsenic oxygen stretching vibrations. The effect of coordination on the As-O stretching frequency should be very small since there is almost no π -bonding in the As-O bond.

In addition to the above studies, the only other lanthanide complexes of group V oxide donors which have been investigated are those of N-oxides.¹¹ In 1967 Krishnamurthy and Soundararajan reported several complexes of lanthanide perchlorates with pyridine N-oxide. The complexes were all found to contain eight coordinated pyridine N-oxide groups, and all of the perchlorate groups were ionic. The infrared spectra of the complexes showed a decrease in the N-O stretching frequency upon complexation from 1265 cm^{-1} in the free ligand to 1224 cm^{-1} in the complexes, which was attributed to oxygen coordination. The similar europium perchlorate and chloride complexes of 4-methyl pyridine N-oxide (picoline N-oxide) were reported in a study of fluorescent europium complexes.⁹

The lanthanides were also found to complex readily with the chelating N-oxide 2,2'-bipyridine 1,1'-dioxide (bipyO₂) in a study reported by Mehs and Madan.¹² These compounds were all found to contain four coordinated bidentate bipyO₂ ligands and three ionic perchlorate groups, making the

coordination number of all of the lanthanides eight. The infrared spectra of all of the compounds indicated oxygen coordination of the ligand just as in the case of pyridine N-oxide.

Among those neutral oxygen donor ligands which have been found to complex readily with the lanthanides, the final important class is made up of those which contain a carbonyl group. Because of the large degree of negative charge localized on the oxygen in amides, these ligands, in particular, have been found to form very stable complexes with the lanthanides. However, although amide complexes of the lanthanides are numerous, the majority of the complexes which have been reported are with simple disubstituted amides such as DMF, and N,N'-dimethyl acetamide (DMA).

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In 1966 Moeller and Galasyn reported several lanthanide iodide and acetate complexes of DMF. In the case of the iodide complexes only the larger lanthanides were used, and all of the complexes obtained were found to have eight coordinated DMF molecules and were ionic. The acetate compounds had only one DMF molecule for the lanthanides with the largest ionic radii, and none for the smaller lanthanides. On the basis of the infrared spectra of the complexes, which showed no change in the amide C-O stretching frequency upon complexation, it appeared as though the DMF was very weakly coordinated to the lanthanide ion. In another study, the perchlorate complexes of DMF

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were prepared, and the coordination number of all of the lanthanides decreased from eight to six, just as in the case of the dimethyl and diphenyl sulfoxide

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complexes. Krishnamurthy and Soundararajan reported the lanthanide nitrate complexes of DMF and found only four coordinated DMF molecules per lanthanide ion. On the basis of conductance measurements in DMF and nitromethane, these authors believe that two of the nitrate groups are bonded as bidentates, while the third is coordinated as a monodentate ligand. The coordination number of

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of all of the lanthanides in these complexes is then nine.

In addition to DMF, complexes of the lanthanides with DMA are also well known. In 1963 the compound $[\text{La}(\text{DMA})_4(\text{NO}_3)_3]$ was reported,¹⁷ and in 1966 the other members of the series were synthesized.¹⁸ It was found that while the larger lanthanides had four coordinated DMA molecules, the smaller ones had only three. Both conductance and infrared spectral data indicated that the nitrate groups were all coordinated. X-ray diffraction measurements showed that the compounds with three coordinated DMA molecules were divided into two groups of isomorphous compounds. The chloride complexes were also synthesized and were found to be quite different from those of the corresponding nitrates.¹⁹ The larger lanthanides had 3.5 coordinated DMA molecules per metal atom, while the smaller ones had only three. The authors attributed the formula of the larger lanthanide complexes to a binuclear structure with a bridging amide ligand. No molecular weight measurements were performed, however.

As in the case of many of the other compounds discussed previously, the lanthanide perchlorate complexes of DMA exhibited different behavior from that of the other complexes.²⁰ In 1966 Moeller and Vicentini reported the syntheses of all of the lanthanide perchlorate complexes of DMA, and found that as the ionic radius of the lanthanide ion decreased, the number of coordinated amide ligands decreased from eight to seven to six. X-ray diffraction measurements showed clearly that the six coordinated complexes had structures different from the others. As expected, the perchlorate groups were all found to be ionic. A similar study was made with lanthanide perrhenate complexes of DMA²¹ and it was found that the number of coordinated DMA ligands was four in all cases. The perrhenate groups were also found to be coordinated.

The only other study of amide complexes which has been reported is that of the synthesis of several lanthanide perchlorate complexes of N-methyl ²² γ -butyrolactam. These compounds were found to exhibit a decrease in coordination number from eight to seven as the lanthanide ionic radii decreased.

It is well known that the coordination number of lanthanide ions plays an important role in determining both the physical and chemical properties of lanthanide complexes. Separation techniques for these elements such as ion-exchange, solvent extraction, and fractional crystallization are all at least indirectly dependent upon the coordination numbers of the lanthanide ions. The efficiency of light emission in lanthanide phosphors and laser systems is also very sensitive to the environment of the metal ion. Although the coordination number of the metal in many different lanthanide complexes is known, few correlations between coordination numbers and ligand properties are possible because of the vast number of differences which are present among the ligands used. With this information in mind, the work described in Part I of this thesis was initiated with the hope that a better understanding of the effects of certain ligand properties on the coordination number of lanthanide ions could be obtained. This information might then be useful in improving some of the processes mentioned in the above discussion.

In Section B of the first part of this thesis, several lanthanide complexes with two different amides were prepared in which the anion was non-coordinating. The amides differed only in their degree of substitution, and the two groups of complexes were compared in order to determine whether the coordination number would be affected by increasing the degree of substitution on the ligand. In Section C, the noncoordinating perchlorate anion was replaced by the nitrate ion, which has the ability to complex with the lanthanides. The properties of these complexes were determined in the

solid compounds as well as in two different solvents, in order to determine whether any changes in the coordination number would occur in going from the crystalline state into solution. In the last part of the study, described in Section D, a new type of ligand was found to stimulate fluorescence in some lanthanide perchlorate complexes in both the solid state and in solution. The coordination number and other properties, as well as the fluorescence behavior were investigated for these complexes and were compared with other fluorescent systems.

B. Complexes of Lanthanide Perchlorates With
 γ -Butyrolactam and N-Methyl γ -Butyrolactam

1. Introduction

Although many lanthanide complexes with amides and other oxygen donors have been reported, comparisons are sometimes difficult because of the number of differences among the ligands used. While it is generally known that those disubstituted amides or sulfoxides with the largest substituent groups give the lowest coordination number complexes, inductive effects may also be involved. Furthermore, although many lanthanide complexes have been prepared with disubstituted amides, no complexes have been reported with amides of a lower degree of substitution. Since both γ -butyrolactam (BuL) and N-methyl γ -butyrolactam (NMBuL) have been found to complex readily with both transition and non-transition elements,^{23,24} the lanthanide perchlorate complexes of both BuL and NMBuL have now been prepared, and the effects of changing the degree of substitution of the ligand on the coordination number and other physical properties of these complexes are reported in this study.

2. Experimental Section

- a. **Materials:** The lanthanide oxides were all obtained from Semi Elements Inc. in 99.9% purity. The BuL was Eastman yellow label grade, and the reagent NMBuL was obtained from Aldrich Chemical Company. All perchloric acid used was reagent grade and was obtained from G.F. Smith, Inc.
- b. **Preparation of hydrated perchlorates:** A slight excess of lanthanide oxide was treated with hot 30% perchloric acid. The solution was then

filtered and evaporated to dryness on a steam bath. The hydrated product obtained was used directly without analyses.

- c. Preparation of BuL complexes: Each of the BuL complexes was prepared by the same procedure. One gram of the hydrated perchlorate was dissolved in 50 ml of absolute ethanol. Upon addition of an excess of BuL, the complex precipitated immediately in microcrystalline form. The precipitate was washed several times with absolute ethanol followed by anhydrous ether and dried in vacuo. The BuL complexes were all obtained in approximately 80 percent yield and were non-hygroscopic.
- d. Preparation of NMBuL complexes: All of the NMBuL complexes were prepared in a similar manner. One gram of the hydrated perchlorate salt was dissolved in 50 ml of a 1:1 mixture of absolute ethanol and 2,2-dimethoxypropane. After 30 minutes an excess of NMBuL was added, followed by 200 ml of anhydrous ether. The oil which formed immediately became more viscous upon trituration. When the oil was redissolved in enough ligand to form a clear solution, addition of a large amount of ether caused the complex to precipitate immediately. In the case of the heavier lanthanides, the precipitates appeared waxy and were reprecipitated from NMBuL. The precipitates were all washed several times with a large portion of anhydrous ether and were dried in vacuo. The compounds were obtained in approximately 85% yield and appeared to be increasingly hygroscopic as the atomic number of the lanthanide increased.
- e. Analyses: Each lanthanide ion was determined by an EDTA titration using Eriochrome black T as an indicator. An excess of EDTA was added to the lanthanide solution, followed by the indicator and

pH 10 ammonia-ammonium chloride buffer. The solution was then back titrated with 0.01M zinc nitrate. Perchlorate analyses was performed²⁵ by precipitation with Nitron. All carbon, hydrogen, and nitrogen analyses were performed by Weiler and Strauss, Microanalytical Laboratory, Oxford, England.

f. Physical Measurements:

- i. Infrared Spectra: All infrared spectra were obtained using a Perkin Elmer Model 521 recording spectrophotometer. Spectra in the region of $4000\text{--}400\text{ cm}^{-1}$ were obtained by using the Nujol mull technique with potassium bromide windows.
- ii. Electronic Absorption Spectra: The electronic absorption spectra were obtained with a Cary Model 14M recording spectrophotometer. The spectra were obtained in solution using matched quartz cells of 1 cm path length. Molar absorptivities, ϵ , were calculated by using the equation $A = \epsilon bc$ where A is the measured absorbance, b is the path length of the cell in cm and c is the concentration of absorbing species in mole ℓ^{-1} .
- iii. Electrical Conductivity: All conductance measurements were performed with an Industrial Instruments Model-RC-18 bridge using a conventional cell calibrated with an aqueous KCl solution. The cell constant, k , was found to be 0.4975 cm^{-1} . All measurements were conducted at 25 C in nitromethane. Molar conductances, λ_m , were calculated from the equation $\lambda_m = 1000 k/RC\text{ cm}^2\text{ohm}^{-1}\text{mole}^{-1}$, where R is the measured resistance of the solution and C is the concentration of complex in mole ℓ^{-1} .

iv. Molecular Weights: Molecular weight measurements were performed with a Hewlett Packard Model-301A vapor pressure osmometer. All determinations were made with a nonaqueous probe, at 37°C, using nitromethane as a solvent. Standard solutions of benzil in nitromethane were used to calibrate the instrument.

v. X-ray diffraction: The x-ray powder diffraction patterns for each complex were measured with a General Electric Model XRD-5 x-ray diffractometer. Copper K_{α} radiation was used as the source. Values of θ were obtained from the recorder and were used to calculate the d spacings by using the Bragg formula $n\lambda = 2d \sin \theta$ where $n=1$, and λ is the source wavelength (1.541Å).

3. Results and Discussion

The analytical data for both the BuL and NMBuL complexes of the lanthanide perchlorates are summarized in Table I. The data clearly show that all of the BuL compounds are similar, while those of NMBuL are divided into two separate groups with the lighter lanthanides having eight coordinated ligands and the heavier lanthanides and yttrium having only seven.

The infrared data summarized in Table II show that the spectra of all of the BuL complexes are very similar, as are those of the NMBuL compounds. No apparent changes in the spectra are observed when the number of coordinated NMBuL ligands is decreased from eight to seven. In general, the data show a decrease in the C-O stretching frequency and an increase in the C-N stretching frequency of the ligand upon coordination. These results are

Table 1
ANALYTICAL AND OTHER DATA FOR RARE EARTH
BuL AND NMBuL COMPLEXES

Compound	Metal		Perchlorate		Carbon		Hydrogen		Nitrogen	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
[La(C ₄ H ₇ NO) ₈](ClO ₄) ₃	12.42	12.28	26.68	27.01	34.34	35.13	5.05	5.20	10.02	10.05
[Pr(C ₄ H ₇ NO) ₈](ClO ₄) ₃ ^a	12.57	12.67	26.63	26.48	34.27	34.02	5.04	5.29	10.00	10.22
[Nd(C ₄ H ₇ NO) ₈](ClO ₄) ₃ ^b	12.83	12.82	26.55	26.67	34.17	34.24	5.02	5.31	9.98	10.54
[Sm(C ₄ H ₇ NO) ₈](ClO ₄) ₃ ^c	13.30	13.41	26.41	26.63	33.99	34.49	5.00	5.21	9.92	10.02
[Gd(C ₄ H ₇ NO) ₈](ClO ₄) ₃	13.84	14.00	26.25	26.01	33.78	34.30	4.97	5.18	9.86	10.25
[Dy(C ₄ H ₇ NO) ₈](ClO ₄) ₃	14.23	14.12	26.13	25.86	33.63	33.42	4.93	4.87	9.81	10.40
[Er(C ₄ H ₇ NO) ₈](ClO ₄) ₃ ^d	14.59	14.37	26.02	25.49	33.49	33.66	4.92	5.08	9.77	10.60
[Yb(C ₄ H ₇ NO) ₈](ClO ₄) ₃	15.02	14.62	25.89	25.91	33.32	33.69	4.90	5.25	9.72	9.69
[Y(C ₄ H ₇ NO) ₈](ClO ₄) ₃	8.32	8.25	27.93	27.88	35.95	36.05	5.29	5.47	10.49	10.88
[La(C ₅ H ₉ NO) ₈](ClO ₄) ₃	11.29	11.08	24.25	24.12	39.05	39.14	5.40	5.90	9.11	8.86
[Pr(C ₅ H ₉ NO) ₈](ClO ₄) ₃ ^a	11.43	11.32	24.21	23.86	38.99	39.49	5.89	6.04	9.09	8.84
[Nd(C ₅ H ₉ NO) ₈](ClO ₄) ₃ ^b	11.67	11.92	24.15	24.52	38.88	38.89	5.87	5.98	9.07	8.79
[Sm(C ₅ H ₉ NO) ₈](ClO ₄) ₃ ^c	12.11	12.05	24.03	23.98	38.69	38.55	5.85	5.60	9.02	9.19
[Gd(C ₅ H ₉ NO) ₈](ClO ₄) ₃	12.59	12.67	23.89	23.89	38.48	38.09	5.81	6.10	8.97	9.51
[Dy(C ₅ H ₉ NO) ₇](ClO ₄) ₃	14.07	13.78	25.84	25.75	36.40	36.38	5.50	5.80	8.49	8.65
[Er(C ₅ H ₉ NO) ₇](ClO ₄) ₃ ^d	14.43	14.28	25.73	25.38	36.26	36.29	5.48	5.28	8.46	8.65
[Yb(C ₅ H ₉ NO) ₇](ClO ₄) ₃	14.85	14.74	25.60	25.52	36.08	36.50	5.45	5.51	8.41	8.65
[Y(C ₅ H ₉ NO) ₇](ClO ₄) ₃	8.22	8.33	27.59	27.59	38.88	39.37	5.87	5.89	9.07	9.05

a. green

b. lavender

c. light yellow

d. pink

all others are colorless

Table II
INFRARED DATA FOR BuL AND NMBuL COMPLEXES

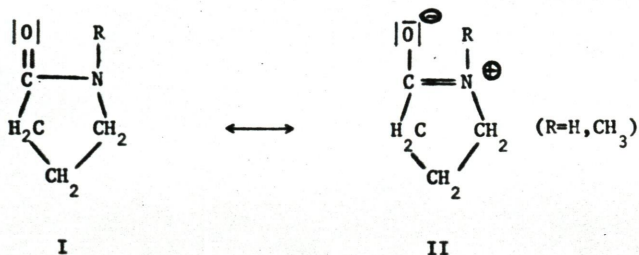
Compound	νCO (cm^{-1}) ^a	$\Delta\nu\text{CO}$ (cm^{-1})	νCN (cm^{-1}) ^b	$\Delta\nu\text{CN}$ (cm^{-1})	νClO_4^- (cm^{-1}) ^c	δClO_4^- (cm^{-1}) ^b
BuL	1691	-	1285	-	-	-
[La(BuL) ₈](ClO ₄) ₃	1665	-26	1289	+ 4	1050-1120	624
[Pr(BuL) ₈](ClO ₄) ₃	1656	-35	1294	+ 9	1090-1130	628
[Nd(BuL) ₈](ClO ₄) ₃	1658	-33	1293	+ 8	1050-1130	624
[Sm(BuL) ₈](ClO ₄) ₃	1658	-33	1295	+10	1050-1120	625
[Gd(BuL) ₈](ClO ₄) ₃	1658	-33	1292	+ 7	1040-1120	623
[Dy(BuL) ₈](ClO ₄) ₃	1657	-34	1292	+ 7	1070-1115	623
[Er(BuL) ₈](ClO ₄) ₃	1659	-32	1295	+10	1040-1130	624
[Yb(BuL) ₈](ClO ₄) ₃	1658	-33	1295	+10	1070-1120	624
[Y(BuL) ₈](ClO ₄) ₃	1663	-28	1293	+ 8	1040-1130	623
NMBuL	1680	-	1286	-	-	-
[La(NMBuL) ₈](ClO ₄) ₃	1646	-34	1307	+21	1060-1120	625
[Pr(NMBuL) ₈](ClO ₄) ₃	1642	-38	1309	+23	1070-1095	625
[Nd(NMBuL) ₈](ClO ₄) ₃	1642	-38	1310	+24	1060-1105	625
[Sm(NMBuL) ₈](ClO ₄) ₃	1641	-39	1309	+23	1070-1110	623
[Gd(NMBuL) ₈](ClO ₄) ₃	1642	-38	1309	+23	1075-1110	624
[Dy(NMBuL) ₇](ClO ₄) ₃	1642	-38	1310	+24	1060-1120	624
[Er(NMBuL) ₇](ClO ₄) ₃	1641	-39	1310	+24	1070-1105	622
[Yb(NMBuL) ₇](ClO ₄) ₃	1643	-37	1310	+24	1060-1110	623
[Y(NMBuL) ₇](ClO ₄) ₃	1645	-35	1310	+24	1060-1110	624

a. very strong

b. strong

c. very broad

similar to those reported by Madan and Sturr for both BuL and NMBuL complexes of transition metals, and were interpreted to indicate coordination of the amide through the oxygen rather than the nitrogen atom. The shift in frequencies upon coordination can readily be explained on the basis of the two resonance forms shown below.



Any coulombic interaction of the oxygen atom of the amide with the positive lanthanide ion would tend to polarize the C-O bond, and pull electron density towards the oxygen. The result would be a greater contribution of resonance form II to the overall structure of the coordinated amide, relative to that of the free ligand. Since resonance form II contains a lower C-O bond order and a higher C-N bond order than form I, the net result would be a lowering of the C-O stretching frequency and a raising of the C-N frequency upon coordination through oxygen, which is observed.

The data in Table II also indicate that the perchlorate bands for all of the complexes appear as two singlets, one being a very strong broad band in the 1100 cm⁻¹ region and the other being a medium intensity band at approximately 625 cm⁻¹. Group theory predicts that the ionic perchlorate group, with T_d symmetry, has four fundamental modes of vibration, two of which are infrared active. Upon coordination as a monodentate, however, the symmetry is lowered to C_{3v} and there are six fundamental modes of vibration,

all of which are infrared active. The vibrations of the ClO_4^- group as a function of symmetry are summarized below.

$T_d \text{ ClO}_4^-$	ν_1	ν_2	ν_3		ν_4	
	sym. st.	sym. bend	asym. st.		asym. bend	
	↓	↓	↓	↓	↓	↓
$C_{3v} \text{ -O-ClO}_3$	ν_2	ν_6	ν_1	ν_4	ν_3	ν_5
	ClO st.	rocking	ClO ₃ sym.st.	asym. bend	ClO ₃ sym. bend	ClO ₃ asym. bend

In the case of the ionic perchlorate group the singly degenerate ν_1 mode and the doubly degenerate ν_2 modes are only Raman active, however, the triply degenerate ν_3 and ν_4 modes are both Raman and infrared active and appear at approximately 1100 cm^{-1} and 626 cm^{-1} , respectively. In the case of the coordinated perchlorato group the degeneracy of the ν_3 and ν_4 modes is removed and a splitting of the bands occurs. Since the infrared spectra of all of the BuL and NMBuL complexes shows no splitting of the ν_3 and ν_4 perchlorate bands, it appears as though all of the compounds contain ionic perchlorate groups only.

The presence of ionic perchlorate groups in all of the compounds is further substantiated by the conductance measurements in nitromethane. The values which were obtained at 25°C are summarized in Table III. Nitromethane was chosen as a solvent because of its very poor donor properties, and its ability to dissolve the compounds. It can be seen from the data that under the conditions which existed, the values for the molar conductivity of all of the complexes were in the range expected for a 1:3 electrolyte. The value of 262 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ for a 1:3 electrolyte, determined by Gill and Nyholm, was used as a reference. The value assigned to a 1:2 electrolyte is

Table III
CONDUCTANCE MEASUREMENTS FOR BuL AND NMBuL COMPLEXES

BuL Complexes			NMBuL Complexes		
Ln	Concn x 10 ³ , M	$\lambda_m, \text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$	Ln	Concn x 10 ³ , M	$\lambda_m, \text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$
La	3.19	228	La	3.04	278
	1.06	276		1.18	285
Pr	3.04	231	Pr	3.13	282
	1.03	275		1.01	310
Nd	2.98	238	Nd	2.95	289
	1.03	282		1.14	325
Sm	3.16	229	Sm	3.34	294
	1.03	286		1.03	332
Gd	3.20	224	Gd	5.79	279
	1.07	296		2.57	303
Dy	3.14	232	Dy	6.00	277
	1.08	298		2.46	318
Er	3.04	242	Er	9.67	284
	1.05	301		3.87	336
Yb	3.19	236	Yb	7.05	295
	1.01	300		4.23	321
Y	3.01	236	Y	7.83	298
	1.03	297		6.26	308

$177 \text{ cm}^2\text{ohm}^{-1}\text{mole}^{-1}$, and is out of the range of the values obtained for these complexes.

In order to confirm that the species present in solution were identical to those measured in the solid state, molecular weight measurements of several of the complexes in nitromethane were determined by vapor pressure osmometry. The results of this study are summarized in Table IV. It can be seen from the data that the observed molecular weights of the complexes in nitromethane were in the range expected for a compound which ionizes to give four particles in solution. Any dissociation of the complex to give free amide molecules in solution would result in a much lower observed molecular weight than that which was measured. The lack of dissociation of the compounds in nitromethane was also substantiated by the absence of any free amide bands in the infrared spectrum of the complexes in nitromethane solution.

A comparison of the visible spectrum of each BuL complex in BuL solution with that of the corresponding NMBuL complex in NMBuL is shown in Table V. The data show that, in general, for a given lanthanide, the spectrum of the BuL complex and the NMBuL complex are nearly identical. Some changes were observed, however, in the absorption bands due to the $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^2\text{G}_{7/2}$ transitions in neodymium and the similar $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ transition in erbium. These transitions as well as those of the other lanthanides, are all crystal field induced electric dipole transitions; however, because only the above transitions in neodymium and erbium are affected to a large degree by the ligand field, they are termed hypersensitive. The changes in the hypersensitive bands are believed to be a result of an inhomogeneous electromagnetic field around the lanthanide ion, and it has been shown that the absorption intensity

Table IV

MOLECULAR WEIGHT DATA FOR BuL AND NMBuL COMPLEXES

Complex	Concn x 10 ³ , M	Apparent Mol.wt. in CH ₃ NO ₂	Theoretical Molecular Weight particles				
			1	2	3	4	5
[La(BuL) ₈](ClO ₄) ₃	10.0	326	1118	559	377	279	224
[Gd(BuL) ₈](ClO ₄) ₃	21.7	305	1137	568	379	284	227
[Yb(BuL) ₈](ClO ₄) ₃	20.0	324	1152	576	384	288	230
[La(NMBuL) ₈](ClO ₄) ₃	9.14	288	1230	615	410	307	246
[Gd(NMBuL) ₈](ClO ₄) ₃	9.84	276	1249	624	416	312	250
[Dy(NMBuL) ₇](ClO ₄) ₃	10.2	255	1154	577	384	288	231
[Yb(NMBuL) ₇](ClO ₄) ₃	10.4	269	1165	582	388	291	233

Table V

VISIBLE AND ULTRAVIOLET SPECTRA OF COLORED BuL AND NMBuL COMPLEXES

BuL Complexes in BuL						NMBuL Complexes in NMBuL					
Ln	$\lambda(\text{m}\mu)$	$\epsilon_{\text{max}}^{\text{max}}$ ($\text{M}^{-1}\text{cm}^{-1}$)	Ln	$\lambda(\text{m}\mu)$	$\epsilon_{\text{max}}^{\text{max}}$ ($\text{M}^{-1}\text{cm}^{-1}$)	Ln	$\lambda(\text{m}\mu)$	$\epsilon_{\text{max}}^{\text{max}}$ ($\text{M}^{-1}\text{cm}^{-1}$)	Ln	$\lambda(\text{m}\mu)$	$\epsilon_{\text{max}}^{\text{max}}$ ($\text{M}^{-1}\text{cm}^{-1}$)
Nd	748	8.28	Sm	344	5.41	Nd	747b	10.0	Sm	374	3.07
	739a	6.10		310	9.19		736b	6.09		361	3.26
	736a	5.87					581b	10.6		344	3.90
	581b	12.4					578b	11.2		298	7.27
	578b	12.4	Dy	387	2.36		572a	5.43			
	569a	5.66		365	4.56		527c	3.03		364	2.95
	523b	4.22		351	6.39		523c	4.43		350	3.94
	511b	2.14		326	5.70		512c	2.74		325	3.87
	355c	4.22	Er	652	5.58		356c	6.98			
	349c	3.44		524b	16.3		350c	6.89		656c	1.79
Pr	347c	3.16		520b	21.6		348c	6.08		652c	2.56
				487	7.74		266	6.89		650c	2.62
										524b	5.48
	593	2.22		380b	25.4	Pr	593	2.52		520b	9.47
	482	5.54		377b	34.2		482	7.65		488	4.85
	469	4.73		363	6.10		469	4.95		407	2.81
	445	10.3					445	11.9		381b	10.6
							266	12.0		377b	17.9
Sm	404	5.53				Sm	403	4.45		364	6.26
	374	3.64									
	361	3.93									

** a. shoulder
 b. doublet
 c. triplet

of these bands is influenced by the symmetry of the field around the lanthanide ion.²⁹ In a study of the effect of coordination number on the hypersensitive lanthanide transitions,³⁰ Karraker found that, in each case, as the coordination number of the lanthanide ion decreased, so did the intensity of the hypersensitive bands in the visible spectrum.

The visible spectra of the neodymium and erbium BuL complexes dissolved in BuL and the NMBuL complexes dissolved in NMBuL are reproduced in Figure 1. It can be seen that in the case of neodymium, the molar absorptivities of the hypersensitive bands at 581 and 578 mμ are nearly the same value for both complexes. In the case of erbium, however, there is a large decrease in the molar absorptivity of the bands at 524 and 520 mμ in going from the BuL to the NMBuL complex. The decrease in molar absorptivity for the NMBuL complex of erbium is consistent with a decrease in coordination number from eight to seven as shown by the chemical analyses.

In order to determine whether any structural differences exist between the BuL and NMBuL series, the x-ray powder diffraction pattern for each compound was measured. The results are summarized in Tables VI, VII, and VIII. It can be seen from the data that while all of the BuL compounds are isomorphous, the NMBuL compounds can be divided into two isomorphous groups, one containing the eight-coordinated complexes and the other containing the seven-coordinated compounds. These results are quite different from those²⁰ reported by Moeller for the lanthanide perchlorate complexes of DMA, which showed that the seven and eight-coordinated species were isomorphous.

These results are not unusual, however, since it has been established that complexes with coordination numbers of eight and seven can have several

**Fig. 1. Hypersensitive Transition Bonds In
the Visible Spectra of the Trivalent Neodymium and Erbium
Ion in Both BuL and NMBuL**

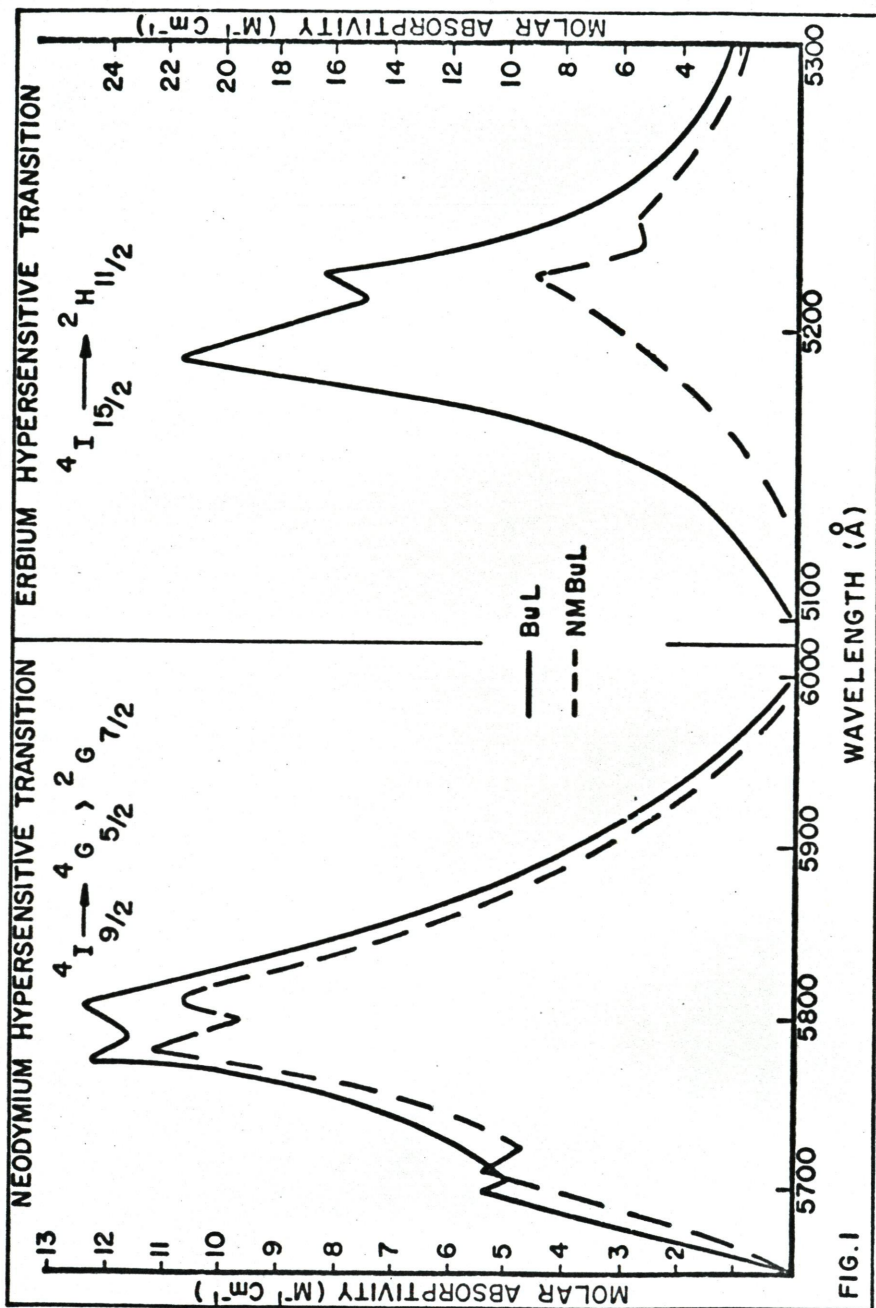


FIG. 1

Table VI
X-RAY DIFFRACTION DATA FOR $[\text{Ln}(\text{BuL})_8](\text{ClO}_4)_3$ COMPLEXES

La	Pr	Nd	Sm	Gd	Dy	Er	Yb	Y
d I/I_{100}	d I/I_{100}	d I/I_{100}	d I/I_{100}	d I/I_{100}	d I/I_{100}	d I/I_{100}	d I/I_{100}	d I/I_{100}
11 11.62	10 11.62	9 11.47	4 11.47	8 11.62	7 11.62	5 11.33	22 11.33	7 11.18
-	-	-	-	5 10.04	5 10.04	4 10.04	11 9.71	4 9.82
-	-	-	-	-	-	10 8.11	20 8.04	6 8.11
17 6.86	25 6.96	22 7.02	26 7.25	41 7.49	45 7.37	100 7.37	100 7.25	41 7.31
-	-	-	-	-	-	5 6.70	11 6.65	-
8 5.98	11 5.94	8 5.94	10 5.82	9 5.90	9 5.90	8 5.82	21 5.71	61 5.75
7 5.82	8 5.82	8 5.79	-	-	-	8 5.75	-	-
-	-	-	-	-	-	6 5.37	7 5.27	-
47 4.62	43 4.62	31 4.60	25 4.53	26 4.53	28 4.48	22 4.46	57 4.41	61 4.44
10 3.83	-	-	45 3.83	32 3.86	46 3.90	63 3.83	62 3.83	60 3.83
41 3.75	41 3.78	37 3.80	-	-	32 3.86	9 3.66	-	-
8 2.67	4 2.86	5 2.85	-	-	-	-	-	-
6 2.83	4 2.83	4 2.81	5 2.76	4 2.81	-	-	-	-
-	-	-	-	4 2.68	-	-	7 2.73	7 2.76

Table VII

X-RAY DIFFRACTION DATA FOR $\text{Ln}(\text{NMBuL})_8 (\text{ClO}_4)_3$ COMPLEXES

La		Pr		Nd		Sm		Gd	
I/I_{100}	d	I/I_{100}	d	I/I_{100}	d	I/I_{100}	d	I/I_{100}	d
16	10.27	8	10.04	19	10.04	13	10.16	14	9.71
-	-	7	8.93	11	8.93	-	-	-	-
8	1.37	-	-	12	7.25	-	-	7	6.96
12	6.51	9	6.37	20	6.41	14	6.41	14	6.23
12	6.23	10	6.15	20	6.15	15	6.15	15	5.98
11	4.53	8	4.48	21	4.46	17	4.48	15	5.98
8	4.37	-	-	9	4.31	-	-	7	4.48
-	-	5	4.15	14	4.15	13	4.15	-	-
10	4.07	-	-	-	-	15	4.06	-	-
-	-	5	4.02	14	4.02	13	4.02	-	-
7	3.78	-	-	12	3.75	22	3.75	-	-
-	-	-	-	8	3.69	-	-	8	3.67

Table VIII

X-RAY DIFFRACTION DATA FOR $[\text{Ln}(\text{NMBuL})_7](\text{ClO}_4)_3$ COMPLEXES

Dy		Er		Yb		Y	
I/I ₁₀₀	d	I/I ₁₀₀	d	I/I ₁₀₀	d	I/I ₁₀₀	d
23	10.77	25	10.77	11	11.04	7	10.91
11	8.93	12	8.93	12	9.02	10	8.84
10	5.90	10	5.90	9	5.94	8	5.60
13	5.03	10	5.06	11	5.06	14	5.09
13	4.09	7	4.09	14	4.13	10	4.13
11	3.97	8	3.97	7	3.98	6	3.98
7	3.73	6	3.69	15	3.70	10	3.70

different symmetries as a result of small changes in the positions of ligands around the metal ion.

4. Summary and Conclusions

In this study the lanthanide perchlorate complexes of both γ -butyrolactam and N-methyl- γ -butyrolactam were characterized by infrared and visible spectroscopy, conductance and molecular weight measurements, and x-ray diffraction measurements. On the basis of the data it appears as though all of the lanthanides are eight-coordinated in the BuL series, while in the NMBuL series the larger lanthanides (La-Gd) are eight-coordinated, while those of smaller ionic radii (Dy-Yb) are only seven-coordinated. Since BuL has a slightly puckered ring system, it is not likely that large repulsive forces would be present between neighboring ligands, and the coordination number of the BuL complexes is identical to that of similar
11
complexes of the planar pyridine N-oxide molecule. In the case of NMBuL, however, the substituted methyl group is out of the plane of the ring, and hence more crowding of neighboring ligands in the coordination sphere can occur as the ionic radius of the metal ion decreases. When the ionic radius of the metal reaches a certain lower limit, the coordination number decreases and hence the repulsion between ligands is reduced. It is not surprising then, that in the case of DMA, which has two substituted methyl groups on the nitrogen atom, the smallest lanthanides (thulium,
20
ytterbium, and lutetium) have only six coordinated DMA molecules.

The increasingly hygroscopic nature of the NMBuL compounds as the lanthanide atomic weight increases is most likely due to a partial replacement of the bulky NMBuL ligands by much smaller water molecules, which would reduce ligand repulsions in the coordination sphere.

C. Complexes of Lanthanide Nitrates With γ -Butyrolactam

1. Introduction

The ability of the nitrate ion to coordinate with transition metals either as a monodentate or a bidentate ligand has been established by Curtis and Curtis.³² In the case of the lanthanides, several series of compounds have also been reported which are believed to contain coordinated nitrato groups. In the triphenylphosphine and triphenylarsine oxide complexes reported by Cousins and Hart^{8,10} the nitrato groups were believed to be bidentate, while in the DMSO complexes reported by Ramalingam and Soundararajan,⁶ one of the nitrato groups was believed to be bidentate and the other two monodentate ligands. In the DMF complexes reported by Krishnamurthy and Soundararajan,¹⁶ it was believed that only one of the nitrato groups was bidentate whereas the other two were monodentate ligands.

Since the lanthanide perchlorate complexes of BuL were found to be very stable, as a logical continuation of the study, the lanthanide nitrate complexes of BuL were prepared. The study was undertaken in order to determine the effects of the coordinating ability of the nitrate ion on the coordination number and other physical properties of these BuL complexes.

2. Experimental Section

a. **Materials:** The lanthanide oxides were all obtained from Semi-Elements Inc., in 99.9% purity. The BuL was obtained as Eastman yellow label

grade, and the nitric acid was Fisher reagent grade.

b. Preparation of hydrated nitrates: A slight excess of lanthanide oxide was heated on a steam bath with 30% nitric acid until most of the oxide was dissolved. The solution was then filtered and evaporated to dryness on a steam bath. The hydrated product which was obtained was used directly without further purification.

c. Preparation of BuL complexes: The same procedure was used in the preparation of all of the BuL complexes. One gram of the hydrated nitrate was dissolved in 10 ml of BuL followed by 10 ml of absolute ethanol to form a clear solution. After the addition of enough anhydrous ether to produce a slightly cloudy solution, stirring resulted in the immediate precipitation of the lanthanum, neodymium, and gadolinium complexes in microcrystalline form. The dysprosium, erbium and ytterbium complexes crystallized more slowly as fine long needles. The crystals were all washed several times with anhydrous ether and were dried in vacuo. All of the BuL complexes were obtained in approximately 85% yields and appeared to be nonhygroscopic.

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d. Analyses: Nitrate ion was analyzed by precipitation with Nitron. All carbon, hydrogen, and nitrogen analyses were performed by Weiler and Strauss, Microanalytical Laboratory, Oxford, England.

e. Physical Measurements: All infrared spectra were obtained using a Perkin-Elmer Model 521 recording spectrophotometer. Spectra in the region of $4000-400\text{ cm}^{-1}$ were obtained by using the Nujol mull technique with potassium bromide windows. Solution spectra in the region of $4000-600\text{ cm}^{-1}$ were obtained with matched cells of 0.5 mm

path length, using both chloroform and nitromethane as solvents. Conductance and molecular weight measurements were performed as described in part B.

3. Results and Discussion

The analytical data for all of the lanthanide nitrate complexes of BuL which were prepared are summarized in Table IX. It can be seen from the analyses that two different types of compounds are obtained, those of the larger lanthanides having eight-coordinated BuL ligands and those of the smaller lanthanides having only three. A comparison of the infrared spectra of these two types of compounds in a Nujol mull indicates that definite structural differences exist between them.

The ionic nitrate group has D_{3h} symmetry, and has four fundamental modes of vibration, three of which are infrared active. Upon coordination as either a monodentate or a bidentate ligand, however, the symmetry is lowered to C_{2v} which has six fundamental modes of vibration, all of which are infrared active.³³ The modes of vibration of the NO_3^- group as a function of symmetry are shown below.

$D_{3h} NO_3^-$	ν_1 sym st	ν_2 out of plane sym bend	ν_3 asym stretch	ν_4 in plane asym bend		
	↓	↓	↓	↓		
$C_{2v} O-NO_2$	ν_2 O- NO_2 st	ν_6 out of plane bend	ν_1 NO_2 sym st	ν_4 NO_2 asym st	ν_3 sym in plane bend	ν_5 asym in plane bend

In a study of a series of uranyl complexes containing bidentate nitrate groups, Bullock³⁴ has found that there are two infrared bands

Table IX
ANALYTICAL AND OTHER DATA FOR BUL COMPLEXES

Compound	Mp. C	Carbon		Hydrogen		Nitrogen		Nitrate	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[\text{La}(\text{C}_4\text{H}_7\text{NO})_8](\text{NO}_3)_3$	106-108	38.21	38.04	5.61	5.81	15.31	15.36	18.49	18.29
$[\text{Nd}(\text{C}_4\text{H}_7\text{NO})_8](\text{NO}_3)_3^a$	95-97	38.01	37.82	5.58	5.59	15.23	15.15	18.39	18.47
$[\text{Gd}(\text{C}_4\text{H}_7\text{NO})_8](\text{NO}_3)_3$	74-76	37.52	37.59	5.51	5.30	15.03	14.60	18.16	18.53
$[\text{Dy}(\text{C}_4\text{H}_7\text{NO})_3(\text{NO}_3)_3]^b$	154-155	23.79	23.86	3.49	3.42	13.80	14.90	30.70	30.40
$[\text{Er}(\text{C}_4\text{H}_7\text{NO})_3(\text{NO}_3)_3]^b$	157-158	23.68	23.77	3.47	3.63	13.80	13.69	30.56	30.12
$[\text{Yb}(\text{C}_4\text{H}_7\text{NO})_3(\text{NO}_3)_3]^b$	155-157	23.46	23.35	3.44	3.12	13.67	13.20	30.27	30.03

a. lavender

b. pink

Between 700 and 750 cm^{-1} . One band was observed in the 710-725 cm^{-1} range and was assigned to the ν_5 vibration, and a stronger band in the 735-750 cm^{-1} region was assigned to the ν_3 vibration of the nitrato group. Furthermore, in the series of lanthanide nitrate complexes with triphenylphosphine oxide reported by Cousins and Hart⁸ it was found that those complexes with ionic nitrate groups had a band at 830 cm^{-1} , which was assigned to the ν_2 vibration of the nitrate ion. On the other hand, those complexes which had coordinated nitrato groups present had an infrared band between 813 cm^{-1} and 819 cm^{-1} , which the authors assigned to the ν_6 vibration of the nitrato group. A similar band was also found at 819 cm^{-1} in the spectrum of the DMF complexes of lanthanide nitrates,¹⁶ which contained only coordinated nitrato groups.

The infrared spectrum of the lanthanide complex $[\text{La}(\text{BuL})_8](\text{NO}_3)_3$ in Nujol is reproduced in Figure 2, and is very similar to those of the corresponding Neodymium and gadolinium complexes. It is clear from the spectrum that there is only one band in the 700-750 cm^{-1} region at 701 cm^{-1} , and a medium intensity band at 829 cm^{-1} . On the basis of the above discussion, these bands are assigned to the ν_4 and ν_2 vibrations of the nitrate ion, respectively.

The infrared spectrum of the complex $[\text{Dy}(\text{BuL})_3(\text{NO}_3)_3]$ is shown in Figure 3, and is very similar to those of the corresponding erbium and Ytterbium compounds. In this spectrum it is clear that two bands are present between 700 and 750 cm^{-1} . The one at 705 cm^{-1} is assigned to the ν_5 vibration, and the one at 746 cm^{-1} is assigned to the ν_3 vibration of the coordinated nitrato group. The band at 817 cm^{-1} is also in the range expected for the ν_6 vibration of the nitrato group.

The C-O stretching frequency of the coordinated amide in the spectrum of the complexes with ionic nitrate groups (Fig. 2) is shifted from

Fig. 2. Infrared Spectra of the complex

$[\text{La}(\text{BuL})_3](\text{NO}_3)_3$ in Nujol, A—, And BuL in Nujol, B----

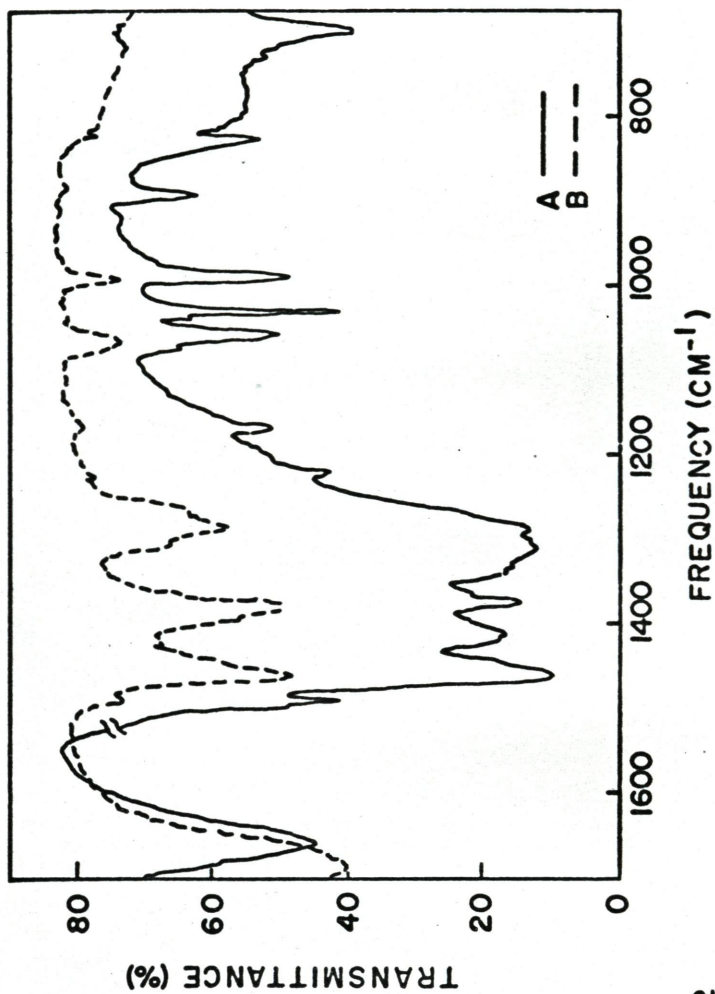


FIG. 2

Fig. 3. Infrared Spectra of the Complex

$[\text{Dy}(\text{BuL})_3(\text{NO}_3)_3]$ in Nujol, A—, and BuL in Nujol, B----

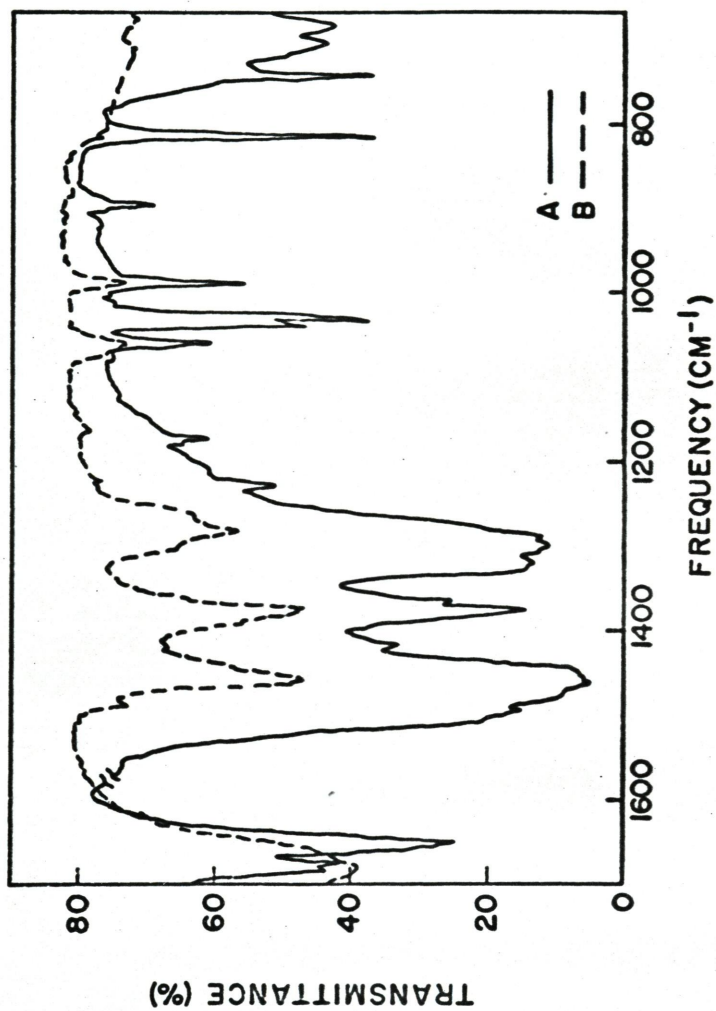


FIG. 3

1691 cm^{-1} in BuL to 1648 cm^{-1} in the complexes. This decrease is similar to that observed in the perchlorate complexes and is attributed to oxygen coordination of the amide. The C-O stretching band in the spectra of the compounds containing coordinated nitrato groups (Fig. 3) also shows a decrease in frequency; however, it is split into a triplet at 1649, 1675, and 1684 cm^{-1} . The splitting may be due to the nonequivalence of the three amide groups in the complex as a result of the presence of both monodentate and bidentate nitrato groups in the coordination sphere. The split band may also be due to coupling of the C-O stretching vibration with one or more vibration of the nitrato group. The ability of the nitrato group to form combination bands has been demonstrated in previous studies.^{32,34}

Both the conductance and molecular weight measurements, summarized in Table X, and XI, respectively, substantiate the infrared data for the complexes containing coordinated nitrato groups. The data clearly show that in the poor coordinating solvent, nitromethane, the complexes are nonelectrolytes and are neutral species. Molecular weight measurements also show that the species are undissociated and monomeric. In the better donor solvent, DMF, however, the complexes were found to be 1:2 electrolytes, demonstrating behavior similar to that of the DMSO complexes of lanthanide nitrates prepared by Ramalingam and Soundararajan.⁶ Values of λ_m of 140-170 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ for a 1:2 electrolyte in DMF were used as a reference.³⁵ The value for a 1:1 electrolyte is 88 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$.³⁵

Since only two of the nitrato groups are replaced by the monodentate DMF molecule, it appears as though one of the nitrato groups is bound more strongly than the other two. This suggests that two of the groups may be monodentate, while the third is probably coordinated as a bidentate ligand.

Table X

Conductance Data For BuL Complexes In Nitromethane And DMF At 298 K

Compound	Solvent	concn. x $10^3 M$	$\lambda_m (cm^2 ohm^{-1} mole^{-1})$
$[La(BuL)_8](NO_3)_3$	NM	1.01	20.2
	DMF	1.02	201
$[Nd(BuL)_8](NO_3)_3$	NM	1.06	12.1
	DMF	1.04	191
$[Gd(BuL)_8](NO_3)_3$	NM	1.17	6.2
	DMF	1.10	165
$[Dy(BuL)_3(NO_3)_3]$	NM	1.17	7.6
	DMF	1.00	163
$[Er(BuL)_3(NO_3)_3]$	NM	1.02	10.2
	DMF	1.05	168
$[Yb(BuL)_3(NO_3)_3]$	NM	1.15	12.5
	DMF	1.27	168

Table XI

Molecular Weight Measurements For BuL Complexes In Nitromethane At 310°K

Compound	Apparent Mol. Wt. In NM	Theoretical Molecular Weight For Particles					
		1	2	3	4	5	6
$[\text{La}(\text{BuL})_8](\text{NO}_3)_3$	190	1006	503	335	252	201	167
$[\text{Nd}(\text{BuL})_8](\text{NO}_3)_3$	178	1011	506	337	253	202	169
$[\text{Gd}(\text{BuL})_8](\text{NO}_3)_3$	178	1024	512	341	256	205	171
$[\text{Dy}(\text{BuL})_3(\text{NO}_3)_3]$	503	604	302	201	151	121	101
$[\text{Er}(\text{BuL})_3(\text{NO}_3)_3]$	471	609	304	203	152	122	101
$[\text{Yb}(\text{BuL})_3(\text{NO}_3)_3]$	455	614	307	204	154	123	102

The solution behavior of the complexes of the type $[\text{Ln}(\text{BuL})_8](\text{NO}_3)_3$, however, is not in agreement with what one would expect for an ionic compound. In nitromethane the complexes are nonelectrolytes (Table X), indicating that coordinated, rather than ionic, nitrate groups are present. In DMF the compounds demonstrated behavior similar to that of the complexes of the type $[\text{Ln}(\text{BuL})_3(\text{NO}_3)_3]$ and were found to be 1:2 electrolytes. Further evidence for the presence of coordinated nitrate groups is obtained from the infrared spectra of the complex $[\text{La}(\text{BuL})_8](\text{NO}_3)_3$ nitromethane solution, which are represented in Fig. 4. The band which was at 829 cm^{-1} in the Nujol mull spectra has shifted to 817 cm^{-1} in nitromethane, and the band at 701 cm^{-1} in Nujol has split into two bands, one at 704 and the other at 739 cm^{-1} . A comparison of the $700\text{--}900\text{ cm}^{-1}$ region in Figures 3 and 4 shows that the species present are very similar.

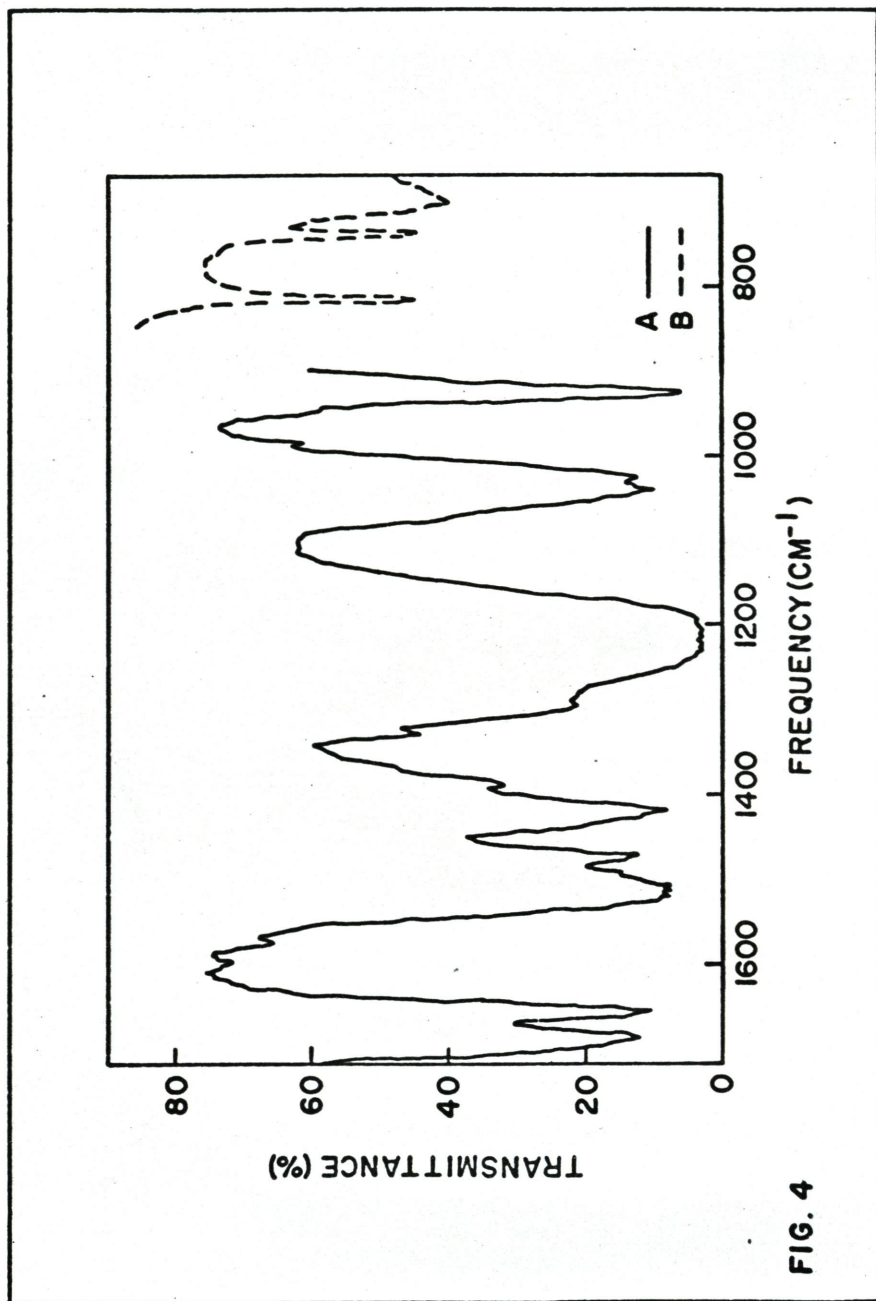
Furthermore, the infrared spectra of these complexes in both nitromethane and chloroform show a strong band at 1690 cm^{-1} as well as the band at 1648 cm^{-1} . The band at 1690 cm^{-1} can only be explained by the presence of free amide molecules in solution. On the basis of the conductance and infrared data for the $[\text{Ln}(\text{BuL})_8](\text{NO}_3)_3$ complexes in solution, it appears as though the nitrate groups are partially replacing BuL in the coordination sphere. The replacement is most likely a result of the full negative charge on the nitrate ions, which would result in a stronger ion-dipole type bond than would the partial negative charge localized on the oxygen of a BuL molecule.

Fig. 4. Infrared Spectra of the Complex

$[\text{La}(\text{BuL})_8](\text{NO}_3)_3$ in Nonaqueous Solvents,

A— Representing the Spectra in Chloroform (1700 cm^{-1} – 900 cm^{-1}),

and B— Representing the Spectra in Nitromethane (850 – 675 cm^{-1})



In order to estimate the degree of dissociation of BuL from the complexes in nitromethane, molecular weight measurements were obtained for 0.01M solutions of each complex. The data which were obtained are summarized in Table XI. The experimental molecular weight values which were obtained indicate that five particles are present when the lanthanum complex dissociates, while six particles are present when the neodymium and gadolinium complexes dissociate. Since the conductance data have shown that no ions are present in solution, it would seem that the only species present in nitromethane are the complex and BuL. On the basis of this data it appears as though the lanthanum complex dissociates to give four BuL molecules in solution, while the neodymium and gadolinium complexes dissociate to give five BuL molecules. The degree of dissociation of each complex was further substantiated by measuring the intensity of the ν_{CO} bond of the free amide in a solution obtained by dissolving enough of the lanthanide complex to form an 0.01 M solution. The intensity of the bands were then compared with those of BuL solutions in the concentration range of 0.03-0.05 M. The measurements showed that the concentration of BuL obtained from the lanthanum complex was slightly over 0.04 M, while in the case of the neodymium and gadolinium complexes, the BuL concentrations were nearly 0.05 M.

4. Summary and Conclusions

In this section, the lanthanide nitrate complexes of BuL were characterized by infrared spectroscopy, conductance measurements, and molecular weight determinations. On the basis of the data it

was found that the complexes of the larger lanthanides lanthanum, neodymium, and gadolinium were ionic in the solid state. In nitromethane solution, however, the nitrate groups replaced some of the BuL from the coordination sphere, and neutral species were obtained. The complexes of the smaller lanthanides, dysprosium, erbium, and ytterbium were found to be neutral in both the solid state and in solution. Under the conditions studied, the data indicate that in the solid complexes of the larger lanthanides the metal is eight-coordinated, while for the smaller lanthanides the coordination number is seven. In solution, however, only the largest ion, lanthanum, appears to be eight-coordinated, while all others have coordination numbers of seven. In the case of neodymium and gadolinium it appears that a reduction in coordination number occurs when the crystalline compounds are dissolved in nitromethane.

D. Fluorescent Lanthanide Complexes with 2,2'-Bipyridine 1,1'-Dioxide

1. Introduction

In recent years, a considerable amount of interest has been shown in the fluorescence behavior of many europium and terbium compounds in solution, because of their potential use as laser sources. In all of the compounds which were studied, the fluorescence was believed to be a result of intramolecular energy transfer from a ligand excited state to the rare earth ion. Absorption of ultraviolet radiation by the ligand would produce an excited triplet state, which could then transfer energy intramolecularly to an excited state of the lanthanide ion. Subsequent decay of the lanthanide excited state to a lower energy level would then result in the observed fluorescence. In most of the complexes which were studied, the ligand was coordinated to the lanthanide ion through an oxygen atom bonded directly to a carbon. In only two cases were N-oxide ligands reported to cause fluorescence in lanthanide complexes. Both pyridine N-oxide³⁶ and 4-picoline N-oxide³⁷ were found to cause fluorescence in europium complexes in the solid state. However, no attempt was made to determine whether fluorescence existed in solution also.

The chelate 2,2'-bipyridine 1,1'-dioxide has previously been reported to complex with several of the lanthanide elements,¹² although the europium and terbium complexes were not prepared. The compounds $[\text{Eu}(\text{bipyO}_2)_4](\text{ClO}_4)_3$ and $[\text{Tb}(\text{bipyO}_2)_4](\text{ClO}_4)_3$ have now been prepared in this study in order to determine their fluorescence properties in solution.

2. Experimental Section

- a. **Materials:** The Eu_2O_3 and Tb_4O_7 were obtained from Semi-Elements Inc., in 99.9% purity. The bipyO_2 was prepared by the method of Madan and Bull.⁴³
- b. **Analyses:** Perchlorate analyses were determined by a gravimetric procedure using Nitron.²⁵ All carbon hydrogen and nitrogen analyses were performed by Weiler and Strauss Microanalytical Laboratory, Oxford, England.
- c. **Preparation of Compounds:** The compounds were prepared by a method reported by Mehs and Madan¹² for the preparation of other lanthanide complexes of bipyO_2 . Both compounds were obtained as a white microcrystalline powder.
- Anal. Calcd. for $[\text{Eu}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4)_4](\text{ClO}_4)_3$: C, 39.94; H, 2.68; N, 9.26; ClO_4^- , 24.81. Found: C, 39.96; H, 2.95; N, 9.43; ClO_4^- , 24.36. Calcd. for $[\text{Tb}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4)_4](\text{ClO}_4)_3$: C, 39.71, H, 2.67; N, 9.26; ClO_4^- , 24.67. Found: C, 39.13; H, 2.58; N, 9.97; ClO_4^- , 24.28.
- d. **Physical Measurements:** Infrared and visible spectra, as well as conductance measurements, were performed as described in Section B. The fluorescence spectra were measured in nitromethane solution at 300°K, using a Beckman DU2 spectrophotometer with a spectral fluorescence attachment. No corrections were made for variations in the detector response at different wavelengths, and the fluorescence intensity values were obtained directly from the instrument.

3. Results and Discussion

The infrared spectra of both the europium and terbium complexes in Nujol were found to be very similar to the spectra of the other lanthanide perchlorate complexes of bipyO₂ reported by Mehs and Madan.¹² The ν NO band for the coordinated bipyO₂ appeared as a triplet at 1258, 1237, and 1211 cm⁻¹ for both complexes, as compared with values of 1264 and 1256 cm⁻¹ for the free ligand.⁴⁵ The δ NO band appeared at 830 cm⁻¹ for the europium complex and at 832 cm⁻¹ for the terbium complex, as compared with the value of 841 cm⁻¹ for bipyO₂.⁴⁵ The decrease in frequency of both the ν NO and δ NO bands upon coordination, has been interpreted by Mehs and Madan to indicate oxygen coordination of the ligand to the lanthanide ion. Further substantiation for oxygen coordination was the observance of a new band in the spectra of the complexes at 343 cm⁻¹ for the europium compound and at 346 cm⁻¹ for the terbium complex. These bands are attributed to the metal-oxygen stretching vibration. In both spectra, the perchlorate bands appeared as a broad single ν_3 band in the 1100 cm⁻¹ region, a very weak forbidden ν_1 band at 929 cm⁻¹, and a medium intensity ν_4 band at 622 cm⁻¹, all characteristic of the ionic perchlorate group with T_d symmetry.²⁶

In nitromethane solution, the conductance behavior of both the europium and terbium complexes was identical to that of the other lanthanide complexes of bipyO₂,¹² and demonstrated that the complexes were typical 1:3 electrolytes. The complexes did not appear to be soluble in other organic solvents such as alcohol or acetonitrile.

The nitromethane solutions of both complexes did not absorb throughout the visible region except for a very weak band in the case of the europium complex at 465 mμ. The band had a molar absorptivity of $0.68 \text{ M}^{-1} \text{ cm}^{-1}$ and is due to the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition in the europium ion.

The fluorescence of the solid europium complex is a very intense red-orange color, characteristic of the trivalent europium ion, while the terbium complex fluoresces a somewhat less intense yellow-green color. Both of the compounds were found to retain their fluorescence in nitromethane solution. The fluorescence spectrum of the europium complex at 300°K in nitromethane is shown in Fig. 5.

The spectrum shows a very broad band with a maximum fluorescent intensity at 612.5 mμ. Previous work has determined that the fluorescence in the region between 560 mμ and 660 mμ in many europium compounds is due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ transitions in the europium ion. The maximum fluorescence at 612.5 mμ is assigned to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. The transition from the ${}^5\text{D}_0$ excited state to the ${}^7\text{F}_0$ state has the highest energy, since the ${}^7\text{F}_0$ state is the ground state for the tripositive europium ion which has six unpaired f electrons. The fluorescence intensity in the 600-610 mμ region is rather high relative to the maximum, and may be due to transitions from the ${}^5\text{D}_1$ state.

The fluorescence spectrum of the terbium complex in nitromethane is reproduced in Fig. 6. The spectrum shows a weak doublet at 480 mμ, and a more intense single band at 544 mμ. On the basis of previous

Fig. 5. Fluorescence Spectrum of $1.09 \times 10^{-3}M$
 $[Eu(bipyO_2)_4](ClO_4)_3$ in Nitromethane at $300^\circ K$

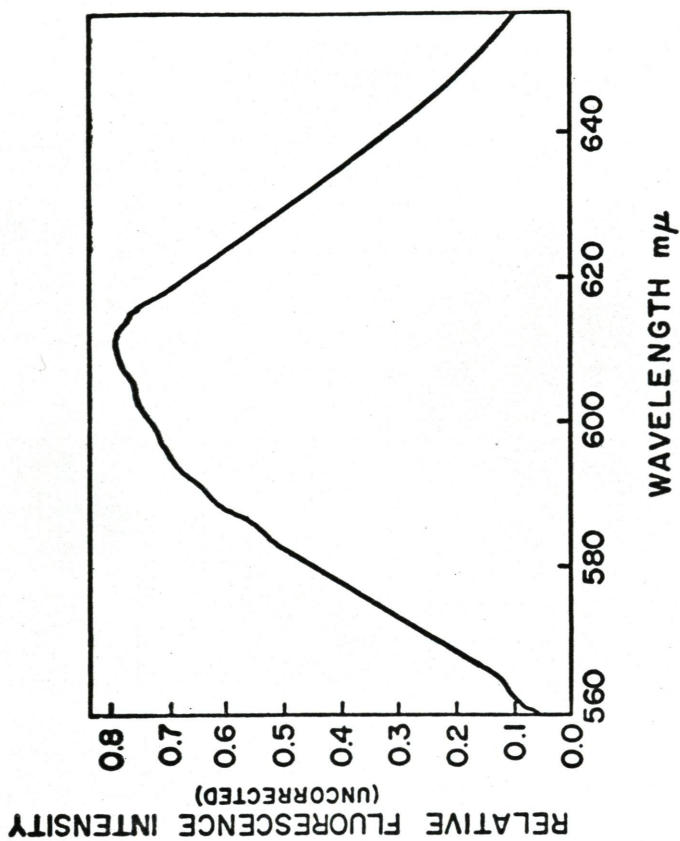


FIG. 5

Fig. 6. Fluorescence Spectrum of 1.08×10^{-2}
M $[\text{Tb}(\text{bipyO}_2)_4](\text{ClO}_4)_3$ in Nitromethane at 300°K

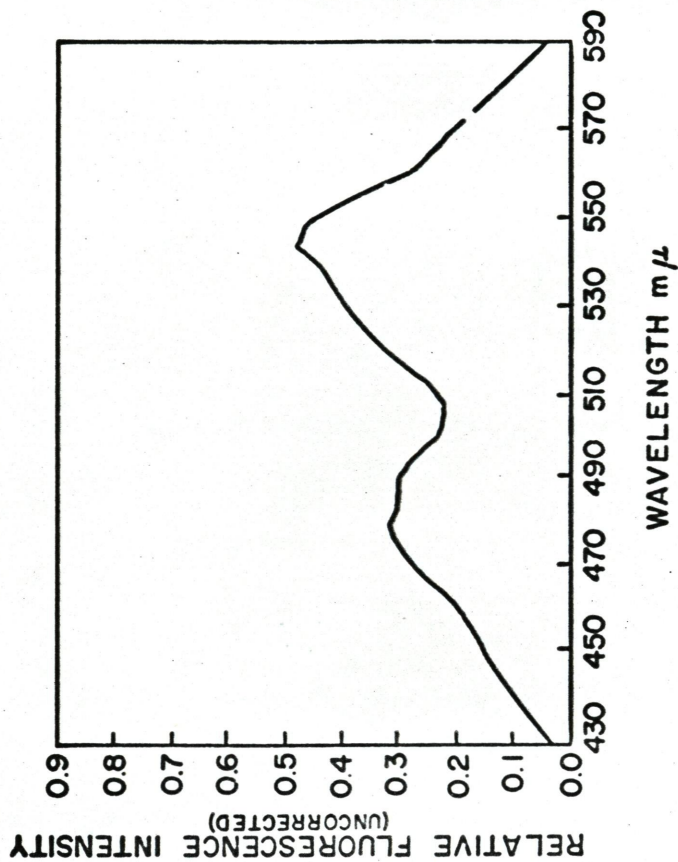


FIG. 6

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work, the doublet is assigned to the $^5D_4 \rightarrow ^7F_6$ transition, and the singlet is assigned to the $^5D_4 \rightarrow ^7F_5$ transition. The 7F_6 state is the ground state for the tripositive terbium ion which has six unpaired and two paired f electrons.

4. Summary and Conclusion

The eight coordinated chelates of both europium and terbium with bipyO_2 were found to fluoresce in solution. Since the ligand is a bidentate, solvolyses of the complex is minimal even in dilute solution, and hence efficient intramolecular energy transfer from the ligand to the metal can occur. As seen in Figures 5 and 6, the fluorescence spectra are very broad and are poorly resolved. This behavior is quite different from that usually observed in the spectra of the solid compounds at low temperature. The broadening of the spectra under the conditions used in this study is most likely due to vibrational fine structure which can only be eliminated by reducing the temperature.

E. Direction of Future Research

Because the lanthanide elements have found commercial use in the field of heterogeneous catalysis and in the manufacture of phosphors and lasers, a considerable need for some of these elements has developed in recent years. Since they occur together in nature and are chemically very similar, separation of these elements is much more difficult than in the case of the transition metals. At present, the most effective large scale separation method for these elements is the use of ion-exchange in aqueous media. The method is based upon the slight difference in the size of the solvated ion due to the change in charge to radius ratio of the elements. In proceeding from lanthanum to lutetium, it has been found by various investigators,^{47,48} that the coordination number of the metal ion decreases from nine to eight in aqueous solution as the ionic radius of the lanthanide ion decreases. On the other hand, the second hydration sphere around the lanthanide ion is larger for the smaller lanthanides because of the higher charge to radius ratio of the metal ion. The effect of the larger solvation shell is to decrease the tendency of the hydrated ion to go into the resin phase, and hence the heavier lanthanide ions are eluted first. While the slight difference in the size of the hydration spheres of neighboring elements does allow them to be separated by ion-exchange techniques, there is still a considerable overlap in the elution curves of these elements in aqueous media.

With this information in mind, it seems highly possible that by using some of the information presented in Part I of this thesis, the present ion-exchange techniques for the separation of the lanthanides could be improved through the use of non-aqueous solvents. Since many common industrial solvents such as DMSO or DMA have been found to complex with the lanthanide ions, and since more drastic changes in coordination number are observed in many cases, it seems as though these solvents would be useful in ion-exchange separations of these elements. As an example, while the coordination number changes from nine to eight in aqueous media, a gradual change from eight to six is observed for the DMA complexes of the lanthanides.²⁰ Furthermore, since the second solvation shell should be greatly reduced in non-aqueous media, the effect of the coordination number on the size of the solvated ion should be greatly enhanced. Therefore, by using either DMA or DMA-water mixtures, it may be possible to obtain a much better separation of the elution curves for these elements. By using the hypersensitive transition bands in the visible spectra of the neodymium and erbium species, any changes in the coordination number with a change in the composition of a mixed solvent can be observed.^{30,48} In this manner the change in coordination number in going from one end of the series to the other could be maximized.

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PART II

Kinetics of the Acid Hydrolysis of Some Distorted

Octahedral Cobalt(III) Complexes

A. Introduction

In an attempt to explain more clearly the nature of the metal-ligand bond in coordination compounds, many kinetic studies have been reported in which one ligand in a coordination complex is replaced by another. In particular, the substitution reactions of octahedral Cr(III) and Co(III) complexes have been investigated extensively, since reactions of these relatively inert species are easily studied by classical methods. The nucleophilic substitution reactions which occur in these complexes can best be described as involving either a unimolecular or a bimolecular displacement to form a five-coordinate or a seven-coordinate transition state, respectively.

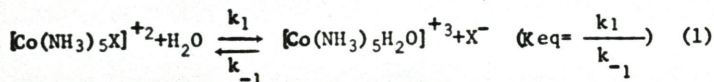
In a pure S_N1 mechanism, the transition state is formed by breaking the metal-ligand bond to form a five-coordinate intermediate species. This type of mechanism requires at least a partial separation of oppositely charged species in the transition state. Hence, the factors which favor an S_N1 reaction mechanism are a low charge to radius ratio on both the metal ion and the leaving group, and increased size of neighboring ligands. In the case of an S_N2 mechanism, the formation of an additional metal-ligand bond to form a seven-coordinate activated complex is the rate determining step. Since bond making, rather than bond breaking, is most important in this type of mechanism, factors which tend to produce an S_N2 reaction

are a high charge to radius ratio on the metal ion and the entering group, and a decrease in the size of neighboring ligands.

In most of the kinetic studies which have been reported for octahedral Co(III) and Cr(III) complexes, the intermediates are not observed, and the kinetic data can often be explained on the basis of either an S_N1 or an S_N2 mechanism. As a result, ascertaining the exact mechanism is often difficult, and it is probably much more correct to assume that most of the nucleophilic substitution reactions which occur in these complexes are neither of pure S_N1 nor S_N2 character, but are in fact intermediate between the two.

A study of the acid hydrolysis reactions of several bis(ethylenediamine)cobalt(III) complexes of the type $[\text{Co}(\text{en})_2\text{LCl}]^+$ and $[\text{Co}(\text{en})_2\text{LCl}]^{+2}$ showed that there is indeed a considerable variation in the relative degree of S_N1 or S_N2 character in the reaction, depending upon the nature of the L group cis or trans to the chloride leaving group. It was found that as the electron-donating properties of donor L groups decrease, so does the reaction rate constant for the replacement of the chloride group by water. This observation is consistent with an S_N1 mechanism, since electron donation from the L group would tend to lower the positive charge on the cobalt ion and facilitate charge separation in the transition state. It was also observed, however, that as acceptor L groups become increasingly electron-withdrawing, the rate constant increases substantially. This type of behavior is characteristic of an S_N2 mechanism because the charge on the cobalt atom would be increased and would enable an entering group to be more strongly attracted by the metal ion.

It was noted that the reactions which demonstrated the most S_N1 character were those of strong electron donor L groups such as NH_2^- or OH^- , while strong electron acceptors like NO_2^- and CN^- give rise to reactions with the most S_N2 character. With L groups such as H_2O , Cl^- , and NH_3 , reactions of mixed character were observed. In another study,² the acid hydrolysis of several dichlorotetramine cobalt(III) complexes were investigated in order to determine the effect of the size of the amine groups in the rate of the hydrolysis reaction. It was found that as the degree of substitution on the amine groups increased, the rate of the hydrolysis increased drastically. These results seem to indicate that in complexes of this type, bond breaking is more important than bond making in the transition state, inasmuch as these results are inconsistent with an S_N2 mechanism. Similar conclusions were obtained from the hydrolysis behavior of several pentammine cobalt(III) complexes.³ It was found that for reactions of the type



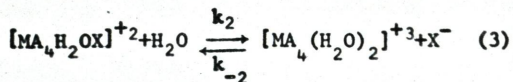
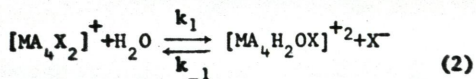
the rate of hydrolysis of the complex decreases as the equilibrium constant for equation 1 decreases. These results are also consistent with an S_N1 mechanism.

Regardless of the type of mechanism, it has been found that the rates of hydrolysis of most Co(III) and Cr(III) amine complexes decrease as the degree of chelation by the amine ligand increases.⁴

In a study of the acid hydrolysis reactions of a series of trans-dichlorotetraminecobalt(III) complexes, it was shown that

when two NH_3 groups are replaced by a bidentate ethylenediamine group, the hydrolysis rate decreases by a factor of eight. Replacement of the remaining two NH_3 groups by a second ethylenediamine molecule again results in an eightfold decrease in the hydrolysis rate. Similar decreases were observed in the hydrolysis rates of the cis complexes when NH_3 is replaced by ethylenediamine, and then by the tetradentate amine, triethylenetetramine (trien). This effect is termed the chelate effect, and cannot be explained by differences in the basicity of the amine groups. It is believed that the lower hydrolysis rates which are observed for the highly chelated complexes are due to a lesser degree of solvent stabilization of the transition state because of a lower charge to radius ratio in the larger chelated complexes.

A survey of the literature makes it readily apparent that the majority of the kinetic data available in the area of octahedral substitution reactions is for reactions of dihalotetramine complexes of both Co(III) and Cr(III) . In particular, the acid hydrolysis and related isomerization reactions of these complexes have been studied extensively and have all been found to react in two separate steps as shown in equations 2 and 3.



($\text{M}=\text{Cr(III)}, \text{Co(III)}$; $\text{A}=\text{monodentate or chelate amine}$; $\text{X}=\text{F}^-, \text{Cl}^-, \text{Br}^-$)

While the primary acid hydrolysis step has been studied for many complexes of both Co(III) and Cr(III), the subsequent step has been well characterized only for the Cr(III) system. Since this thesis deals with the secondary acid hydrolysis step of two dihalo triaminotriethylaminecobalt(III) complexes, a brief summary of the behavior to the other related systems of both Cr(III) and Co(III) is presented for comparison.

For Cr(III), the primary acid hydrolysis reaction of $\text{cis-}[\text{Cr}(\text{en})_2\text{F}_2]^+$ has been studied⁵ as well as that of both the^{6,8} corresponding cis- and trans-dichloro and dibromo complexes.⁹ The acid hydrolysis of the difluoro complex was found to proceed at a much faster rate in a highly acidic solution than in solutions of higher pH. The ability of the reaction to be acid-catalyzed was attributed to a rapid acid-base pre-equilibrium, which results in the formation of a faster reacting protonated complex. The complex was believed to react to form the cis-fluoroaquo species as the major product, although some evidence for the formation of a polymeric species was obtained. No attempt was made to measure the secondary acid hydrolysis rate constant for the reaction of the fluoroaquo species, however.

The primary acid hydrolysis reactions of cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ ^{6,7} ion were found to be considerably more complicated^{6,8} than that of the difluoro system. The acid hydrolysis of the trans complex involves isomerization to the cis isomer, as well as hydrolysis to produce a mixture of cis- and trans-chloroaquo species. In addition,

a small percentage of trans-[Cr(en)(H₂O)₂Cl₂]⁺ and an unknown diaquo species were also observed. The reaction of the cis-dichloro complex was found to be equally as complicated. The observed isomerization reactions were attributed to the formation of a five-coordinate intermediate in an S_N1 mechanism, which could then rearrange to form either a cis or trans product.

The kinetics of the acid hydrolysis of both the cis and trans chloroaquo species were reported by MacDonald and Garner in another study.¹⁰ The cis isomer appears to react in a straightforward manner to give the cis diaquo species as the only product. The diaquo complex then hydrolyzes further, with the loss of one ethylenediamine molecule, to form the tetraaquo species. In the case of the trans isomer,¹⁰ however, isomerization as well as hydrolysis occurs. No systematic effort was made in this study to determine the effects of ionic strength or acid concentration on the reaction rates.

Both the primary and secondary acid hydrolysis reactions of the bromo analogs have also been studied.¹¹ It was discovered that the cis-dibromo complex reacts with water to form the cis-bromoaquo species, exclusively, and that the reaction rate is independent of acid concentration at low pH values. The cis-bromoaquo species was found to react at a much slower rate to form the cis-diaquo complex as the major product, although a small amount of the trans isomer is also formed. The rate of hydrolysis was found to be acid independent in the range of 0.06 and 0.14M hydrogen ion concentration. The trans-dibromo salt was observed to react in a manner similar to that

of the cis compound to produce the trans-bromoquo species as the major product. The bromoquo species, however, was found to isomerize as well as hydrolyze to produce a mixture of cis and trans diaquo species, as well as a tetraquo complex.

In summary, the primary acid hydrolysis rate for all of the dihalo tetramine chromium(III) complexes is known to be considerably faster than the rate for the corresponding secondary acid hydrolysis reaction of the haloquo complex. Furthermore, the reaction rate in a series of similar complexes decreases in the order $\text{Br} > \text{Cl} > \text{F}$. Both of these observations are consistent with a mechanism which has a considerable amount of $\text{S}_{\text{N}}1$ character, since the fastest rate in an $\text{S}_{\text{N}}1$ mechanism should occur in the complex with the lowest charge to radius ratios on both the metal ion and the leaving group.

Although many similarities are observed between the kinetics of the acid hydrolysis reactions of Cr(III) and Co(III) complexes, some differences between the two systems are also apparent. Basolo,¹² Matoush, and Pearson reported a kinetic study of the acid hydrolysis of trans- $[\text{Co}(\text{en})_2\text{F}_2]^+$ ion and found the reaction to be acid-catalyzed,⁵ just as in the case of the cis- $[\text{Cr}(\text{en})_2\text{F}_2]^+$ ion. The final product of the hydrolysis was found to be the fluoroquo species, which in turn isomerized to a cis - trans mixture. No attempt was made to determine the secondary acid hydrolysis rate, however. The acid hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{F}]^{+2}$ ¹³ was also found to be acid-catalyzed.

In the case of the dichlorotetraamine complexes of Co(III), an extensive amount of kinetic data is available for their primary acid

hydrolysis reactions. Kinetic investigations of dichloro complexes⁴ with ammonia,⁴ ethylenediamine² and other related bidentate amines,^{4,14} and trien, all indicate that the chloroaquo species is the major product. Furthermore, in general, it appears that the cis complexes react stereospecifically while those of the trans configuration isomerize to form mixtures of the cis and trans chloroaquo product. In acidic solution the primary acid hydrolysis reaction rates appear to be little affected by either pH or ionic strength changes.

The chloroaquo species of Co(III) have been considerably less characterized than the dichloro complexes. The acid hydrolysis of cis-[Co(NH₃)₄H₂OCl]²⁺ has been reported.¹⁵ and the rate was found to be much slower than that for the hydrolysis of the corresponding dichlorotetraammine complex. The only other acid hydrolysis study of a Co(III) chloroaquo complex is that of Chan in 1963.¹⁶ In this study it was found that the rate of isomerization of the chloroaquo species is much faster than the rate of hydrolysis, so that the rate of hydrolysis which is observed is a sum of the reaction rates for both isomers. It was also found that the reaction was acid-inhibited, an effect which is attributed to an acid-base equilibrium between the chloroaquo species, and the more labile chloro hydroxo species. However, no activation parameters or ionic strength effects were reported.

In the corresponding bromo series, the kinetic data is very sparse.¹⁷ The primary acid hydrolysis reactions of cis and trans - [Co(en)₂Br₂]⁺ ion have been studied and their behavior is similar^{12,18}

to that of the corresponding chloro analogs. It was found that the rates of hydrolysis of the bromo complexes are faster than those of the corresponding chloro complexes, just as in the case of the Cr(III) system. It was also noted that the rates are not dependent upon the pH or the ionic strength of the solution, and the bromoaquo species are the only product.

No kinetic data are available for the acid hydrolysis of any Co(III) bromoaquo species. However, a study was reported which dealt with the rate of isomerization of cis and trans-[Co(en)₂H₂OBr]⁺²₁₈ to an equilibrium mixture. It was found that the isomerization of the bromoaquo species could be measured without any interference from the much slower acid hydrolysis reaction, and that the equilibrium ratio of cis and trans isomers was not temperature-dependent.

In summary, it can be said that the kinetics of the acid hydrolysis of most Co(III) complexes are quite similar to those of the Cr(III) systems. In both cases, the hydrolysis rates for a given amine complex always increase in the order F < Cl < Br, the reactions of the cis complexes are generally more stereospecific than those of the trans complexes, and the chelate effect is observed. The observation that the Co(III) complexes always react at a slower rate than their Cr(III) analogs is generally believed to be due to a greater loss in crystal field stabilization energy in forming the transition state for a d⁶ Co(III) complex than for one of Cr(III) with a d³ electronic configuration.

While the kinetic behavior of most Co(III) amine complexes can be explained in terms of the theories described above, occasionally an unusual complex is found whose kinetic behavior does not follow the trends which can be expected. The octahedral Co(III) complexes of β, β', β'' -triaminotriethylamine (tren) are a good example. While the chelate effect is observed in the kinetics of most Co(III) amine complexes, the acid hydrolysis rates of cis-[Co(tren)Cl₂]⁺ and cis-[Co(tren)Br₂]⁺ do not fit the observed trend in rate constants. Since tren is a branched isomer of trien it is therefore a tetradentate ligand, and its complexes would normally be expected to show acid hydrolysis rates similar to those of trien. However, the primary acid hydrolysis rate constant for [Co(tren)Cl₂]⁺ was found to be nearly twenty times faster than that of cis-[Co(trien)Cl₂]⁺ and nearly 12 times faster than that of cis-[Co(en)₂Cl₂]⁺ under similar conditions at 25.0°C.¹⁹ The corresponding dibromo complex [Co(tren)Br₂]⁺ was found to react even faster, and has an acid hydrolysis rate 27 times faster than that of cis-[Co(en)₂Br₂]⁺.²⁰

The increased rate of hydrolysis of the tren species is attributed to the peculiar geometry of the complex invoked by the tren ligand. Since tren has a branched structure rather than a linear one, the alkyl groups are not long enough to enable a primary nitrogen to be trans to the tertiary nitrogen atom in an octahedral complex. As a result, only the cis isomer can be formed. Furthermore, it has been shown in an x-ray structure determination of cis-dithiocyanato(triaminotriethylamine)nickel(II)²¹ that the complex is a distorted octahedron, with the primary nitrogens above and below the plane being pulled back towards the tertiary

nitrogen. Since it is not unreasonable that a similar structure is present in the Co(III) tren species, this type of distortion would tend to expose the two cis halide groups more fully to solvent attack. The increased exposure of the halide groups to the solvent should tend to increase the rates of acid hydrolysis of the tren complexes relative to those with no distortion.

Since only the primary acid hydrolysis reactions of $[\text{Co}(\text{tren})\text{Cl}_2]^+$ ¹⁹ and $[\text{Co}(\text{tren})\text{Br}_2]^+$ ²⁰ have been reported, it seems as though the value of measuring the secondary acid hydrolysis reaction kinetics for these complexes would be twofold. First, since no cis-trans isomerization reactions are possible, the tren haloaquo species are model systems for studying the effects of acid concentration, ionic strength, and temperature on acid hydrolysis reactions of complexes of this type. Secondly, although it is known that the distortion accelerates the primary acid hydrolysis rates of the tren complexes, it is not known whether it has the same effect on the second halide group. With these facts in mind, the kinetics of the acid hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$ and $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$ have been measured under various conditions, and the results are presented in the following pages.

**B. Kinetics of the Acid Hydrolysis of
Bromoquo(triaminotriethylamine)cobalt(III) Ion**

1. Experimental Section

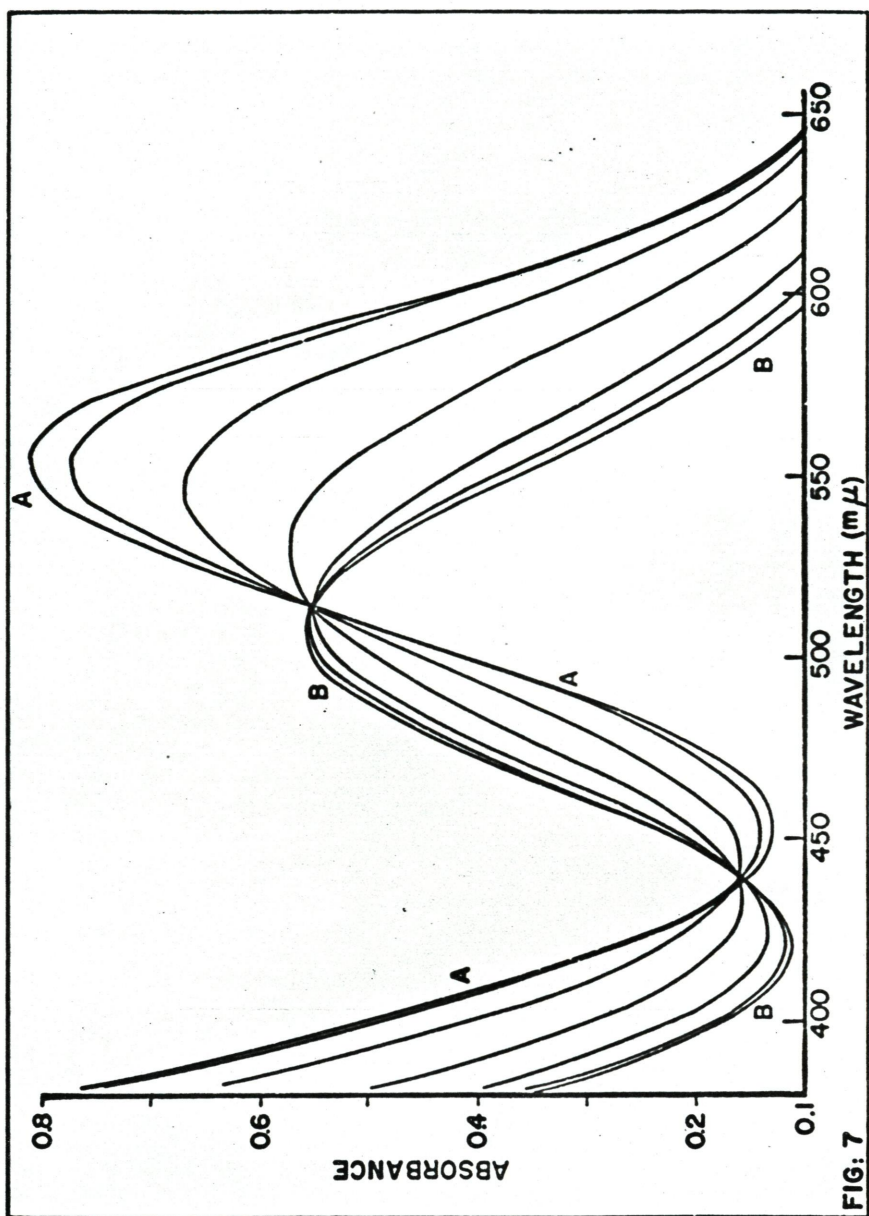
a. Synthesis of Compounds

- i. Dibromo(triaminotriethylamine)cobalt(III)bromide:** This compound was prepared as described by Madan and Peone.²⁰
- ii. Carbonato(triaminotriethylamine)cobalt(III) perchlorate²² monohydrate:** The method of Scheidegger was used to prepare this salt.
- iii. Bromoquo(triaminotriethylamine)cobalt(III) bromide perchlorate:** Addition of 5 ml of 48% HBr to a solution of 1 g of $[\text{Co}(\text{tren})\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$ in 5 ml of H_2O immediately gave a deep purple solution. After slight warming to expel the resulting CO_2 gas, the addition of anhydrous NaClO_4 gave a bright purple precipitate when cooled to 0°C . The precipitate was filtered, washed with ethanol, and dried in vacuo. The yield was 79%. Anal. Calcd. for $[\text{Co}(\text{C}_4\text{H}_{18}\text{N}_4)\text{H}_2\text{OBr}]\text{ClO}_4\text{Br}$: C, 14.94; H, 4.15; N, 11.62; ClO_4^- , 20.65. Found C, 15.14; H, 4.22; N, 11.79, ClO_4^- , 21.80. Recrystallization from a NaClO_4 solution replaced only a small amount of the bromide anion by perchlorate.

- b. **Electronic Absorption Spectra:** The visible spectra of all species were obtained with a Cary Model 14M recording spectrophotometer. The spectra were obtained with 5 millimolar solutions in aqueous perchloric acid using matched cells of 1 cm path length.
- c. **Kinetic Measurements:** The bromoaquo species used in this study was prepared by dissolving $[\text{Co}(\text{tren})\text{Br}_2]\text{Br}$ in water, and allowing it to undergo the primary acid hydrolysis step at room temperature (10 min.). Since the second acid hydrolysis step is much slower than the first, no interference from the first step was present in measuring the acid hydrolysis rate of the bromoaquo species. Because of the slow reaction rate at 25.0°C , most of the kinetic data which are presented in this thesis were obtained at 65.0°C .

A scan of the visible spectrum of the solution at the end of the first hydrolysis step showed that under the conditions used, the species obtained was $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$ whose spectrum was reported earlier.²⁰ A series of scans of the spectrum during the second acid hydrolysis step at 55.0°C , and pH zero is shown in Figure 7. The scans showed two sharp isosbestic points at 438 and 513 m μ , which did not change during the course of the reaction. The final spectrum was identical to that of the diaquo species.²⁰ The isosbestic points occur at the two wavelengths where the molar absorptivities of the bromoaquo and diaquo species are identical. Since the two points are constant

Fig. 7. Spectral Changes During the Acid Hydrolysis
of Bromoaquo(triaminotriethylamine)cobalt(III) Ion In
1 M HClO₄ at 55.0 C
(A) initial trace, [Co(tren)H₂OBr]⁺², 5.28 x 10⁻³M
(B) final trace, [Co(tren)(H₂O)₂]⁺³



throughout the course of the reaction, it appears as though the total concentration of the two species is constant, and no other product is formed to any great extent. The fact that the spectrum of the final solution was identical to that of the diaquo species indicates that no appreciable amount of the bromoaquo ion is present at the end of the reaction. A series of scans at pH 2.3 gave identical results to the scan at pH zero. The wavelength chosen for this kinetic study was 560 m μ , where the molar absorptivity of the bromoaquo species is 153 M⁻¹ cm⁻¹ and that of the diaquo species is only 65 M⁻¹ cm⁻¹. All kinetic measurements were obtained by using a Cary Model 16 spectrophotometer with matched cells of 1 cm path length and approximately 1 mM solutions.

Since the dibromo salt does not dissolve very rapidly in perchloric acid media, the salt was first dissolved in water, and the desired amount of perchloric acid was added afterwards. Each run was allowed to undergo the first acid hydrolysis step and was then placed in a constant temperature bath which was controlled to $\pm 0.05^\circ\text{C}$. The time required to bring the solution to the temperature of the bath was always less than five minutes, and accounted for only a small percentage of the overall reaction time. The data were obtained by withdrawing samples from the bath with a pipet and rapidly cooling the solution to room temperature in a matched cell in order to quench the reaction.

Since water, one of the reactants, is always present in large excess, the kinetics of the acid hydrolysis of the bromoaquo

species are those of a typical pseudo-first-order reaction. Because the reaction goes to completion, the rate equation is that of a standard first-order reaction and is

$$kt = \ln \frac{a}{a-x} \quad (4)$$

where a is the initial concentration in moles per liter, x is the amount which has reacted at time t , and k is the first-order rate constant. In view of the fact that the absorbance of the ions in solution is proportional to their concentration, the rate equation can be expressed in terms of the absorbance of the solution. The initial concentration, a , is proportional to the value of $A_0 - A_\infty$ where A_∞ is the absorbance at the end of the reaction, and A_0 is the absorbance initially. Furthermore, x , the amount which has reacted, can be expressed in terms of $A_0 - A_t$, where A_t is the absorbance at time t . In accordance with this information, absorbance can be substituted for concentration in equation 4 and the rate expression becomes

$$kt = \ln \frac{A_0 - A_\infty}{A_t - A_\infty} \quad (5)$$

Therefore, a plot of $\ln \frac{A_0 - A_\infty}{A_t - A_\infty}$ or $\ln(A_t - A_\infty)$ vs. t gives a straight line with a slope equal to k . Plots of $\ln(A_t - A_\infty)$ vs. t for all of the kinetic data in this study give good straight lines for at least three half lives and were refined by a least squares computer program. Consecutive runs usually agreed to within 2%, and always agreed to within 4%. The standard deviation of each line was usually less than 1%. A typical plot of $\ln(A_t - A_\infty)$ vs. t is illustrated in Figure 8, and the data for the plot are summarized in Table XII.

Fig. 8. Plot of $\ln(A_t - A_\infty)$ vs. t for the Acid Hydrolysis of
Bromoaquo(triaminotriethylamine)cobalt(III) Ion at 65°C , In 1M HClO_4

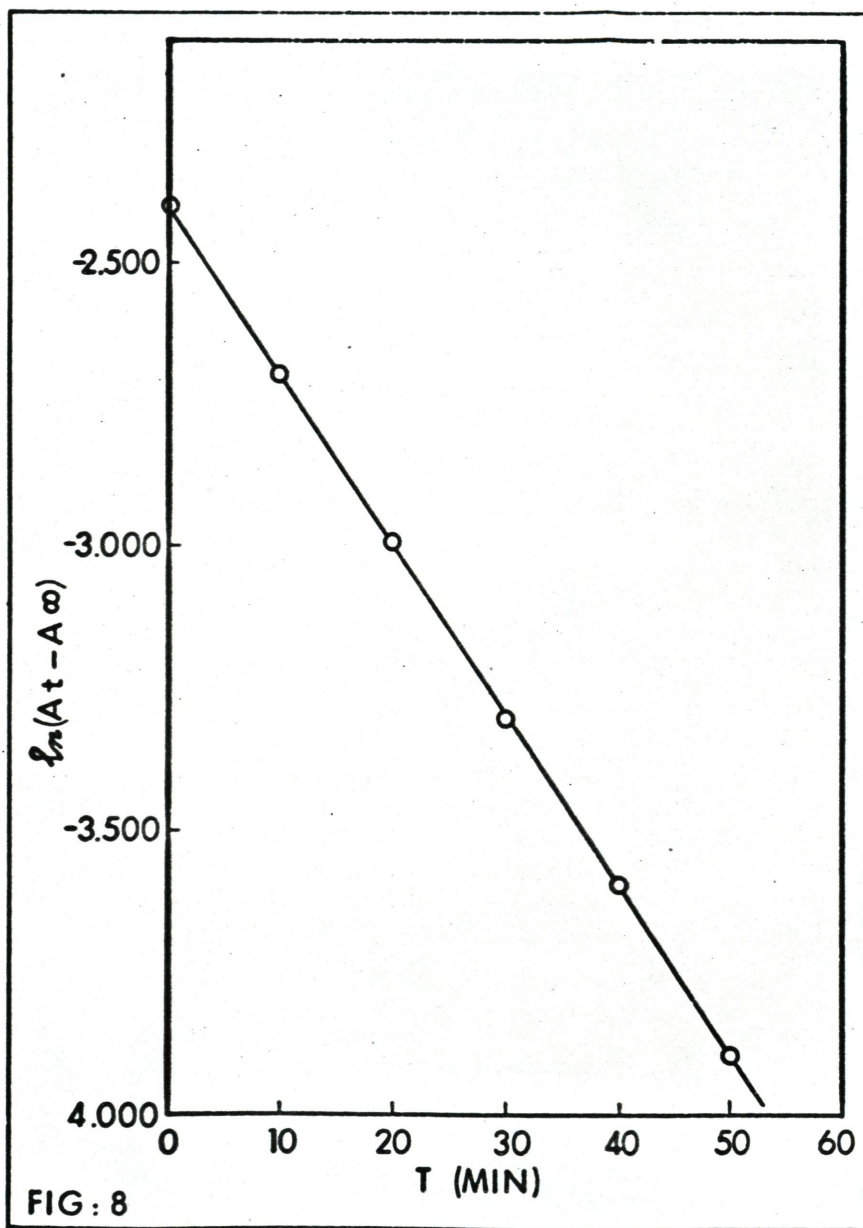


Table XII

Typical Experimental Data for the Acid Hydrolysis of
 Bromoaquo(triaminotriethylamine)cobalt(III) Ion at 65°C,
 in 1M HClO₄ at 560 mμ.

<u>time (min.)</u>	<u>A</u>	<u>A_t - A_∞</u>	<u>ln (A_t - A_∞)</u>
0	.1750	.0908	- 2.399
10	.1515	.0673	- 2.699
20	.1344	.0502	- 2.992
30	.1208	.0366	- 3.308
40	.1117	.0275	- 3.594
50	.1045	.0203	- 3.897
∞	.0842	.0000	---

2. Results and Discussion

In order to substantiate the fact that no side reactions were present in the secondary acid hydrolysis reaction of $\text{Co}(\text{tren})\text{H}_2\text{OBr Br}_2$, the reaction rate was determined in 1M HClO_4 at 65.0°C at three different wavelengths. The values which were obtained for the rate constant, k_2 , at 560, 480, and $390\text{m}\mu$ are 5.04×10^{-4} , 5.06×10^{-4} , and $5.12 \times 10^{-4}\text{sec}^{-1}$ respectively. All three values are in good agreement with each other and with the average value of $4.93 \times 10^{-4}\text{sec}^{-1}$ obtained by measuring the acid hydrolysis rate of $\text{Co}(\text{tren})\text{H}_2\text{OBr ClO}_4\text{Br}$ under identical conditions of temperature, pH, and ionic strength.

The acid hydrolysis of the bromoaquo ion was studied in 1M HClO_4 under various conditions of temperature and ionic strength, and the values of k_2 which were obtained are summarized in Table XIII. The Arrhenius plot for the data in Table XIII between 25.0 and 65.0°C was obtained by plotting $\ln k_2$ vs. $1/T$. The plot gives a straight line with a standard deviation of 1.1% and is shown in Figure 9. From the slope of the line a value of $24.4\text{ kcal mole}^{-1}$ was obtained for the activation enthalpy, ΔH . The free energy of activation was calculated from the equation

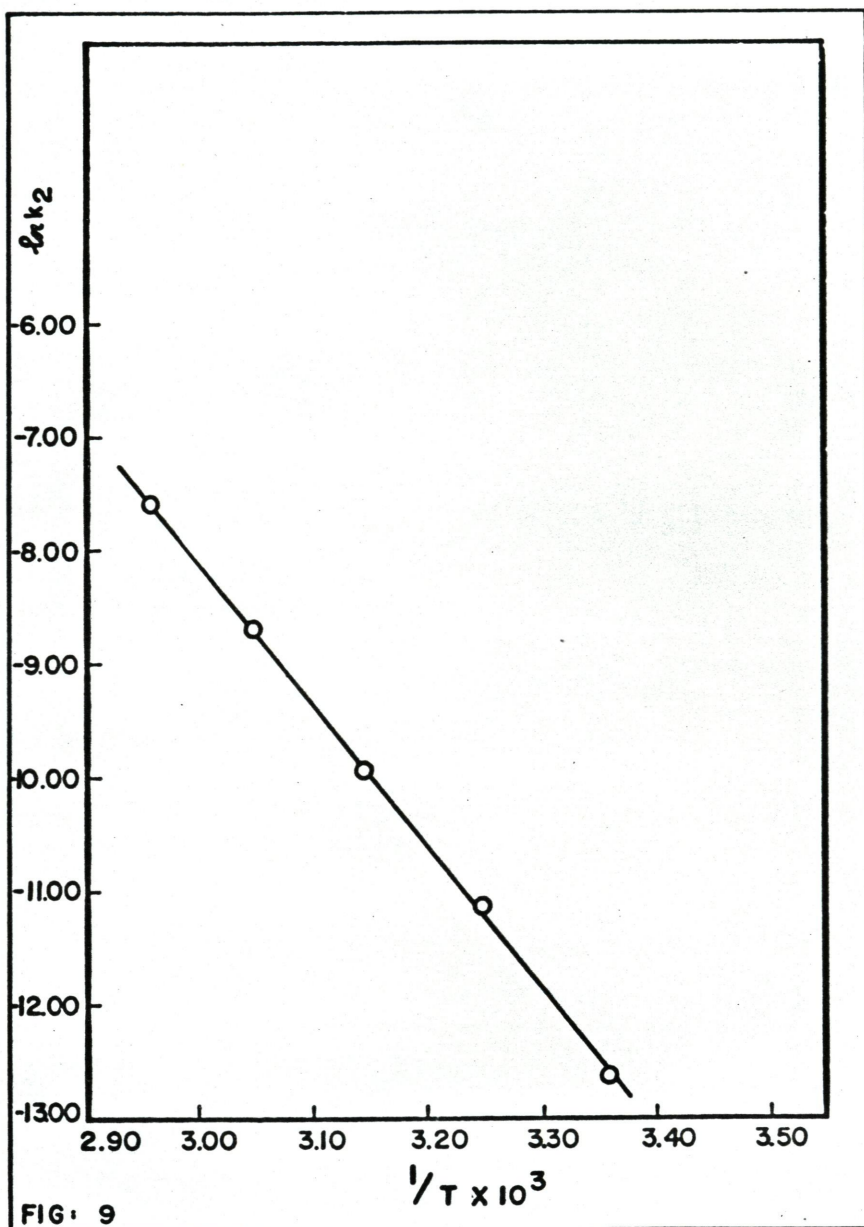
$$k_2 = \frac{RT}{Nh} e^{-\Delta G / RT} \quad (6)$$

where R is the gas constant, N is Avogadro's number, and h is Plank's constant. The value obtained for ΔG is $24.9\text{ kcal mole}^{-1}$

Table XIII. Rates of Acid Hydrolysis of
 Bromoaquo(triaminotriethylamine)cobalt(III)
 Ion Under Various Conditions in 1M HClO₄.

<u>Temp. (°C)</u>	<u>Added Electrolyte</u>	<u>Ionic Strength</u>	<u>k₂ (sec⁻¹)</u>
25.0	None	1.00	3.29x10 ⁻⁶
35.0	None	1.00	1.44x10 ⁻⁵
45.0	None	1.00	4.89x10 ⁻⁵
55.0	None	1.00	1.69x10 ⁻⁴
65.0	None	1.00	5.04x10 ⁻⁴
65.0	1.50 M NaClO ₄	2.50	5.03x10 ⁻⁴
65.0	1.00 M NaClO ₄	2.00	5.13x10 ⁻⁴
65.0	0.50 M NaClO ₄	1.50	5.04x10 ⁻⁴
65.0	0.050 M NaBr	1.05	5.05x10 ⁻⁴
65.0	0.10 M Na ₂ SO ₄	1.30	7.11x10 ⁻⁴
65.0	0.050 M Na ₂ SO ₄	1.15	6.11x10 ⁻⁴

Fig. 9. Arrhenius Plot for the Acid Hydrolysis
of Bromoaquo(triaminotriethylamine)cobalt(III) Ion
in 1M HClO₄ between 25.0 and 65.0°C



and the value of ΔS^\ddagger was calculated to be $-1.7 \text{ cal mole}^{-1} \text{ deg}^{-1}$.

The activation enthalpy for the acid hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$ is considerably higher than that reported for the primary acid hydrolysis reaction of $[\text{Co}(\text{tren})\text{Br}_2]^+$ ($15.1 \text{ kcal mole}^{-1}$).²⁰ The increased activation enthalpy is most likely a result of the higher charge of the bromoaquo species, which makes charge separation in the transition state more difficult. The value of ΔH^\ddagger for the hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$ is, however, nearly identical to that of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{+2}$ ($24 \text{ kcal mole}^{-1}$), which is also a dipositive ion.²³ A comparison of ΔS^\ddagger for the primary and secondary acid hydrolyses of $[\text{Co}(\text{tren})\text{Br}_2]^+$ shows that the value for the bromoaquo ion ($-1.7 \text{ cal mole}^{-1} \text{ deg}^{-1}$) is considerably less negative than that for the dibromo species ($-14.8 \text{ cal mole}^{-1} \text{ deg}^{-1}$).²⁰ Since an S_N2 mechanism involves the formation of a single activated complex from two species in solution, the system becomes more ordered and a negative entropy of activation is expected. In the case of a S_N1 mechanism, the degree of disorder increases, and hence, a large positive entropy of activation is expected. On the basis of the activation parameters, it appears as though there is a definite decrease in S_N2 character in the acid hydrolysis mechanism for the bromoaquo species relative to that of the dibromo ion. This observation is somewhat unexpected since the higher charge on the former species would be more apt to facilitate an S_N2 mechanism and make bond breaking more difficult in the transition state. The change in ΔS^\ddagger in proceeding from the primary to the secondary acid hydrolysis step may be due to a subtle change in the geometry of the complex after the primary acid hydrolysis reaction, and will be discussed

in greater detail in a later part of this thesis.

The data in Table XIII also indicate that in highly acidic solution, the acid hydrolysis rate of $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$ is ionic strength-independent, when an "inert" electrolyte such as NaClO_4 is present. This behavior is similar to that of the primary acid hydrolysis of the dibromo species, and is expected for an acid hydrolysis reaction on the basis of the Debye-Huckel equation. If one assumes that the complex, A, reacts with water, B, to form an activated complex, AB, the thermodynamic equilibrium constant K can be expressed by the following equation involving activity coefficients

$$K^\dagger = \frac{[\text{AB}]}{[\text{A}][\text{B}]} \cdot \frac{\gamma_{\text{AB}}}{\gamma_{\text{A}} \cdot \gamma_{\text{B}}} \quad (7)$$

However, since the observed acid hydrolysis rate is only dependent upon the concentration of the activated complex, the rate equation becomes

$$\text{rate} = k[\text{AB}] = k K^\dagger [\text{A}][\text{B}] \frac{\gamma_{\text{A}} \cdot \gamma_{\text{B}}}{\gamma_{\text{AB}}} \quad (8)$$

According to the Debye-Huckel equation, at low ionic strengths

$$\log \frac{\gamma_{\text{A}} \cdot \gamma_{\text{B}}}{\gamma_{\text{AB}}} \approx -\frac{1}{2} \mu (Z_{\text{A}}^2 + Z_{\text{B}}^2 - Z_{\text{AB}}^2) \quad (9)$$

where Z is the charge of the species and μ is the ionic strength of the solution. Since Z_{AB} is the sum of $Z_{\text{A}} + Z_{\text{B}}$, equation 9 can be rearranged to give

$$\log \frac{\gamma_A \gamma_B}{\gamma_{AB}} = Z_A Z_B \sqrt{\mu} \quad (10)$$

Therefore, since the charge on water, one of the reactants, is zero, the right hand side of equation 10 becomes zero, and the activity coefficient ratio will be unity. It is then apparent that reactions of this type should not be ionic strength-dependent. At high ionic strengths, however, equation 9 may not always be applicable.

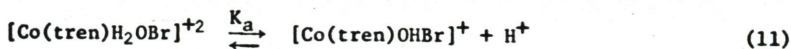
The addition of an excess of bromide ions also did not affect the rate. This observation further substantiates the spectral scans, which show that any equilibrium present between the bromoaquo and diaquo species lies far towards the latter. However, an excess of sulfate ions was found to cause an appreciable increase in the rate of hydrolysis, just as in the case of the dibromo species.²⁰ The acceleration is attributed to the formation of an ion pair between the complex and the sulfate ion, which effectively lowers the charge on the complex, and enables a dissociative mechanism to operate more easily. The acceleration of the acid hydrolysis rate for the bromoaquo species is more pronounced than for the dibromo complex in the presence of sulfate ions, presumably because the higher positive charge on the bromoaquo ion enables it to undergo ion pair formation more readily.

A study of the acid hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$ was also performed at higher pH values, and the kinetic data obtained at 65°C are presented in Table XIV. From the data it is clear that the hydrolysis of the bromoaquo complex is acid inhibited. Similar behavior has been observed in the acid hydrolysis reactions of cis- and trans- $[\text{Co}(\text{en})_2\text{H}_2\text{OCl}]^{+2}$,¹³ $[\text{Cr}(\text{en})\text{NH}_3(\text{H}_2\text{O})_2\text{Br}]^{+2}$,²⁴ $[\text{Cr}(\text{en})(\text{H}_2\text{O})_3\text{Br}]^{+2}$,²⁵ and $[\text{CrNH}_3(\text{H}_2\text{O})_4\text{Cl}]^{+2}$.²⁶

Table XIV. Rates of Acid Hydrolysis of
 Bromoaquo(triaminotriethylamine)cobalt(III)
 Ion between pH 1.0 and pH 3.0 with added
 NaClO_4 at 65.0°C .

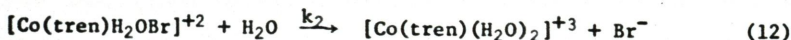
H^+ (mM)	Ionic Strength	$k_{\text{obsd}} \times 10^4 (\text{sec}^{-1})$
5.00	0.025	8.75
6.00	0.025	7.94
7.50	0.025	7.55
10.0	0.025	6.81
15.0	0.025	6.10
17.5	0.025	6.00
100.0	0.100	5.10
4.00	1.00	7.99
5.00	1.00	7.39
6.07	1.00	7.13
10.0	1.00	6.39
15.0	1.00	6.03
40.0	1.00	5.45

The acid inhibition in the kinetics of these aquo complexes has been attributed to the presence of an acid-base equilibrium between the haloaquo complex and the much faster reacting halohydroxo complex. For $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$ this equilibrium would lead to the following reaction scheme.



very fast

K_a very small



very fast

Since K_a is very small, and k_2' is much larger than k_2 , the amount of bromohydroxo species present does not affect the visible spectrum, but merely offers a faster pathway for the reaction to occur. The observed rate of hydrolysis of the bromoaquo species can then be expressed as a sum of the rates for the bromoaquo and the bromohydroxo species according to the equation

$$\text{Rate} = k_2[\text{bromoaquo complex}] + k_2'[\text{bromohydroxo complex}] \quad (15)$$

However, the concentration of the bromohydroxo species can be expressed as $K_a[\text{bromoaquo complex}]/[\text{H}^+]$, and therefore equation 15 becomes

$$\text{Rate} = (k_2 + k_2'K_a/[\text{H}^+])[\text{bromoaquo complex}] \quad (16)$$

and the observed rate constant, k_{obsd} , is then

$$k_{\text{obsd}} = k_2 + k_2'K_a/[H^+] \quad (17)$$

From equation 17 it is apparent that the observed rate constant should increase as the pH of the solution is raised. Furthermore, a plot of k_{obsd} vs. $1/[H^+]$ should give a straight line, with a slope equal to the product $k_2'K_a$ and an intercept equal to k_2 . A plot of this type was made for the data in Table XIV at ionic strengths 1.0 and 0.025, and the results are shown in Figures 10 and 11. The slope and intercept of the line in Figure 10 were used to obtain the rate constant expression at ionic strength 1.00

$$k_{\text{obsd}} = 5.2 \times 10^{-4} \text{ sec}^{-1} + 1.1 \times 10^{-6} \text{ sec}^{-1}/[H^+] \quad (18)$$

At ionic strength 0.025 the line in Figure 11 gives the expression

$$k_{\text{obsd}} = 4.9 \times 10^{-4} \text{ sec}^{-1} + 1.9 \times 10^{-6} \text{ sec}^{-1}/[H^+] \quad (19)$$

The values of k_2 obtained from equations 18 and 19 are very close to the experimental value of $5.04 \times 10^{-4} \text{ sec}^{-1}$ which was obtained in 1 M HClO_4 , and show that the value of k_2 is not ionic strength-dependent. However, it is clear from the second terms in equations 18 and 19 that the $k_2'K_a$ product does show a dependence upon the ionic strength of the solution. The decrease in the $k_2'K_a$ term with increasing ionic strength is most likely due to changes in the activity coefficients of the three species present. From equation 8, the concentration quotient, K_a , is

$$K_a = \frac{[\text{bromohydroxo complex}][H^+]}{[\text{bromoquo complex}]} \quad (20)$$

Fig. 10. Plot of k_{obsd} vs. $1/[\text{H}^+]$ for the Acid Hydrolysis of Bromoaquo(triaminotriethylamine)cobalt(III) Ion at 65.0°C , with $\mu=1.00$

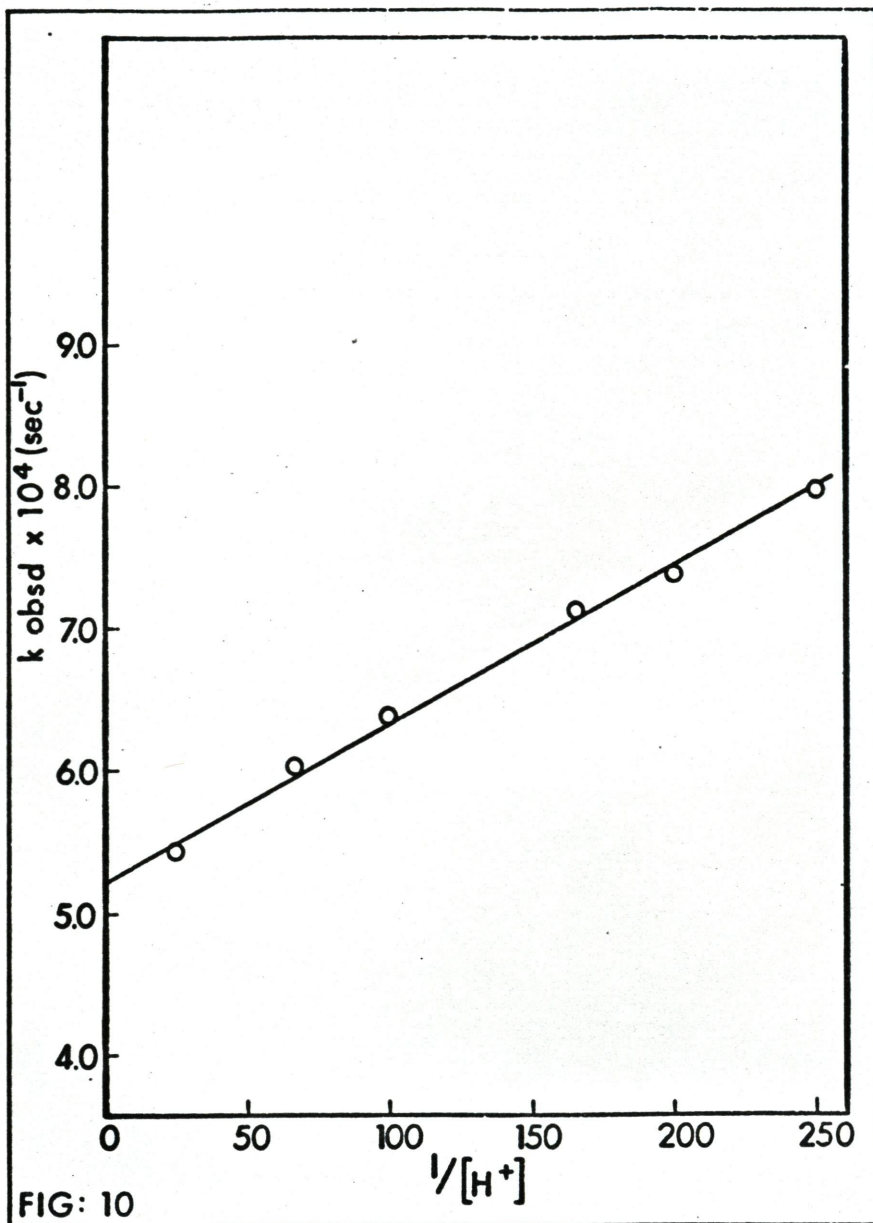


FIG: 10

Fig. 11. Plot of k_{obsd} vs. $1/[\text{H}^+]$ for the Acid Hydrolysis of Bromoaquo(triaminotriethylamine)cobalt(III) Ion at 65.0°C, with $\mu=0.025$

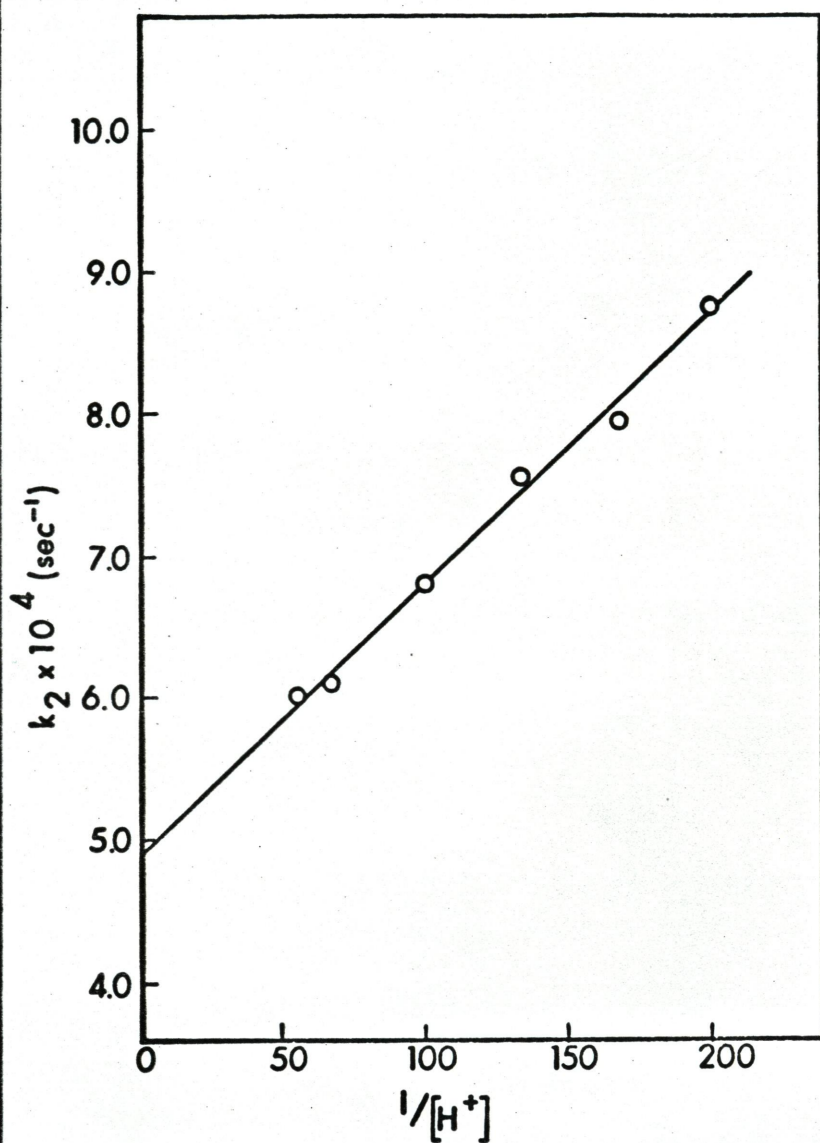


FIG: 11

and is related to the thermodynamic equilibrium constant, K_a' , by the equation

$$K_a' = K_a \frac{\gamma[\text{Co}(\text{tren})\text{OHBr}]^+ \cdot \gamma\text{H}^+}{\gamma[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}} \quad (21)$$

where γ is the activity coefficient.

As the ionic strength of the solution increases, so does the activity coefficient ratio, and hence, K_a decreases. Therefore, it can be seen from equation 17 that as K_a decreases, so does k_{obsd} . A similar but opposite effect has been observed in the kinetics of the acid-catalyzed hydrolysis reactions of $[\text{Cr}(\text{H}_2\text{O})_5\text{OAc}]^{+2}$,²⁷ cis- $[\text{Cr}(\text{H}_2\text{O})_4(\text{CN})_2]^+$,²⁸ and $[\text{Cr}(\text{H}_2\text{O})_5\text{CN}]^{+2}$,²⁹ in which the K_a term appears in the denominator rather than the numerator of the rate equation.

In order to substantiate further the fact that the acid inhibition is due to an acid dissociation of the bromoaquo species, the reaction rate was also measured at pD zero and pD 2.0 in deuterium oxide and compared with that in water under identical conditions. At pD zero where k_{obsd} is approximated by k_2 , the observed rate constant in D_2O at 65.0°C is $3.49 \times 10^{-4} \text{ sec}^{-1}$ and is 31% less than the corresponding value in H_2O . Decreases of the same order of magnitude have previously been reported by Adamson and Basolo when H_2O is replaced by D_2O in the acid hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]^{+2}$.²³ The slower rate in D_2O has been attributed to a smaller degree of solvent-aided dissociation of the halide group in the transition state. In H_2O at 65.0°C and pH 2.0 the value of k_{obsd} is 27% higher than at pH zero because of the acid dissociation of the bromoaquo species. In D_2O , however, the increase in k_{obsd} in going from pH zero to

pH 2.0 is only 17%. This observation is consistent with an acid-base equilibrium in which the acidic species hydrolyzes more slowly, since it has been established previously that weak acids are less dissociated in D_2O than in H_2O .³⁰ The opposite effect has been observed in the acid-catalyzed hydrolysis of trans- $[Co(en)_2F_2]^+$ ¹² since in this case, the protonated species reacts faster.

A comparison of the primary and secondary acid hydrolyses rates of $[Co(tren)Br_2]^+$ with those of other amine complexes indicates that the nature of the primary acid hydrolysis reaction in the dibromo tren complex is quite different from that of the bromoaquo species. As stated previously, the value of k_1 for the acid hydrolysis of $[Co(tren)Br_2]^+$ is 27 times larger than that for cis- $[Co(en)_2Br_2]^+$ at $25.0^\circ C$,²⁰ and 10 times larger than that of cis- $[Cr(en)_2Br_2]^+$.⁹ This increased rate of hydrolysis in the tren compound is attributed to a distortion of the complex by the tren ligand, which results in both a strain in the complex, and an increased exposure of the bromide ligands to the solvent.²⁰ The effect of this distortion would then be to labilize the bromide groups in either a S_N1 or a S_N2 mechanism.

A similar comparison of the second acid hydrolysis step of these complexes, however, shows that the value of k_2 for the hydrolysis of the bromoaquo tren complex at $25.0^\circ C$ is almost 58 times smaller than that for cis- $[Cr(en)_2H_2OBr]^{+2}$.⁹ Furthermore, although no data are available for the acid hydrolysis of cis- $[Co(en)_2H_2OBr]^{+2}$, a comparison of the value of k_2 for the hydrolysis of cis- $[Co(en)_2H_2OCl]^{+2}$ ¹³ with that of $[Co(tren)H_2OBr]^{+2}$ at $25.0^\circ C$ shows that the tren complex hydrolyzes only twice as fast, while

$[\text{Co}(\text{tren})\text{Br}_2]^+$ reacts over 100 times faster than cis- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ at the same temperature.⁴

The marked decrease in labilization of the second bromide ion relative to the first can only be explained by a reduction in the distortion of the complex after the loss of the first bromide group. This is not unreasonable, since the replacement of a bulky cis bromide group by water, combined with the increased positive charge of the complex, would allow the second bromide group to be pulled in closer to the cobalt and hence would decrease its vulnerability to solvent attack by an $\text{S}_{\text{N}}2$ mechanism. The increase in AS^\ddagger for the secondary acid hydrolysis step relative to the first is consistent with a decrease in $\text{S}_{\text{N}}2$ character for the hydrolysis of the bromoaquo species.

C. Kinetics of the Acid Hydrolysis of Chloroaquo

(triaminotriethylamine)cobalt(III) Ion

1. Experimental Section

a. Preparation of Compounds

i. Dichloro(triaminotriethylamine)cobalt(III) perchlorate:

Dichloro(triaminotriethylamine)cobalt(III) chloride hydrate,
¹⁹
 prepared by a method reported by Madan and Peone, was dissolved
 in a minimum amount of water at 25 C. The addition of a large
 excess of NaClO_4 followed by cooling to 0 C resulted in
 the formation of deep blue crystals. The compound was
 filtered, washed with absolute ethanol, and dried in vacuo.
 The yield was 36%.

Anal. Calcd. for $\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_2\text{ClO}_4$: C, 19.25; H, 4.80;
 N, 14.94; ClO_4 , 26.50. Found: C, 19.84; H, 5.08; N, 14.59;
 ClO_4 , 25.95.

- ii. Chloroaquo(triaminotriethylamine)cobalt(III) sulfate: One
 gram of dichloro(triaminotriethylamine)cobalt(III) perchlorate
 was dissolved in 20 ml of H_2O and was allowed to undergo the
 primary acid hydrolysis step at 35.0 C. An excess of ammonium
 sulfate was added to the red solution, and cooling to 0 C
 resulted in the formation of a red-violet precipitate. The
 compound was filtered, washed with ethanol, and dried in vacuo.
 The yield was 69%.

Anal. Calcd. For $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{H}_2\text{OCl}]\text{SO}_4$: C, 20.34; H, 5.69; N, 15.80. Found: C, 19.88; H, 5.90; N, 16.11.

- b. Electronic Absorption Spectra: The visible spectra of all species were obtained as described in Section B.
- c. Kinetic Measurements: The chloroaquo species used in this study was prepared in situ by allowing $[\text{Co}(\text{tren})\text{Cl}_2]\text{ClO}_4$ to undergo the primary acid hydrolysis step at room temperature (1 hr.). Since the secondary hydrolysis step is very slow at 25°C , no appreciable secondary reaction occurred during this period. After the primary acid hydrolysis step, a series of scans of the visible spectrum during the secondary hydrolysis reaction at 55.0°C showed that the initial spectrum was identical to that of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]\text{SO}_4$, and the final spectrum was identical to that of $[\text{Co}(\text{tren})(\text{H}_2\text{O}_2)]^+{}^{20}$. These scans are reproduced in Figure 12. Two isosbestic points were observed in the spectra during the entire course of the reaction, one at 508 and the other at 432 m μ , although a slight shift in the isosbestic points was observed during the initial part of the reaction. The wavelength chosen for this kinetic study was 550 m μ where the maximum difference in absorbance occurs between the reactant and the product.

In general, the kinetic measurements were performed by the same methods described in Section B. Plots of $\ln(A_t - A_\infty)$ vs. t gave straight lines for two or three half lives after the first 10 percent of the reaction, however, a slight curvature in the plot was observed during the initial part of the reaction. While the origin of the curvature was investigated in this study, the

Fig. 12. Spectral Changes During the Acid Hydrolysis of

Chloroaquo(triaminotriethylamine)cobalt(III) Ion

at 50.0°C, in 1M HClO₄

(A) initial trace, [Co(tren)H₂OCl]⁺² 3.63 x 10⁻³M

(B) final trace, [Co tren (H₂O)₂]⁺³

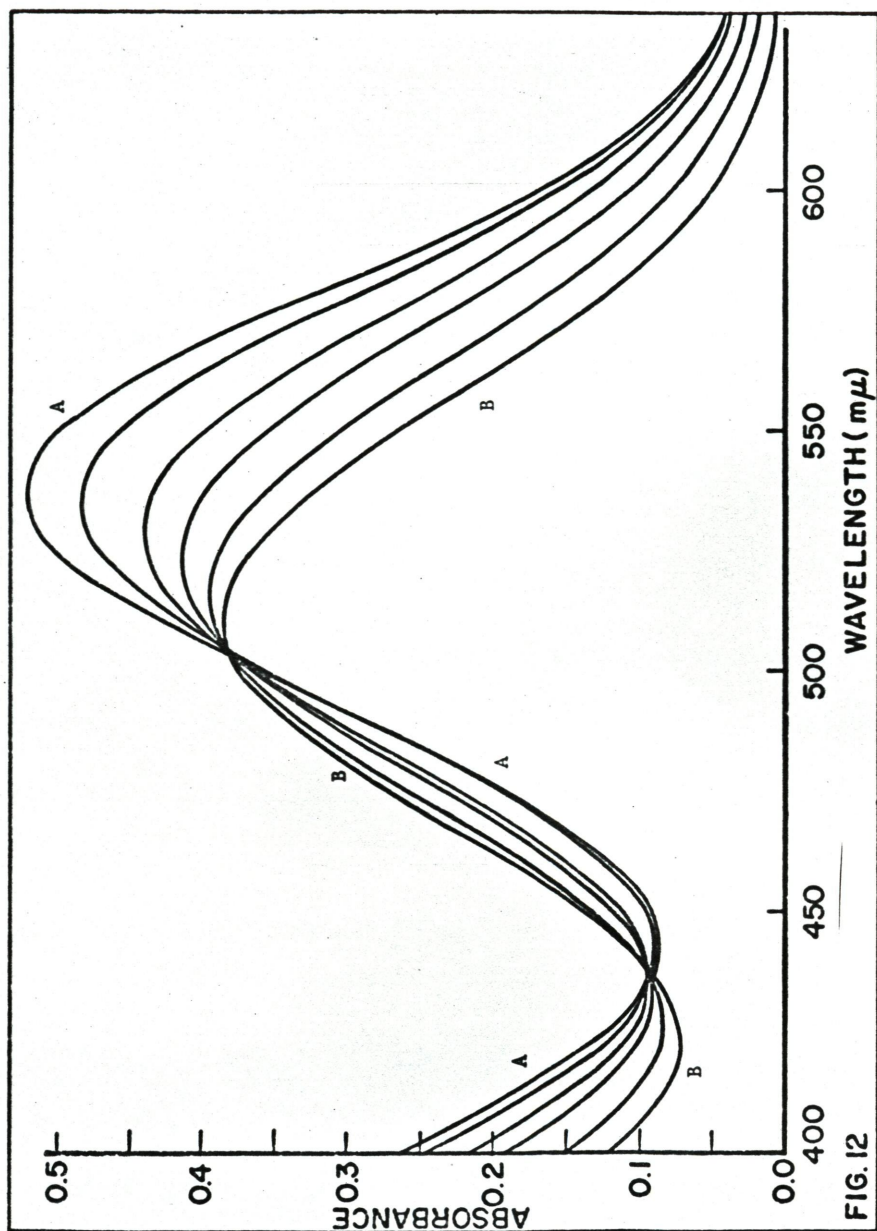


FIG. 12

majority of the kinetic data obtained is for the latter 90% of the reaction where the plot of $\ln(A_t - A_\infty)$ vs. t is linear. In all cases, consecutive runs agreed to within 3%.

2. Results and Discussion

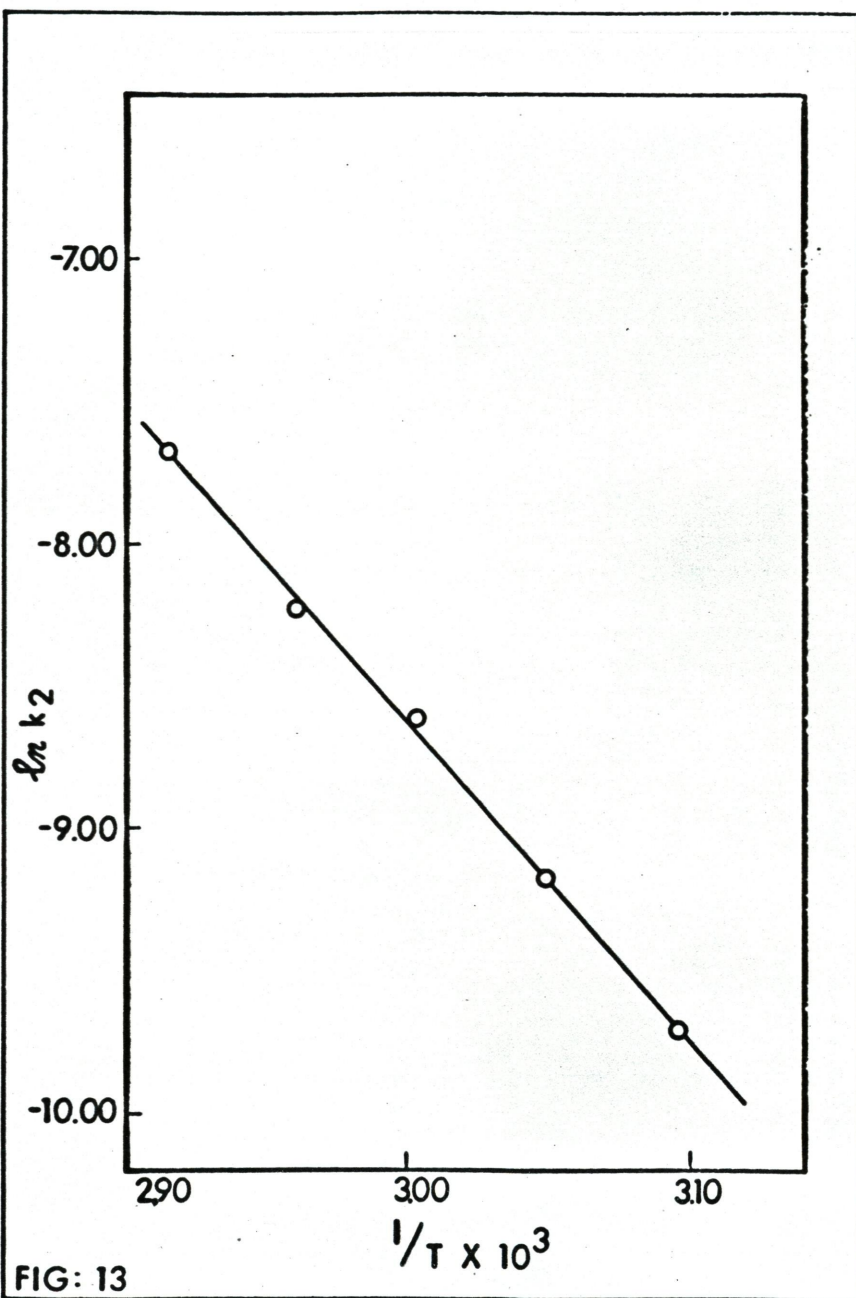
In order to establish that the kinetics of the acid hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^+$ involves no side reactions, the reaction rate was determined at 65.0°C and pH zero at three different wavelengths. The values which were obtained for the rate constant, k_2 , at 565, 550, and 385 mμ are 2.77×10^{-4} , 2.69×10^{-4} , and $2.73 \times 10^{-4} \text{sec}^{-1}$, respectively. These values are all in good agreement with the average value of $2.83 \times 10^{-4} \text{sec}^{-1}$ obtained for the acid hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]\text{SO}_4$.

In general, the kinetics of the acid hydrolysis of the chloroaquo species are similar to those of the bromoaquo complex described in Section B. The rate constants for the hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$ were obtained in 1M HClO_4 under various conditions of temperature and ionic strength, and the data are summarized in Table XV. The Arrhenius plot for the data in Table XV in the range of 50–70°C is shown in Figure 13. The plot gives a straight line with a standard deviation of 2.7%, from which an activation enthalpy, ΔH^\ddagger , of $21.6 \text{ cal mole}^{-1} \text{ deg}^{-1}$ is obtained. The free energy of activation, ΔG^\ddagger , and the entropy of activation, ΔS^\ddagger , were found to be $25.3 \text{ kcal mole}^{-1}$, and $-12.4 \text{ cal mole}^{-1} \text{ deg}^{-1}$, respectively. It is interesting that the activation enthalpy for the primary acid hydrolysis of $[\text{Co}(\text{tren})\text{Cl}_2]^+$ is higher than that for the corresponding reaction of the dibromo salt,²⁰ while in the case of the secondary hydrolysis reaction, the order is reversed. Furthermore, in the hydrolysis reactions of the halopentammine cobalt(III) and cis-

Table XV. Rates of Acid Hydrolysis of Chloroaquo
(triaminotriethylamine)cobalt(III) Ion in
1M HClO₄ under Various Conditions

Temp. °C	Added Electrolyte	Ionic Strength	k_2, sec^{-1}
25.0	None	1.00	2.38×10^{-6}
50.0	None	1.00	6.10×10^{-5}
55.0	None	1.00	1.04×10^{-4}
60.0	None	1.00	1.82×10^{-4}
65.0	None	1.00	2.69×10^{-4}
70.0	None	1.00	4.70×10^{-4}
65.0	1.50M NaClO ₄	2.50	2.32×10^{-4}
65.0	1.00M NaClO ₄	2.00	2.51×10^{-4}
65.0	0.50M NaClO ₄	1.50	2.66×10^{-4}
65.0	0.005M NaCl	1.01	2.73×10^{-4}
65.0	0.10M Na ₂ SO ₄	1.30	3.59×10^{-4}
65.0	0.05M Na ₂ SO ₄	1.15	3.15×10^{-4}

Fig. 13. Arrhenius Plot for the Acid Hydrolysis of Chloroaquo
(triaminotriethylamine)cobalt(III) Ion in
1M HClO₄ between 50 and 70°C



dihalobis(ethylenediamine)cobalt(III) complexes, the value of ΔH^\ddagger is also higher for the reactions of the bromo species. The higher value of ΔH^\ddagger is most likely a result of the larger size of the bromide ion relative to that of the chloride ion, which makes it more difficult for a water molecule to enter the coordination sphere in a cis attack by an S_N2 mechanism. The fact that the opposite is true for the primary acid hydrolysis step of the tren complexes is most likely a result of the high degree of distortion in the dibromo complex, which facilitates a cis attack by incoming water molecules.

The value of ΔS^\ddagger for the acid hydrolysis of the chloroaquo complex, ($-12.4 \text{ cal mole}^{-1} \text{ deg}^{-1}$), is nearly identical to that for the hydrolysis of the dichloro complex ($-10.4 \text{ cal mole}^{-1} \text{ deg}^{-1}$). The reaction of the chloroaquo ion, unlike that of the bromoaquo species, does not seem to show an increase in S_N1 character relative to the reaction of the dichloro species. This is not unreasonable, since the smaller radius and higher nucleophilicity of the chloride ion would tend to diminish the tendency towards a dissociative type of mechanism with a highly charged cation.

The data in Table XV at 65.0°C and pH zero also show that the addition of large amounts of NaClO_4 has only a small effect on the value of k_2 . The slight decrease in the value of k_2 with increasing ionic strength was also observed in the kinetics of the acid hydrolysis of trans- $[\text{Cr NH}_3(\text{H}_2\text{O})_3\text{Cl}_2]^+$ ³¹ but does not seem to be present in the kinetics of the reaction of any of the bromide compounds. Because of the high ionic strengths used, however, to attribute the small ionic strength

dependence of the reaction to any single cause is probably misleading, although a lowering of the water activity by the addition of large amounts of NaClO_4 could be responsible.

The addition of a five-fold excess of chloride ions did not affect the reaction rate as seen from the data in Table XV. Large excesses of chloride ions were found to result in an incomplete reaction, however, with a large amount of the chloroaquo species remaining at equilibrium. The addition of an excess of Na_2SO_4 was found to accelerate the reaction rate, presumably by an ion pair mechanism, just as in the case of the kinetics of $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$.

A study of the dependence of the acid hydrolysis rate of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$ on acid concentration revealed that the kinetics are very similar to those of the bromoaquo species described in Section B. The data for the acid hydrolysis of the chloroaquo species at 65.0 C and ionic strengths 0.10 and 1.00 are summarized in Table XVI, and the plots of k_{obsd} vs. $1/[\text{H}^+]$ are illustrated in Figures 14 and 15. From the plot for the data obtained at $\mu = 0.10$, the rate constant equation was found to be

$$k_{\text{obsd}} = 3.2 \times 10^{-4} + 1.5 \times 10^{-6}/[\text{H}^+] \quad (22)$$

and at $\mu = 1.00$ the rate constant expression was calculated to be

$$k_{\text{obsd}} = 2.8 \times 10^{-4} + 9.3 \times 10^{-7}/[\text{H}^+] \quad (23)$$

The ionic strength dependence of the second term in equations 22 and 23 is similar to that which has been discussed in the kinetics of the bromoaquo system described in Section B.

Table XVI. Rates of Acid Hydrolysis of Chloroaquo
(triaminotriethylamine)cobalt(III) Ion between
pH 1.0 and 3.0 with Added NaClO_4 at 65.0°C

<u>$[\text{H}^+]$</u> <u>mm</u>	<u>Ionic Strength</u>	<u>$k_{\text{obsd}} \times 10^4$</u> <u>$\text{sec}^{-1}$</u>
7.50	0.10	5.12
10.00	0.10	4.75
13.30	0.10	4.22
20.00	0.10	3.94
50.00	0.10	3.49
100.0	0.10	3.29
5.00	1.00	4.54
6.67	1.00	4.23
10.00	1.00	3.74
20.00	1.00	3.11
50.00	1.00	2.99
100.0	1.00	2.87

Fig. 14. Plot of k_{obsd} vs. $1/[\text{H}^+]$ for the Acid Hydrolysis
of Chloroaquo(triaminotriethylamine)cobalt(III) Ion
at 65.0°C, with $\mu = 0.10$

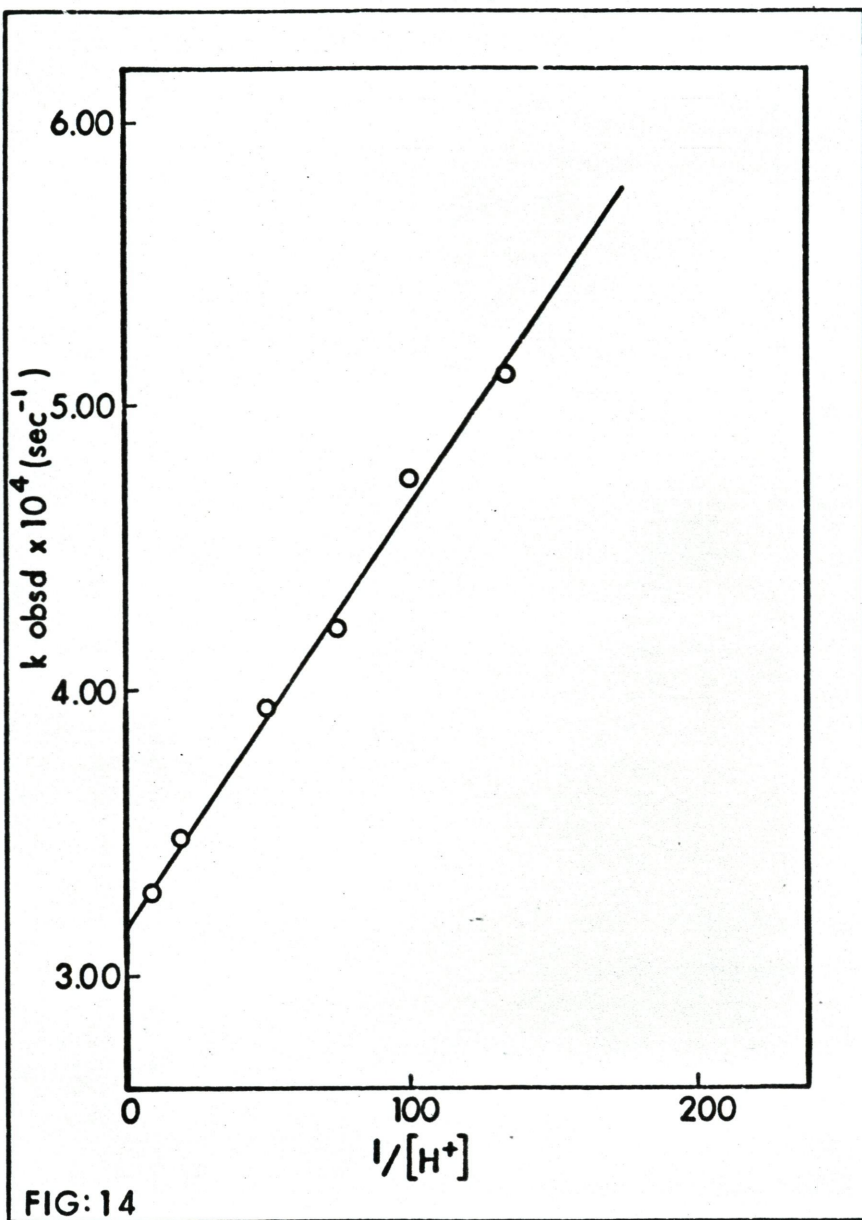


Fig. 15. Plot of k_{obsd} vs. $1/[\text{H}^+]$ for the Acid Hydrolysis
of Chloroaquo(triaminotriethylamine)cobalt(III) Ion
at 65.0°C, with $\mu = 1.00$

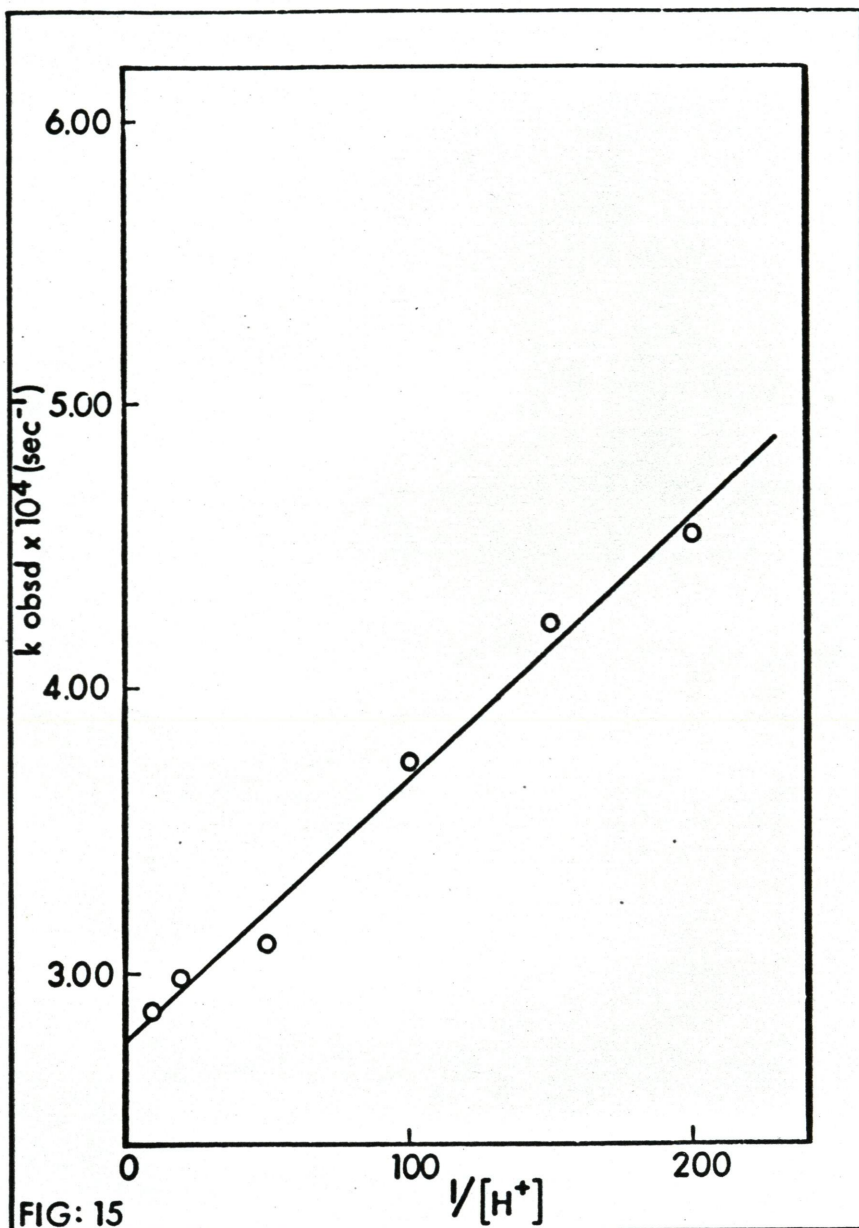


FIG: 15

In comparing the kinetics of the bromoaquo and chloroaquo systems, it becomes readily apparent that the only major difference between the two occurs in the initial stages of their reactions. While the plot of $\ln(A_t - A_\infty)$ vs. t is linear throughout the entire acid hydrolysis reaction of $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$, a noticeable curvature is present in the similar plots for the reactions of the chloroaquo species. A typical plot of $\ln(A_t - A_\infty)$ vs. t for the hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]\text{SO}_4$ at pH zero and 55.0 C is illustrated in Figure 16 and the data are summarized in Table XVII.

A similar type of first-order plot has been observed in the acid hydrolysis of diethyl-³²-t-butyl-carbinyl chloride, and also in the acid hydrolysis of chloro(tetramethylene-pentamine)cobalt(III) ⁴ ion. In both cases the non-linearity of the plot is believed to be a result of the presence of two isomers reacting at different rates. If the faster reacting isomer is less abundant than the slower one, the hydrolysis rate during the initial part of the reaction is a sum of the rates of reaction of both isomers until the former is all reacted. During the later part of the reaction, the measured rate of hydrolysis is simply that of the slower reacting isomer. By extrapolating the linear portion of the plot to $t = 0$, and plotting the difference between a point on this line and a point on the curve at time t vs. t , the rate constant for the first reaction can be obtained.

Since two isomers are possible for all of the haloaquo-(tri-aminotriethylamine)cobalt(III) species it seems reasonable that the kinetics of the acid hydrolysis of the chloroaquo species may involve a similar parallel reaction of two isomers to form the common diaquo product. The two possible isomers of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$

Fig. 16. Plot of $\ln(A_t - A_\infty)$ vs. t for the Acid Hydrolysis of
Chloroaquo(triaminotriethylamine)cobalt(III) Ion
at 55.0°C, in 1M HClO₄

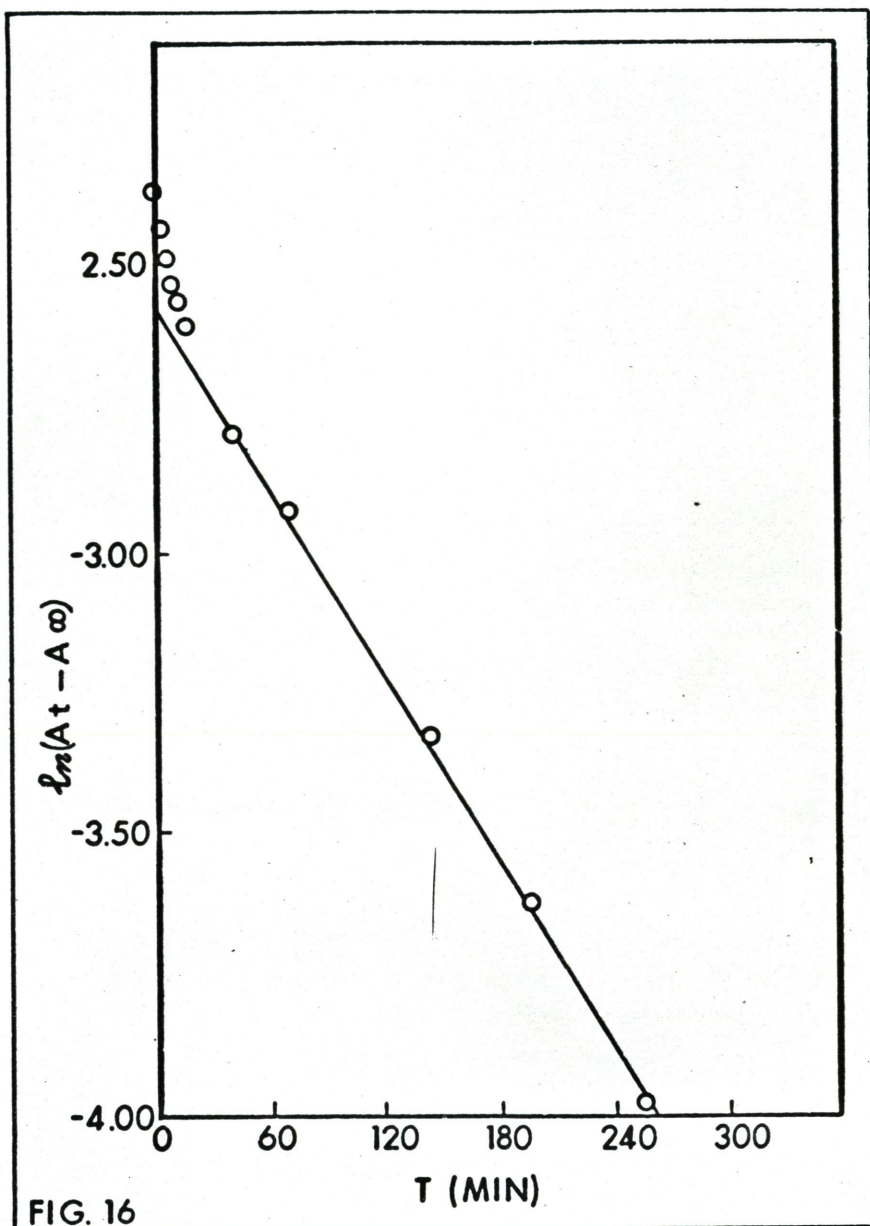


FIG. 16

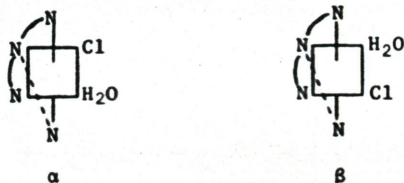
Table XVI

Typical Experimental Data for the Acid Hydrolysis of Chloro-aquo

(triaminotriethylamine)cobalt(III) Ion at 65.0°C in 1M HClO₄ at 550 mμ

<u>time (min)</u>	<u>A</u>	<u>(A_t-A_∞)</u>	<u>ln(A_t-A_∞)</u>
0	0.1786	0.0934	-2.371
3	0.1725	0.0873	-2.438
6	0.1680	0.0828	-2.491
9	0.1647	0.0795	-2.532
12	0.1621	0.0769	-2.565
16	0.1588	0.0736	-2.609
40	0.1460	0.0608	-2.800
70	0.1383	0.0531	-2.935
145	0.1210	0.0358	-3.330
195	0.1119	0.0267	-3.623
255	0.1040	0.0188	-3.974
∞	0.0852	-	-

are represented below.



The α isomer contains the chloride group cis to the tertiary nitrogen, while the β isomer contains the chloride group trans to the tertiary nitrogen atom.

Although these isomers have never been isolated, evidence for the existence of isomers in other tren complexes has been found. In a study of the reaction of $[\text{Co}(\text{tren})(\text{H}_2\text{O})\text{OH}]^{+2}$ with glycine ethyl ester,³³ it was found that two isomers of the chelated glycine complex could be obtained, one with the glycine oxygen cis and the other with it trans to the tertiary nitrogen atom. The two isomers were separated by fractional crystallization, and it was found that the visible spectra of the two species differed slightly. In the same study, Collman and co-workers³³ allowed $[\text{Co}(\text{tren})\text{Cl}_2]^+$ to undergo the primary acid hydrolysis step and then reacted it with glycine ethyl ester. The coordinated water was replaced by the amino acid nitrogen; however, in this case, only one isomer of the product was detected. It was concluded that the isomer which was obtained has the amino acid nitrogen cis to the tertiary nitrogen atom, since these authors believe that the β isomer of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$ is formed preferentially from the primary acid hydrolysis of $[\text{Co}(\text{tren})\text{Cl}_2]^+$. Their conclusion seems consistent with an x-ray diffraction study of

$[\text{Ni}(\text{tren})(\text{NCS})_2]$ ²¹ which shows the Ni-NCS bond distance to be nearly 0.1 Å longer for the NCS group cis to the tertiary nitrogen.

With the above information in mind, an attempt was made to determine the reaction rate for the faster reacting, α , isomer by using the method of Brown and Fletcher.³² The data obtained for the fast initial reaction are summarized in Table XVII and a typical first-order plot for the fast reaction is shown in Figure 17. As seen from the data in Table XVII, the absorbance change during the first reaction is only a small fraction of the total absorbance change, (< 15%), and therefore, the error in calculating k_2 for the α -isomer is much larger than for the β -isomer. In determining the value of k_2 for the α -isomer, consecutive runs usually agreed to within 10%, and the plots of $\ln [(A_t - A_\infty)_{\text{exp}} - (A_t - A_\infty)_{\text{ext}}]$ vs. t gave straight lines with typical standard deviations of 5 or 6%.

The activation parameters for the first reaction were obtained from the rate constants at 60.0, 55.0, 50.0, and 45.0°C, which had values of 2.95×10^{-3} , 1.55×10^{-3} , 8.90×10^{-4} , and $4.40 \times 10^{-4} \text{ sec}^{-1}$, respectively. From these values, an Arrhenius plot was made which gave a straight line over the entire temperature range, with a standard deviation of 3%. The plot is illustrated in Figure 18. From the plot values for the activation parameters, ΔH^\ddagger , ΔG^\ddagger , and ΔS^\ddagger were calculated to be 25.4 kcal mole⁻¹, 23.4 kcal mole⁻¹, and +6.7 cal mole deg⁻¹, respectively.

These activation parameters are quite different from those discussed earlier in this section for the acid hydrolysis of the other isomer of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$. The value of ΔH^\ddagger for the hydrolysis of the α -isomer

Table XVIII. Experimental Data for the Determination of the Rate Constant of the Fast Initial Reaction in the Acid Hydrolysis of Chloroquo (triaminotriethylamine)cobalt(III) Ion at 55.0°C in 1M HClO₄

time (min)	$(A_t - A_\infty)_{\text{experimental}}$	$(A_t - A_\infty)_{\text{extrapolated}}$	$(A_t - A_\infty)_{\text{exp}} - (A_t - A_\infty)_{\text{ext}}$	$\ln[(A_t - A_\infty)_{\text{exp}} - (A_t - A_\infty)_{\text{ext}}]$
0	0.0934	0.0751	0.0183	-4.00
3	0.0873	0.0740	0.0133	-4.32
6	0.0828	0.0729	0.0099	-4.62
9	0.0795	0.0717	0.0078	-4.85
12	0.0769	0.0706	0.0063	-5.06
16	0.0736	0.0694	0.0042	-5.47

Fig. 17. Plot of $\ln[(A_t - A_\infty)_{\text{exp}} - (A_t - A_\infty)_{\text{ext}}]$ vs. t for
the Acid Hydrolysis of the α -Isomer of Chloroaquo
(triaminotriethylamine)cobalt(III) Ion
at 55.0°C, in 1M HClO_4

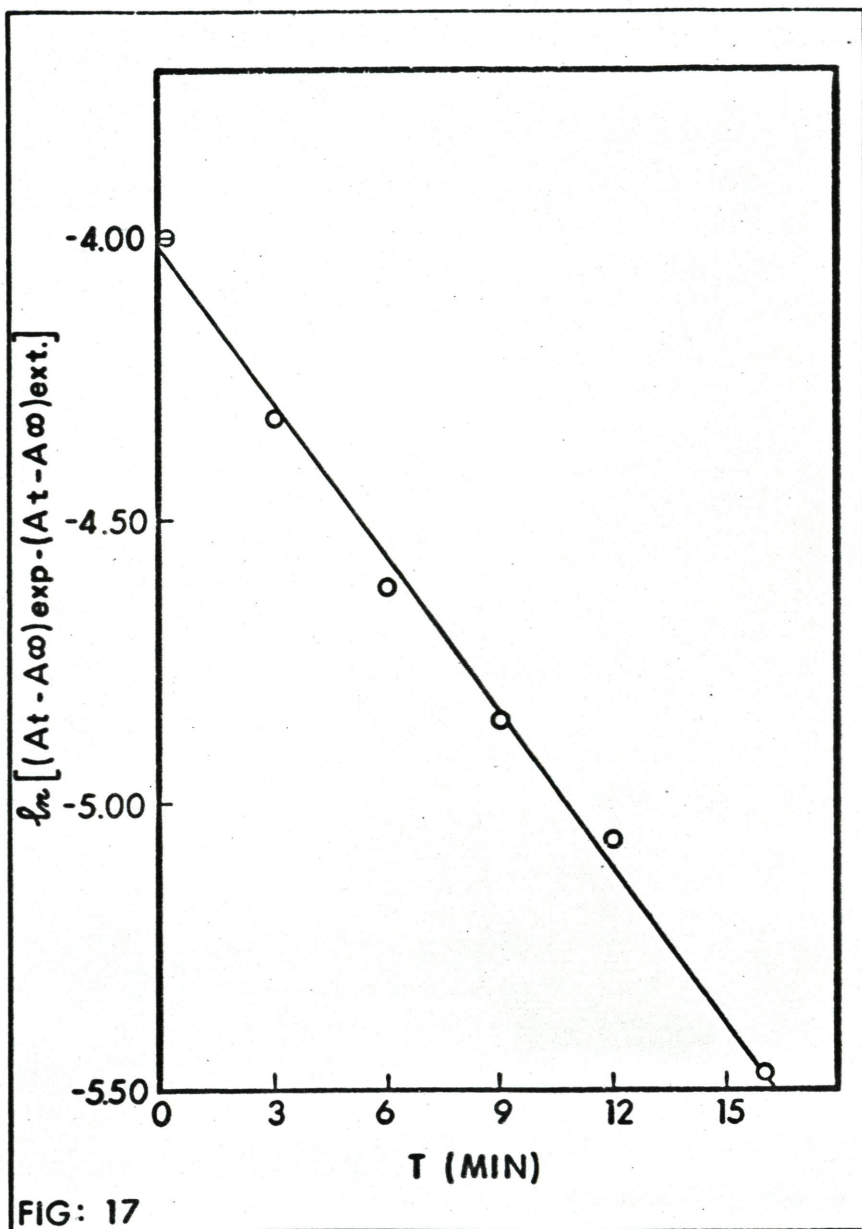


FIG: 17

Fig. 18. Arrhenius Plot for the Fast Initial Reaction in the Acid
Hydrolysis of Chloroaquo(triaminotriethylamine)cobalt(III) Ion
in 1M HClO₄ between 45 and 60°C

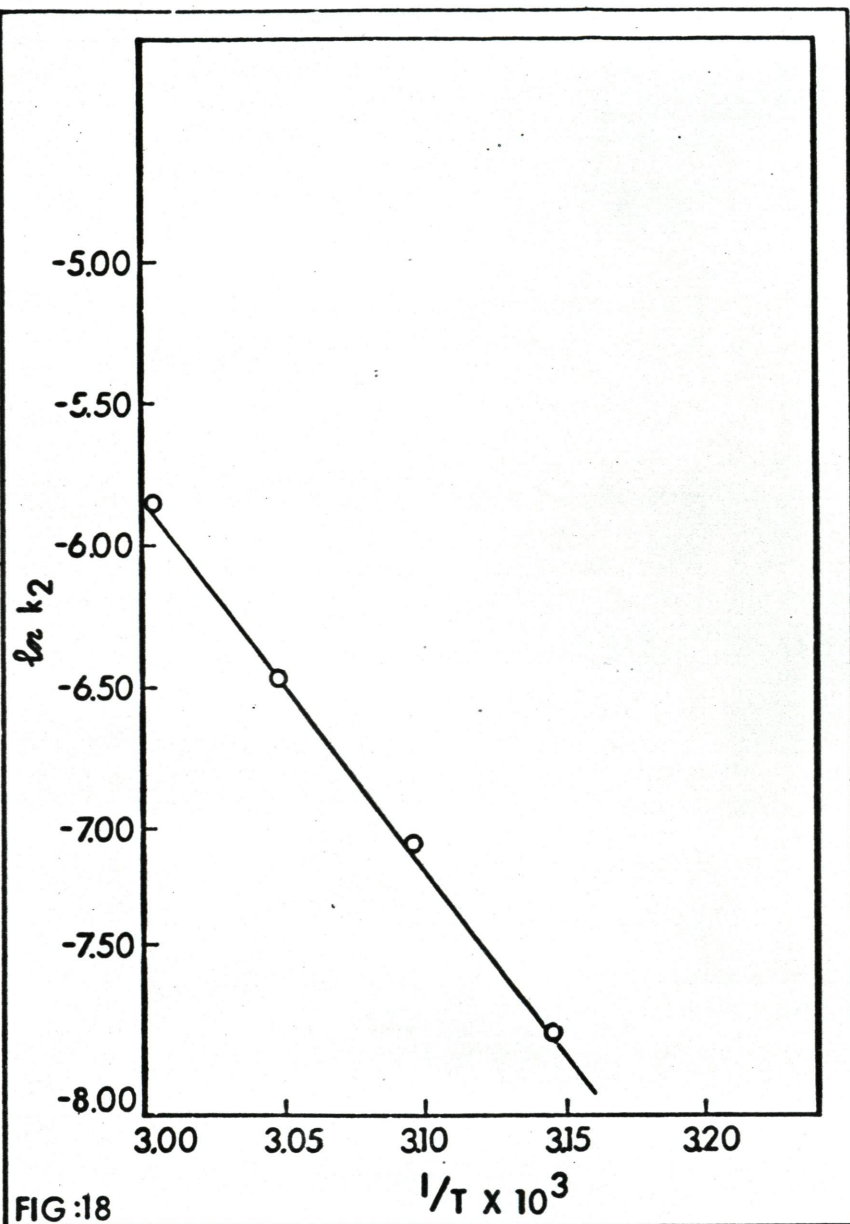


FIG:18

is considerably higher than the value for the reaction of the β isomer, and the positive entropy of activation is quite different from the value of $-12.4 \text{ cal mole}^{-1} \text{ deg}^{-1}$ reported earlier in this section for the reaction of the β -isomer of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$. It is interesting, however, that the value of ΔH^\ddagger for the isomerization of $[\text{Co}(\text{en})_2\text{H}_2\text{OCl}]^{+2}$ reported in a previous study³⁴ is $26.6 \text{ kcal mole}^{-1}$, and is somewhat higher than that for the acid hydrolysis step. Furthermore, the values of ΔS^\ddagger for the isomerization of cis- $[\text{Co}(\text{en})_2\text{H}_2\text{OCl}]^{+2}$ ³⁴ and trans- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{+3}$ ³⁵ are $+6.4$ and $+4.0 \text{ cal mole}^{-1} \text{ deg}^{-1}$, respectively. These data compare favorably with the activation parameters for the reaction of the α -isomer, and seem to suggest that the first reaction may involve a change from one isomer to the other in the transition state. On the basis of the limited data for this reaction, determination of the exact nature of the reaction is not feasible.

A comparison of the rate of acid hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+}$ with that of the corresponding ethylenediamine complex shows that at 25.0°C , the tren complex reacts about 75% faster.¹⁶ On the other hand, the acid hydrolysis of $[\text{Co}(\text{tren})\text{Cl}_2]^{+}$ proceeds at a rate which is nearly 1200% faster than that of cis- $[\text{Co}(\text{en})_2\text{Cl}_2]^{+}$ under similar conditions.¹⁹

These results are in good agreement with those already discussed in the study of the bromoaquo system, and support the hypothesis that the labilization of the second halide group in dihalo(triaminotriethylamine) cobalt(III) complexes is considerably less than that of the first. The observation that the first bromo group appears to be more labilized by the distortion of the complex than the first chloro group may account for

the presence of only one isomer in the bromoaquo system. While the dibromo complex appears to lose the first bromide group exclusively from the position cis to the tertiary nitrogen atom, the less distorted dichloro complex seems to lose the chloride in the cis position preferentially, but with a small amount of the other isomer also being produced.

3. Summary and Conclusions:

In summary, the kinetics of the acid hydrolysis of both $[\text{Co}(\text{tren})\text{H}_2\text{OBr}]^{+2}$ and $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$ were studied spectrophotometrically under various conditions of temperature, pH, and ionic strength. It was found that in both systems, the hydrolysis reaction is acid-inhibited due to an acid-base equilibrium between the haloaquo and the more labile halohydroxo complex. Furthermore, it was found that in both cases the labilization of the second halide group due to distortion of the complex is greatly reduced, relative to that in the dihalo complexes. In the case of the chloroaquo complex, two isomers are believed to exist.

D. Direction of Future Research

In the past, a considerable amount of effort has been devoted to studying the kinetics of substitution reactions in octahedral cobalt(III) tren complexes. The data obtained seem to indicate that the system is, in many ways, considerably more complex than those of other cobalt(III) amine complexes, and it is now apparent that much more work needs to be done in order to understand fully the nature of the system. On the basis of the work described in Section C, it appears as though the chloro-aquo complex exists as a mixture of two isomers. However, the acid hydrolysis data obtained spectrophotometrically do not indicate clearly whether the overall reaction is one of isomerization of one isomer to the other, followed by hydrolysis, or whether the two isomers both hydrolyze independently at different rates to form the common diaquo species. It seems reasonable that a study of the acid hydrolysis of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$ using a conductance or chloride ion electrode technique might be helpful in distinguishing between the two mechanisms. Clearly, if the initial reaction involves isomerization of one isomer to the other, the concentration of chloride ions should be zero during the initial part of the reaction. On the other hand, if the reaction involves acid hydrolysis only, the kinetics should be identical to those measured spectrophotometrically.

If the two isomers of $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]^{+2}$ can be separated by fractional crystallization or column chromatography, it may also be possible to distinguish between the α and β isomer by measuring the kinetics of the base hydrolysis of each isomer. It is known that the base hydrolysis

of a chloride group trans to a primary amine is greatly accelerated by extraction of an amine proton by a hydroxide ion, in an S_N1 conjugate base mechanism.³⁶ On this basis, the α isomer should react much more rapidly than the β isomer, since the latter has the chloride group trans to the tertiary nitrogen.

Another point of interest in the acid hydrolysis of Co(III) tren complexes is the relative effect of the distortion on both an S_N1 and on S_N2 mechanism. While it appears as though the distortion in these complexes can accelerate the hydrolysis rate by either mechanism, it would be interesting to determine which is affected to a higher degree. Since data for the acid hydrolysis of complexes of the type cis- and trans- $[\text{Co}(\text{en})_2\text{LCl}]^+$ are available,⁷ a comparison of these data with similar data for the corresponding tren compounds may be useful. As an example, cis- $[\text{Co}(\text{en})_2\text{N}_3\text{Cl}]^+$ is believed to hydrolyze by a mechanism with a large degree of S_N1 character, while cis- $[\text{Co}(\text{en})_2\text{NO}_2\text{Cl}]^+$ is believed to react by a mechanism which is, for the most part, S_N2 in character. By measuring the acid hydrolysis rates of the corresponding tren complexes and comparing their ratios, an idea as to the effect of distortion on an S_N1 and S_N2 mechanism might be obtained.

Preliminary kinetic measurements have been performed for the hydrolysis reactions of $[\text{Co}(\text{tren})\text{NO}_2\text{Cl}]^+$, $[\text{Co}(\text{tren})(\text{NO}_2)_2]^+$, and $[\text{Co}(\text{tren})(\text{N}_3)_2]^+$, and it is clear from the data that the reactions are not simple first-order as in the case of the ethylenediamine analogs. It seems that the intermediate nitroquo and azidoquo species are quite

labile, so that the primary acid hydrolysis rate of these compounds cannot be measured without interference from the secondary reaction. The kinetics of the acid hydrolysis of these complexes will therefore have to be treated as consecutive first-order reactions.

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