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E. STORE
SYNTHETIC AND KINETIC STUDIES OF SOME
TRANSITION METAL COMPLEXES OF MACROCYCLIC
LIGANDS

A thesis
submitted in partial fulfilment of the
regulations for the degree of
Doctor of Philosophy
by
BAKIR J. A. JERAGH

Department of Chemistry
University of Stirling
Scotland

April 1979
To

my parents,

my wife,

and

my daughters,

Ebtessam, Bothaina and Sallwa.
ACKNOWLEDGEMENTS

I wish to thank

Dr. R. W. Hay, my supervisor, for suggesting the topics of this work, encouragement and friendliness throughout my period in the University of Stirling;

Dr. G. H. Searle (University of Adelaide, Australia) for supplying several milligrams of the complexes cis-α- and cis-β-carbonato-(3,6-dimethyl-1,8-diamino-3,6-diazaoctane)cobalt(III), which were used for kinetic studies, and for carrying out the column chromatography work discussed in Section II Chapter 4;

Dr. K. Hideg (University of Pécs, Hungary) for supplying several grams of the ligand 5,12-dimethyl-7,14-di(2-thienyl)-1,4,8,11-tetra-azacyclotetradeca-4,11-diene;

Mr. D. F. Dance for assistance in recording the n.m.r. spectra;

Mrs. Joan Weber for typing the manuscript.
The thesis is divided into two sections. The first section deals with kinetic studies and the second section with synthetic and stereochemical investigations.

The kinetics and mechanism of the acid-catalysed decarboxylation of a number of complexes of the general type \( \text{cis-}[\text{CoN}_4\text{CO}_3]^+ \) (where \( N_4 \) = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, \( \text{C-meso-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane} \), \( \text{1,4,7,10-tetra-azacyclododecane} \) and \( \text{3,6-dimethyl-1,8-diamino-3,6-diazaoctane} \)).

The acid-catalysed decarboxylation of these complexes has been studied over a range of perchloric acid or nitric acid concentrations, and temperatures 25, 35 and 45°C (except in the case of \( \text{cis-carbonato(C-meso-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane)co} \) cobalt(III) which was studied only at 35°C). The rate expression takes the form

\[
\begin{align*}
k_{\text{obs}} &= k_0 + k_1 [H]^+, \\
k_0 &= \text{the observed first order rate constant at constant hydrogen ion concentration.}
\end{align*}
\]

The activation parameters have been determined and the mechanism of the reactions discussed. The complexes display solvent deuterium isotope effects \( (k_{D_2O}/k_{H_2O}) \) in the range of 2.1 to 2.65. The magnitude of the solvent isotope effects is consistent with a rapid pre-equilibrium protonation followed by rate-determining ring-opening, and excludes a mechanism
involving concerted attack by $\text{H}_3\text{O}^+$. The values of $\Delta S^+$ suggest an A-1 type reaction to give a five-coordinate intermediate.

The second part of this section deals with the kinetics of the acid-aquation of the cis-dichloro(C-meso-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane)chromium(III) cation. The reactions were studied using 0.01 mol dm$^{-3}$ nitric acid as the reaction medium. The hydrolysis occurs in two steps,

\[
\text{cis-[CrLCl}_2\text{]}^+ + \text{H}_2\text{O} \rightarrow \text{cis-[CrLCl(H}_2\text{O)}\text{]}^2+ + \text{Cl}^-
\]

\[
\text{cis-[CrLCl(H}_2\text{O)}\text{]}^2+ + \text{H}_2\text{O} \rightarrow \text{cis-[CrL(H}_2\text{O)}\text{]}^3+ + \text{Cl}^-
\]

and activation parameters for both hydrolyses obtained. Loss of the first chloride ligand is ca. 76 times faster than the second at 25°C. Possible mechanisms for these reactions are considered.

The second section of the thesis deals with synthetic and stereochemical studies of macrocyclic ligands and their metal complexes.

Reduction of the nickel(II) complex of C-meso-5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene gives three diastereoisomeric tetramethylcyclams (as their nickel(II) complexes, (1), (2) and (3)).

One of these complexes, believed to be (2), is formed preferentially (ca 70%) and is readily obtained isomerically pure. Molecular models indicate that the four
methyl groups in (2) are equatorial, and that the axial coordination sites are readily accessible to monodentate ligands. A number of octahedral nickel(II) complexes of (2) have been prepared and characterised. The thermodynamics of the NiL$_2$$^+$ + 2H$_2$O $\rightarrow$ [NiL(H$_2$O)$_2$]$^{2+}$ equilibrium has been studied in detail and values of $\Delta H^0$ and $\Delta S^0$ obtained.

Fractional crystallisation of the nickel(II) complex of 5,6,12,13-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene from aqueous solution led to the characterization of three isomers (arising from chiral nitrogen and carbon centres) designated a, b and c, identified by their $^1$H n.m.r. spectra. Equilibration of a and b in DMSO/KOH gives isomer d. N.m.r. studies confirm that the reaction proceeds via the steps, b $\rightarrow$ a $\rightarrow$ d.

Cobalt(III), copper(II) and nickel(II) complexes of 1,4,7,10,13,16-hexa-azaoctadecane have been prepared and
characterised and the stereochemistry of the cobalt(III) complex discussed. The $^1$H n.m.r. spectrum of the cobalt(III) complex in $d_6$-DMSO solution is consistent with the unsym topology. This assignment is fully confirmed by $^{13}$C n.m.r. The $^{13}$C n.m.r. spectrum unequivocally establishes that the compound consists of the two NH geometrical isomers of the unsym topology which are present in roughly equal amounts, (4) and (5).

A number of metal(II) and cobalt(III) complexes of the macrocyclic ligand 5,12-dimethyl-7,14-di(2-thienyl)-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (6) have been prepared and characterised. The spectroscopic properties of
these complexes are consistent with a square planar geometry for the metal(II) perchlorate salts and a trans-arrangement of the unidentate ligands in the octahedral cobalt(III) complexes.

The structures of all compounds were confirmed by elemental analysis, spectroscopic investigations, and in some cases by conductivity measurements.
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Nomenclature and Abbreviations

The definitive rules of nomenclature and abbreviations for inorganic chemistry proposed by the International Union of Pure and Applied Chemistry\(^a\) (IUPAC) are used throughout this thesis.

International Union names based on the Chemical Society (London)\(^b\), in which the nitrogen atoms are given the lowest numbers, have been used for the macrocyclic ligands.

Abbreviated names have been used for macrocyclic ligands and these are based on suggestions by Busch and coworkers\(^c\). Full names are given wherever these abbreviations are used.

The following abbreviations have been used:

- TFA: Trifluoroacetic acid
- DMSO: Dimethylsulphoxide
- DMF: Dimethylformamide
- T.M.S.: Tetramethylsilane
- NaT.M.S.: 3-(Trimethylsilyl)-1-propanesulfonic acid, sodium salt hydrate
- en: 1,2-diaminoethane
- dien: 2,2'-diaminodiethylamine (diethylenetriamine)
- Medien: 4-Methyldiethylenetriamine
- trien: 1,2-Di(amoethylamino)-ethane(triethylenetetramine).
- phen: 1,10-Phenanthroline
- bipy: 2,2'-bipyridyl
- dmtr: 3,6-Dimethyl-1,8-diamo-3,6-diazaoctane
- OAc: Acetate anion
- (a) and {g} a: Refer to axial and equatorial methyl substituents
- meso: racemic-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
- tet b: racemic-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
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<td>[Me₄S][14]dienel₂HClO₄</td>
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Materials and Methods

All reagents were available as Analar grade and were used without further purification.

Proton n.m.r. spectra were recorded using a Perkin-Elmer R32 instrument at 90 MHz or a Perkin-Elmer R24 at 60 MHz; with d₆-DMSO, CD₃NO₂, D₂O or TFA as solvents and T.M.S. or NaT.M.S as internal standard.

¹³C n.m.r. spectra were recorded by Dr. S. F. Lincoln (University of Adelaide, Australia).

Infrared spectra were recorded as KBr discs using a Perkin-Elmer 457 spectrophotometer.

Visible spectral measurements were made using a Perkin-Elmer 402 instrument with the appropriate solvent as blank.

Reflectance spectra were obtained with MgO as reference on a Unicam SP-700 instrument.

Conductivity measurements were carried out at 25°C using aqueous solutions and a Portland conductivity meter Model P310. The concentrations used were 10⁻³ mol dm⁻³.

Instrumentation used for kinetic studies is discussed in the kinetic section.

Elemental analyses were performed by Dr. F. B. Strauss, Microanalytical Laboratory, 10 Carlton Road, Oxford, OX2 7SA.
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22. Temperature dependence of $k_{obs}$ for the acid hydrolysis of cis-[Cr(Me₂cyclam)(H₂O)Cl]²⁺
1.1 Introduction

The kinetics of the acid-catalysed aquation (or decarboxylation) of a number of carbonatotetramine-cobalt(III) complexes have been investigated and discussed over recent years.\(^ {1-8}\) For such reactions the rate law normally observed is

\[
k_{\text{obs}} = k_0 + k_1[H^+]
\]

where \(k_{\text{obs}}\) is the observed first order rate constant at constant hydrogen ion concentration and \(k_0\) and \(k_1\) are the rate constants for the parallel rate-determining carbonato ring-opening processes (1) and (2) scheme 1, \((N_4\) a tetramine).

The decarboxylation steps represented by equations (3) and (4)

\begin{align*}
\text{Scheme 1} \\
[N_4\text{CoCO}_3]^+ + H_2O & \overset{k_0}{\longrightarrow} \text{cis-}[N_4\text{Co(OH)(CO}_3\text{H)}]^+ \quad (1) \\
[N_4\text{CoCO}_3]^+ + H_3O^+ & \overset{k_1}{\longrightarrow} \text{cis-}[N_4\text{Co(OH}_2\text{)(CO}_3\text{H)}]^2+ \quad (2) \\
\text{cis-}[N_4\text{Co(OH}_2\text{)(CO}_3\text{H)}]^2+ & \overset{k_2}{\longrightarrow} \text{cis-}[N_4\text{Co(OH)(OH}_2\text{)}]^2+ + CO_2 \quad (3) \\
\text{cis-}[N_4\text{Co(OH)(CO}_3\text{H)}]^+ & \overset{k_3}{\longrightarrow} \text{cis-}[N_4\text{Co(OH)}]^+ + CO_2 \quad (4)
\end{align*}

are rapid, and the above reaction scheme is consistent with observed kinetics if \(k_2 \gg k_1[H_3O]^+\) and \(k_2 \gg k_3\).
The reactivity of carbonato complexes is markedly dependent upon the nature of the tetramine ligand. With simple amine ligands such as \( \text{NH}_3 \), ethylenediamine(\( \text{en} \)), 1,2-diaminopropane(\( \text{pn} \)) and 1,3-diaminopropane(\( \text{tn} \)), values of \( k_1 \) are ca. 1 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) at 25°C. However, complexes such as \( \text{cis-8-[Co(trien)CO}_3] \), \( \text{[Co(phen)}_2\text{CO}_3] \), \( \text{[Co(bipy)}_2\text{CO}_3] \) and complexes of the type \( \text{[CoL(CO}_3] \) where \( L \) represents the macrocyclic ligands, C-rac-5,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane ((I) = tet b); 5,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane-4,4-diene ((II) = \text{trans-Me}_6[14]-\text{diene}) and 1,4,8,11-tetra-azacyclotetradecane ((III) = cyclam) have much lower reactivities. Arguments\(^3\) that steric hindrance by the tetradentate amines might explain the low \( k_1 \) values have been questioned,\(^4\) and such hindrance was not considered important for the \( \text{phen and bipy complexes} \). Francis and Jordan\(^5\) have demonstrated a
correlation between ligand basicity and $k_1$ for a number of these complexes, so that variations in electron donor ability of the amines were considered to be generally more important than steric effects.

Three possible mechanisms may be considered to account for the first-order dependence of the reaction on the hydrogen ion concentration.\(^7,9\) These mechanisms are outlined in Scheme 2. A recent paper by Harris and Hyde,\(^12\) considers only mechanisms A and B, however, mechanism C must also be taken into account.

Mechanism A involves a slow concerted proton catalysed dechelation, while mechanisms B and C involve a rapid pre-equilibrium protonation followed by slow rate determining ring opening of chelated carbonate. Mechanisms B and C differ in the involvement of water in the rate-determining step. Mechanism B corresponds to an A-2 reaction in which water is involved, while mechanism C is A-1 process involving a 5-coordinate intermediate. These mechanisms can be differentiated by the use of deuterium solvent isotope effects. For mechanism A, a rate determining proton transfer step is involved and $k_{D_2O}/k_{H_2O} < 1$. In mechanisms B and C, $k_{D_2O}/k_{H_2O} > 1$ as $D_2O$ is less basic than $H_2O$ and hence the substrate will be able to compete with the solvent for the deuteron in $D_2O$ more effectively than for the proton in $H_2O$. For mechanism B, $k_{obs} = k_{B1}K[H^+][H_2O]$ while for mechanism C, $k_{obs} = k_{C1}K[H^+]$. The value of $k_{B1}$ ($D_2O/H_2O$) will be somewhat less than unity,
**Scheme 2: Possible mechanisms for acid catalysed decarboxylation.**

**Mechanism A**

\[ \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} + \text{H}^+ + \text{H}_2\text{O} \xrightarrow{k_{A1} \text{ slow}} \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} \quad \text{2+} \]

\[ \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} \quad \text{2+} \xrightarrow{k_{A2}} \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} \quad \text{3+} + \text{CO}_2 \]

**Mechanism B**

\[ \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} + \text{H}^+ \xrightarrow{K \text{ fast}} \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{H} \quad \text{2+} \]

\[ \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{H} + \text{H}_2\text{O} \xrightarrow{k_{B1} \text{ slow}} \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} \quad \text{2+} \]

\[ \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} \quad \text{2+} \xrightarrow{k_{B2} \text{ fast, H}^+} \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} \quad \text{3+} + \text{CO}_2 \]

**Mechanism C**

\[ \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{O} + \text{H}^+ \xrightarrow{K \text{ fast}} \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{H} \quad \text{2+} \]

\[ \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{H} \quad \text{2+} \xrightarrow{k_{C1} \text{ slow}} \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{H} \quad \text{2+} \]

\[ \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{H} \quad \text{2+} + \text{H}_2\text{O} \xrightarrow{k_{C2} \text{ fast, H}^+} \text{N}_4\text{Co} \stackrel{O}{O} \text{C}=\text{H} \quad \text{3+} + \text{CO}_2 \]
however the value of $k(D_2O/H_2O)$ is much greater, hence $k_{obs}$ increases in $D_2O$ solvent. In addition the magnitude of the solvent isotope effect can be of value in differentiating between A-1 and A-2 processes. Solvent deuterium isotope effects $k_{D_2O}/k_{H_2O}$ in the range (1.9-2.6) are considered typical for A-1 hydrolysis, and are much larger than the values of 1.3-1.4 which have been observed\textsuperscript{10} for A-2 reactions. In addition unimolecular A-1 reactions normally have entropies of activation close to zero, while A-2 reactions have substantial negative entropies of activation of the order of $-60$ to $-80$ J K$^{-1}$ mol$^{-1}$\textsuperscript{11}

On the basis of early solvent deuterium isotope effect studies with cis-[Co(en)$_2$CO$_3$]$^+$, Sastri and Harris\textsuperscript{8} favoured mechanism A, as they observed a deceleration in $D_2O$ solvent. However Harris and Hyde\textsuperscript{12} have recently reinvestigated the solvent deuterium isotope effect for the acid-catalysed decarboxylation of cis-[Co(en)$_2$CO$_3$]$^+$ and now report a value of $k_{D_2O}/k_{H_2O} = 2.3$. In this study we also found that the acid-catalysed decarboxylation of cis-[Co(Me$_2$diene)CO$_3$]$^+$, cis-[Co(cyclen)CO$_3$]$^+$, and cis- and cis-$\beta$-[Co(dmtr)CO$_3$]$^+$ exhibit solvent deuterium isotope effects $k_{D_2O}/k_{H_2O}$ in the range of 2.05 to 2.65 (see Table 12).

When the work began on this project, the only available solvent kinetic isotope data,\textsuperscript{8} favoured a slow concerted proton transfer mechanism (mechanism A). Such mechanisms involving slow proton transfer are rather rare,
and it was for this reason that the acid-catalysed decarboxylation and solvent isotope effect of a number of complexes of the general type, $[\text{CoN}_4\text{CO}_3]^+$ (where $N_4 = \text{Me}_2[14] \text{diene}$; C-meso-$\text{Me}_2 \text{cyclam}$; cyclen, and dmtr was studied. In addition, very little work on the decarboxylation of macrocyclic carbonato complexes of cobalt(III) had been published. The only previous data referred to $\text{Me}_6[14] \text{diene}^{(II)}$, tet $b^1$ and cyclam(III)$^6$. The work on $\text{Me}_6[14] \text{diene}$ and tet $b$ is somewhat provisional. It was of particular interest to study the effect of methyl substitution, ligand unsaturation, and macrocyclic ring size on the rates of the acid-catalysed decarboxylation. For comparison purposes the open chain analogues cis-$a$- and cis-$\beta$-$[\text{Co(dmtr)}\text{CO}_3]^+$ were also investigated over a temperature range. Francis and Searle$^5$ had previously studied these later reactions but only at a single temperature.

1.2 Experimental

Synthesis of 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Dihydroperchlorate; $[\text{Me}_2[14] \text{diene}] \cdot 2\text{HClO}_4$.

The ligand and its nickel(II) complex were prepared essentially as described by Kolinski and Korybut-Daszkiewicz.$^{13}$ Perchloric acid (72%, 165 cm$^3$, 2 moles) was added dropwise to cooled 10% methanolic solution of anhydrous ethylenediamine (134 cm$^3$, 2 moles). The reaction mixture was cooled to $-10^\circ C$ and methyl vinyl ketone (162 cm$^3$, 2 moles) in methanol (160 cm$^3$) was added dropwise. When the addition was complete, stirring was continued for 4 hours. The solid
product was filtered off and washed with methanol then ether and dried in vacuo. Melting point 109-110°C (lit. 109-110°C).


A suspension of powdered nickel(II) carbonate (30g, 0.25 mole) in water (300 cm³) was heated to boiling and a suspension of the ligand [Me₂[14]diene]-2HClo₄ (60g, 0.14 mole) in water (200 cm³) added dropwise through the condenser. The reaction mixture was boiled until evolution of carbon dioxide ceased. The solid was filtered off and the filtrate reduced to half volume and cooled. The product was filtered off and washed with cold methanol. The i.r. spectrum of the complex is identical to that reported¹³ (vC=N(S) 1641; vNH 3217; ClO₄⁻ 1093(S) and 625 cm⁻¹(S)).

C-Meso-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane; [Me₂(cyclam)].

The nickel(II) complex of [Me₂[14]diene][ClO₄]₂ was reduced with nickel-aluminium alloy essentially as described by Kolinski et al.¹³ A solution of the complex [Ni(Me₂[14]diene)][ClO₄]₂ (48.2g, 0.1 mole) in water (900 cm³) was maintained at about 60°C with vigorous stirring.

Sodium hydroxide (13g) and powdered nickel-aluminium alloy (50% nickel, 14g) were added in small portions for about 30 minutes. Heating was continued for a further 30 minutes. Celite (10g) was added and the aluminium(III) precipitated as the hydroxide by the addition of concentrated hydrochloric acid
until pH 8-9 was reached (at lower pH's e.g. 2-3 a violet precipitate forms).\textsuperscript{14} The precipitate was filtered off and the filtrate evaporated to half its volume.

Ethanol (450 cm\textsuperscript{3}) and sodium cyanide (29.4 g, 0.6 mole) were added and the reaction mixture was refluxed for 4 hours. Ethanol was distilled off and the water solution extracted with benzene in a continuous manner. The extract was evaporated to dryness. The product (ca 16g) was crystallised from xylene. Fractional crystallization from xylene and the residues from ether gave only one product with m.p. 144-145\textdegree C. Attempts to obtain the second isomer (m.p. 109-110\textdegree C) were unsuccessful. The i.r. spectrum confirms the absence of the vC:N from the product, thus indicating complete reduction has occurred.

C-Meso-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane Tetrahydrochloride; 
[Me\textsubscript{2}(cyclam)].4HCl

To a solution of Me\textsubscript{2}(cyclam) (1.5g) in aqueous methanol (20 cm\textsuperscript{3}, 1:1 v/v) concentrated hydrochloric acid (6 cm\textsuperscript{3}) was added. The white precipitate was filtered off and dried in vacuo. (Calc. for C\textsubscript{32}H\textsubscript{32}N\textsubscript{4}Cl: C, 38.51; H, 8.62, N, 15.0; Found: C, 38.30; H, 8.30; N, 14.95%).

Cis-carbonato (5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate Sesquihydrate; cis-[Co(Me\textsubscript{2}[14]diene)CO\textsubscript{3}]\textsubscript{2}ClO\textsubscript{4}\textsubscript{.2H}\textsubscript{2}O

This complex was prepared as previously described\textsuperscript{15} as follows: Trisodium tris(carbonato)cobaltate(III)\textsuperscript{17} (1.0g) and Me\textsubscript{2}[14]diene.2HClO\textsubscript{4} (1.0g) were mixed in methanol-water
(40 cm³; 1:1 v/v) and heated on a steam-bath until effervescence ceased. The dark solution was filtered whilst hot. Methanol and ether were then added to the solution which was cooled in an ice-bath for several hours when the pink product crystallised. It was filtered off and recrystallised from hot aqueous methanol with final cooling in a refrigerator overnight. (Found: C, 33.15; H, 5.6; N, 11.9.
Calc. for $C_{13}H_{27}ClCoN_{4}O_{8.5}$: C, 33.2; H, 5.8; N, 11.9%).

Trans-diaquo-(5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Perchlorate; $[\text{Co}(\text{Me}_2[14] \text{ diene})(\text{H}_2\text{O})_2][\text{ClO}_4]_3 \cdot \text{XH}_2\text{O}(X = 1.5 \text{ or } 2$).

This complex was prepared by two routes, (a) by acid catalysed ring opening of cis-$[\text{Co}(\text{Me}_2[14] \text{ diene})\text{CO}_3][\text{ClO}_4]$ and (b) by direct synthesis, and isolated as the perchlorate salt. **Method (a)**: cis-$[\text{Co}(\text{Me}_2[14] \text{ diene})\text{CO}_3][\text{ClO}_4]$ · 1.5 $\text{H}_2\text{O}(0.1g)$ was dissolved in the minimum volume of perchloric acid (0.5 mol dm⁻³) and the solution heated on a water bath for ca 5 minutes. The solution was then allowed to stand at room temperature for ca one week, during which time reddish-green crystals began to appear. The product was filtered off, washed with cold ethanol then ether and dried in vacuo
(Found: C, 22.6; H, 4.9; N, 8.4. Calc. for CoC₁₂H₂₈N₄O₁₄Cl₃ · 1.5 $\text{H}_2\text{O}$: C, 22.35; H, 4.85; N, 8.7%).

**Method (b)**: A solution of Me₂[14]diene.2HClO₄ (4.25g; 0.01 mol) in ethanol-water (50 cm³, 1:1 v/v) was added to a solution of Co(ClO₄)₂.6H₂O (3.66g, 0.01 mol) in ethanol-water (50 cm³, 1:1 v/v)
and the mixture heated on a steam-bath for ca 1 hour. During heating, air was passed through the mixture and this was continued for a further 3 hours. The mixture was filtered and the filtrate made up to ca 30% in HClO₄ and heated for a further 0.5 hour. The volume of the solution was reduced on a rotary evaporator to ca 30 cm³ and the solution allowed to stand at room temperature. After several hours green crystals of the product appeared, which were filtered off, washed with cold ethanol, then ether and finally dried in vacuo. (Found: C, 21.9; H, 4.70; N, 8.6. Calc. for Co₁₂H₂₈N₄O₄Cl₃.2H₂O: C, 22.05; H, 4.90; N, 8.60%).

Cis-carbonato-C-meso-(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane)cobalt(III) Chloride Monohydrate; cis-[Co(Me₂(cyclam)CO₃].Cl.H₂O.

To a solution of the ligand Me₂(cyclam).4HCl (2.1g) in water (20 cm³) sodium triscarbonatocobaltate (2.5g) was gradually added with stirring. The resultant solution was heated on a steam-bath for 15 minutes. The red solution was cooled to room temperature and filtered. Ethanol and acetone were then added in excess and the solution was left in the refrigerator overnight. The red-violet product was filtered off and recrystallized from methanol. Calc. for Co₁₃N₄Cl₁₃H₃₀O₄: C, 38.95; H, 7.3; N, 14.0. (Found: C, 39.00; H, 7.54; N, 14.10%).
Trans-dichloro-C-meso-(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane)cobalt(III) Perchlorate; C-meso-[Co(Me₂(cyclam)Cl₂][ClO₄].

Sodium tris(carbonato)cobaltate(III) (2g, 5.5 mmol) and the ligand C-meso-Medcyclam) (1.3g, 5.7 mmol) were mixed in methanol-water (100 cm³, 1:1 v/v) and heated on a steam-bath for half an hour. Concentrated hydrochloric acid (20 cm³) was added to the red solution and the volume reduced on a steam-bath. The green product obtained by adding a saturated solution of sodium perchlorate followed by cooling in an ice-bath. The product was filtered off and recrystallised from hot methanol. Calc. for CoC_{12}N_{4}O_{6}Cl_{2}H_{28}: C, 31.5; H, 6.2; N, 12.2%. Found: C, 31.8; H, 6.4; N, 12.0%.

Attempted preparation of trans-diaquo-C-meso-(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane)cobalt(III) Perchlorate Monohydrate; trans[Co(Me₂(cyclam)(H₂O)₂][ClO₄]₃.H₂O.

A solution of the ligand C-meso-Me₂(cyclam) (1.2g., 5 mmoles) in ethanol-water (40 cm³, 1:1 v/v) was added to a solution of Co(ClO₄)₂·6H₂O (1.9g, 5 mmoles) in ethanol-water (40 cm³, 1:1 v/v) and the mixture heated on a steam-bath for ca 1 hour. During heating air was passed through the mixture and this was continued for a further 2 hours. The mixture was filtered and the filtrate made up to ca 30% in HClO₄ and heated for a further half hour. The volume of the solution was reduced on a rotary-evaporator to ca 20 cm³. After long
standing in the refrigerator (3 days) green crystals began to appear. These were collected by filtration and recrystallised from dilute perchloric acid. The electronic spectrum of this compound suggests that it is not isomerically pure. Calc. for CoC₁₂N₄Cl₃·1.5H₃₄: C, 22.53; H, 5.36; N, 8.76; Found: C, 22.80; H, 5.35; N, 8.81%.

Cis-dichloro(1,4,7,10-tetra-azacyclododecane)-cobalt(III) Chloride; cis[Co(cyclen)Cl₂].Cl.

Cyclen was prepared, as its tetrahydrochloride salt, as discussed later (see Appendix I); cis-[Co(cyclen)Cl₂]Cl was prepared as follows. The ligand cyclen.₄HCl (1g, 3.1 mmoles) was dissolved in methanol-water (100 cm³; 1:1 v/v) and trisodium tris(carbonato)cobaltate(III) trihydrate (1.14g, 3.1 mmol) added. The mixture was heated on a water-bath for 0.5 hour. The solution was filtered hot and concentrated HCl (7 cm³) added to the reddish solution, and the volume reduced on a steam bath. Purple-violet crystals of the product were obtained on cooling in an ice-bath. The complex was recrystallised from methanol. Calc. for CoC₈H₂₀N₄Cl₃; C, 28.5; H, 6.0; N, 16.6; Cl, 31.5. Found: C, 28.4; H, 6.1; N, 16.4; Cl, 31.3%.

Cis-carbonato(1,4,7,10-tetra-azacyclododecane)-cobalt(III) Chloride Dihydrate; cis[Co(cyclen)CO₃].Cl.2H₂O

This complex was prepared via two routes, (a) by reacting the ligand cyclen.₄HCl with sodium tris(carbonato)-
cobaltate(III) trihydrate (0.57 g, 1.6 mmol) was added. The solution was then heated on a steam bath for 0.5 hours and filtered hot. The volume of the filtrate reduced to about 10 cm$^3$. The product was crystallised by careful addition of ethanol and acetone and cooling in the refrigerator overnight. The product was filtered off and recrystallised from ethanol-water. Yield 97.5% ($\lambda_{\text{max}}$ 370 nm (170), 530 nm (224), Lit. $\lambda_{\text{max}}$ 368 (210), 530 (280)). Method (b) A solution of cis$[\text{Co(cyclen)}\text{Cl}_2] \cdot \text{Cl}$ (0.27 g, 0.8 mmol) and Li$_2$CO$_3$ (0.15 g, 2 mmol) in water (15 cm$^3$) was heated for six hours on a steam bath at 85°C. Calcium chloride (0.12 g, 1.1 mmol) was added, and the mixture was allowed to stand overnight. The calcium carbonate was removed by filtration, and the filtrate was then concentrated to about 2 cm$^3$. Upon careful addition of 4 mls of ethanol and 4 mls of acetone, a purple-red product isolated. This was filtered off, washed with ether, and recrystallised from water-ethanol. Calc. for Co$_4$H$_2$C$_9$ClO$_4$: C, 29.80; H, 6.7; N, 15.44; Found: C, 29.40; H, 6.4; N, 15.12%).

Cis$\alpha$-carbonato-(3,6-dimethyl-1,8-diamino-3,6-diazaoctane)cobalt(III) Perchlorate and cis$\beta$-carbonato-(3,6-dimethyl-1,8-diamino-3,6-diazaoctane)cobalt(III) Perchlorate Monohydrate.

These two complexes were kindly supplied by Dr. G. H. Searle. The complexes were prepared as previously described. (Found: C, 29.4; H, 6.2; Cl, 8.9; Co, 14.7; N, 15.93.

Calc. for cis$\beta$-[Co(C$_8$H$_{22}$N$_4$)CO$_3$][ClO$_4$]$_2$H$_2$O, C, 26.3; H, 5.9;
Cl, 8.6; Co, 14.4; N, 13.6%. Found: C, 27.6; H, 5.7; Cl, 9.3; N, 14.3. Calc. for cis-[Co(C$_8$H$_{22}$N$_4$)$_2$CO$_3$][ClO$_4$], C, 27.5; H, 5.6; Cl, 9.0; N, 14.3%.

1.3 **Kinetics**

The kinetics of decarboxylation of cis[Co(Me$_2$[14]-diene)CO$_3$][ClO$_4$] 1.5 H$_2$O, C-meso-cis[Co(Me$_2$(cyclam)CO$_3$]Cl.H$_2$O, cis[Co(cyclen)CO$_3$]Cl.2H$_2$O, cis-[Co(dmtr)CO$_3$][ClO$_4$] and cis-$eta$-[Co(dmtr)CO$_3$][ClO$_4$] .H$_2$O were monitored spectrophotometrically by following the decrease in absorbance at 280 nm, 530 nm, 530 nm, 320 nm and 370 nm respectively. The reactions were initiated by addition of a small amount of the solid complex (on a "plumper") to the appropriate thermostatted solution. The concentration of the complexes was ca 10$^{-3}$ mol dm$^{-3}$. Reactions were normally carried out either triplicate or duplicate (depending on the availability of the material in study), and plots of log($A_t - A_0$) were linear in all cases. Values of $k_{obs}$ (the observed rate constant at constant hydrogen ion concentration) were obtained from these plots. Values of $k_{obs}$ within each kinetic measurement were in close agreement. The reactions were carried out with either perchloric acid or nitric solutions as appropriate. These solutions were adjusted to the required ionic strength (0.5 or 1 mol dm$^{-3}$) with sodium perchlorate in the case of perchloric acid solutions or with potassium nitrate in the case of nitric acid solutions. The concentration of all the acid solutions was determined by titration with standard sodium hydroxide solution. The solvent
deuterium isotope effect studies were carried out using 0.5 mol dm$^{-3}$ DC1 in D$_2$O. The DC1 solutions were prepared by diluting deuterium chloride (20% solution in D$_2$O with isotopic purity > 99%) with the appropriate volume of D$_2$O (isotopic purity 99.8%). In the case of cis$\alpha$ and cis$\beta$-[Co(dmtr)CO$_3$][ClO$_4$] the ionic strength of the DC1 solution was adjusted to 1.0 mol dm$^{-3}$ with potassium chloride. The comparative experiments were carried out using 0.49 or 0.50 mol dm$^{-3}$ hydrochloric acid solutions (adjusted to an ionic strength of 1.0 mol dm$^{-3}$ with potassium chloride in the case of cis$\alpha$- and cis$\beta$-[Co(dmtr)CO$_3$][ClO$_4$]). The HCl and DC1 solutions were standardised with standard sodium hydroxide solutions. Kinetic measurements were carried out with a Gilford 2400S instrument, the cell temperature being maintained to within 0.05°C by circulating water through a metal cell block holder. The temperature was monitored throughout the reactions. Routine spectral measurements, including interval scan spectra were carried out with a Perkin-Elmer 402 instrument.
The acid-catalysed decarboxylation of \( \text{cis-}[\text{Co(Me}_2\text{[14] diene})\text{CO}_3]^+ \). 

**Results**

The complex \( \text{cis-}[\text{Co(Me}_2\text{[14] diene})\text{CO}_3]^+ \) has \( \lambda_{\text{max}} \) 504 nm (\( \epsilon = 133 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \)) and \( \lambda_{\text{max}} \) 360 nm (\( \epsilon = 167 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \)).\(^{15}\) In acidic solution (0.1 - 0.5 mol dm\(^{-3}\) HClO\(_4\)) the absorbance decreases with time at both wavelengths, with the band at 504 nm moving to ca 490 nm. The resulting spectrum is consistent with the formation of a cis-diaquo complex, Fig. 1(a). Thus \( \text{cis-}[\text{Co(cyclam)}(\text{H}_2\text{O})_2]^3+ \) has \( \lambda_{\text{max}} \) 506 nm (\( \epsilon = 110 \)) and \( \lambda_{\text{max}} \) 367 nm (\( \epsilon = 99 \)).\(^{16}\) This relatively rapid reaction is followed by a much slower reaction, in which the absorbance decreases with time, suggesting isomerisation to the trans-diaquo complex, Fig. 1(b). The final product has \( \lambda_{\text{max}} \) 362 nm (\( \epsilon = 79 \)), 424 nm (\( \epsilon = 49 \)) and 564 nm (\( \epsilon = 27 \)). This spectrum is identical to that of an authentic sample of \( \text{trans-}[\text{Co(Me}_2\text{[14] diene})(\text{H}_2\text{O})_2]^3+ \) which has \( \lambda_{\text{max}} \) 362 nm (\( \epsilon = 77 \)), 424 nm (\( \epsilon = 48 \)) and 564 (\( \epsilon = 26 \)), Table 1.

The spectral changes are thus consistent with the reaction scheme,

\[
\begin{align*}
\text{cis-}[\text{Co(Me}_2\text{[14] diene})\text{CO}_3]^+ & \xrightarrow{\text{H}^+} \text{cis-}[\text{Co(Me}_2\text{[14] diene})(\text{OH}_2)_2]^3+ \\
\text{cis-}[\text{Co(Me}_2\text{[14] diene})(\text{H}_2\text{O})_2]^3+ & \xrightarrow{\text{trans-}[\text{Co(Me}_2\text{[14] diene})(\text{H}_2\text{O})_2]^3+}
\end{align*}
\]

The kinetics of the acid-catalysed ring opening step were monitored spectrophotometrically using the decrease in
Figure 1(a). Absorbance changes for the acid-catalysed decarboxylation of \( \text{cis-[Co(Me}_2\text{14} \text{ diene})CO}_3 \)\(^+\) in 0.2 mol dm\(^{-3}\) HNO\(_3\) at 25\(^\circ\)C. (First reaction: \( \text{cis-[Co(Me}_2\text{14} \text{ diene})CO}_3 \)\(^+\) → \( \text{cis-[Co(Me}_2\text{14} \text{ diene})(H}_2\text{O})_2 \)\(^{3+}\)).
Figure 1(b). Absorbance changes for the acid-catalysed decarboxylation of cis-[Co(Me,J diene)CO] in 0.2 mol dm$^{-3}$ HNO$_3$ at 25°C. (Second reaction: cis-[Co(Me$_2$14) diene]($H_2O$)$_2$ $\rightarrow$ trans-[Co(Me$_2$14) diene]($H_2O$)$_2^{3+}$. 27
TABLE 1

Electronic Absorption Spectra\(^a\) of some cis and trans cobalt(III) complexes of macrocyclic ligands.

<table>
<thead>
<tr>
<th>Complex(^b)</th>
<th>d-d bands</th>
<th>Reference</th>
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<tbody>
<tr>
<td>cis-[Co(Me(<em>{14}) diene)Co(</em>{3})](^+)</td>
<td>504(133)</td>
<td>15</td>
</tr>
<tr>
<td>cis-[Co(Me(<em>{14}) diene)(H(</em>{2})O)(_{2})](^3+)</td>
<td>490(^c)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>362</td>
<td></td>
</tr>
<tr>
<td>cis-[Co(cyclam)(H(<em>{2})O)(</em>{2})](^3+)</td>
<td>506(110)</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>367(99)</td>
<td></td>
</tr>
<tr>
<td>trans-[Co(Me(<em>{14}) diene)(H(</em>{2})O)(_{2})](^3+),(^d)</td>
<td>364(27)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>424(49)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>362(79)</td>
<td></td>
</tr>
<tr>
<td>trans-[Co(Me(<em>{14}) diene)(H(</em>{2})O)(_{2})](^3+),(^e)</td>
<td>564(26)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>424(48)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>362(77)</td>
<td></td>
</tr>
</tbody>
</table>

\(a = \) Band maxima in nm; extinction coefficients (\(\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}\)) in parentheses.

\(b = \) Spectra recorded in aqueous solutions unless otherwise stated.

\(c = \) Extinction coefficients not measured, band maxima obtained from Fig.1(a).

\(d = \) Complex prepared by acid-catalysed ring opening, see experimental, method (a).

\(e = \) Complex prepared by direct synthesis, see method (b).
absorbance at 280nm. As the isomerization reaction is very slow, it was possible to obtain values of \( A_m \) (\( A_m \) represents the absorbance at completion of the reaction) with little difficulty. The acid-catalysed aquation was studied over the range of perchloric acid concentrations 0.1-0.5 mol dm\(^{-3}\) at \( I = 0.5 \text{ mol dm}^{-3} \), adjusted with sodium perchlorate. Values of \( k_{\text{obs}} \) (the observed first order rate constant at constant hydrogen ion concentration) were obtained from plots of log \( (A_t-A_m) \) against time (\( A_t \) represents absorbance at time \( t \)). The plots were linear in every case. A typical kinetic plot is shown in Fig. 2. The rate constants (\( k_{\text{obs}} \)) at 25\(^\circ\)C, 34.8\(^\circ\)C and 45.4\(^\circ\)C are listed in Table 2. Values of \( k_{\text{obs}} \) are almost directly proportional to \( [H^+] \) over the acidity range studied, Fig. 3, indicating that \( k_o \) does not make a significant contribution to the overall reaction. Linear regression analysis gives \( k_1 = 1.46 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and \( k_o = 7.5 \times 10^{-5} \text{ s}^{-1} \) at 25\(^\circ\)C. At the acidities used in the present study it is difficult to determine \( k_o \) with any degree of precision. Attempts to determine \( k_o \) at lower acidities were frustrated by the cis - trans isomerization reaction of the diaquo-species. Dasgupta\(^6\) has reported a small contribution from \( k_o \) in the ring opening of \([\text{Co(cyclam)C}_2\text{O}_3]\)^+ where \( k_o = 2.5 \times 10^{-4} \text{ s}^{-1} \) and \( k_1 = 7.1 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 40\(^\circ\)C. The requisite constants \( k_1 \) at 34.8\(^\circ\)C and 45.4\(^\circ\)C are \( 4.25 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and \( 12.89 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). Activation parameters for the acid-catalysed pathway were determined from the temperature dependence of the \( k_1 \) rate constants, Fig. 4. The rate parameters derived from Fig. 4 are
Figure 2. Kinetic plot for the acid-catalysed decarboxylation of the complex \text{cis-}[\text{Co}(\text{Me}_2[14\text{diene}])\text{CO}_3]^+ in 0.3 \text{ mol dm}^{-3} \text{HClO}_4, I = 0.5 \text{ mol dm}^{-3} \text{ at } 25^\circ\text{C}
**TABLE 2**

Kinetic data for the acid-catalysed aquation of cis-[Co(Me2[14]diene)(CO3)]+ at I = 0.5 mol dm⁻³ (NaClO4)*

<table>
<thead>
<tr>
<th>Temp.</th>
<th>[HClO₄] / mol dm⁻³</th>
<th>10⁵kₑₒₒᵱ/s⁻¹⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.099</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>0.196</td>
<td>2.90</td>
<td></td>
</tr>
<tr>
<td>0.320</td>
<td>4.78</td>
<td></td>
</tr>
<tr>
<td>0.400</td>
<td>5.93</td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>7.33</td>
<td></td>
</tr>
<tr>
<td>k₁ = 1.46 x 10⁻² dm³ mol⁻¹ s⁻¹⁺</td>
<td>kₒ = 7.5 x 10⁻⁵ s⁻¹⁺</td>
<td></td>
</tr>
<tr>
<td>34.8°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>2.55</td>
<td></td>
</tr>
<tr>
<td>0.099</td>
<td>4.73</td>
<td></td>
</tr>
<tr>
<td>0.151</td>
<td>7.49</td>
<td></td>
</tr>
<tr>
<td>0.196</td>
<td>9.38</td>
<td></td>
</tr>
<tr>
<td>0.250</td>
<td>10.98</td>
<td></td>
</tr>
<tr>
<td>0.320</td>
<td>12.76</td>
<td></td>
</tr>
<tr>
<td>0.400</td>
<td>18.65</td>
<td></td>
</tr>
<tr>
<td>k₁ = 4.25 x 10⁻² dm³ mol⁻¹ s⁻¹⁺</td>
<td>kₒ = 6.34 x 10⁻⁴ s⁻¹⁺</td>
<td></td>
</tr>
<tr>
<td>45.4°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>7.07</td>
<td></td>
</tr>
<tr>
<td>0.099</td>
<td>15.36</td>
<td></td>
</tr>
<tr>
<td>0.151</td>
<td>20.33</td>
<td></td>
</tr>
<tr>
<td>0.196</td>
<td>25.40</td>
<td></td>
</tr>
<tr>
<td>0.250</td>
<td>35.04</td>
<td></td>
</tr>
<tr>
<td>0.320</td>
<td>42.84</td>
<td></td>
</tr>
<tr>
<td>k₁ = 12.89 x 10⁻² dm³ mol⁻¹ s⁻¹⁺</td>
<td>kₒ = 1.59 x 10⁻³ s⁻¹⁺</td>
<td></td>
</tr>
</tbody>
</table>

For k₁, ΔH* = 82.9 kJ mol⁻¹, ΔS*₂₉₈ = -0.4 JK⁻¹ mol⁻¹, ΔG*₂₉₈ = 83.0 kJ mol⁻¹

* Values of k₁ and kₒ were obtained by linear regression analysis, the kₒ constants are subject to considerable error.
+ Mean of three kinetic runs.
Figure 3. Plot of $k_{obs}$ versus the perchloric acid concentration at the indicated temperatures for the acid-catalysed decarboxylation of cis-$\text{Co}($Me$_2$[14]diene)$\text{CO}_3^+$, $I = 0.5$ mol dm$^{-3}$.
Figure 4. Temperature dependence of $k_r$ for the acid-catalysed decarboxylation of cis-[Co(Fe$_2$[14]dien)$_2$CO$_3$]$. 
\[ \Delta H^\ddagger = 82.9 \text{ kJ mol}^{-1} \text{ and } \Delta S^\ddagger_{298} = -0.47 \text{ JK}^{-1} \text{ mol}^{-1}, \text{ Table 2}. \]

At 25°C, the rate of the acid-catalysed aquation of \( \text{cis-}[\text{Co(Me}_2 14\text{ diene})\text{CO}_3]^+ \) is \( \text{ca} \) twice that for \( \text{cis-}[\text{Co(Me}_6 14\text{ diene})\text{CO}_3]^+ \) and \( \text{ca} \) 11.5 times faster than for \( \text{cis-}[\text{Co(cyclam)}\text{CO}_3]^+ \).

In order to clarify the mechanism of the decarboxylation (see later for details), the solvent deuterium isotope effect was determined. For solutions \( \text{ca} 0.5 \text{ mol dm}^{-3} \) in hydrogen ion at 25°C, the value of \( k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.6 \), Table 3, fully consistent with a rapid pre-equilibrium protonation mechanism.
### TABLE 3

Solvent deuterium isotope effect for cis-[Co(Me$_2$[14]diene)(CO$_3$)]$^+$ at 25°C.

<table>
<thead>
<tr>
<th>[HCl]/mol dm$^{-3}$</th>
<th>$10^2k_{obs}/s^{-1}$</th>
<th>$10^2k_{obs}/[H^+]/dm^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.493</td>
<td>8.3*</td>
<td>1.63</td>
</tr>
<tr>
<td>[DC1]/mol dm$^{-3}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.545</td>
<td>23.7*</td>
<td>4.35</td>
</tr>
</tbody>
</table>

$k_{D_2O}/k_{H_2O} = 2.6$

* Mean of three kinetic runs.
1.5 The acid-catalysed decarboxylation of cis-carbonato-C-meso-(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane)cobalt(III); cis-[Co(Me₂cyclam)CO₃]⁺.

Results

The ligand C-meso-Me₂cyclam(IV) is the saturated analogue of Me₂[14]diene. Differences might be expected in

(IV)

C-meso-Me₂cyclam
the reactivity of the two complexes since the unsaturated ligand could possibly stabilise 5-coordinate intermediates by $d_{\pi}-p_{\pi}$ bonding and so accelerate the reaction. Thus, for this reason the saturated derivative was studied.

The complex cis-$[\text{Co(Me}_2\text{cyclam)}\text{CO}_3]^+$ was prepared by reacting C-meso-$\text{Me}_2\text{cyclam}$.$4\text{HCl}$ with sodium tris(carbonato)-cobaltate(III). The complex has $\lambda_{\text{max}}$ 530nm ($\epsilon = 202$) and 378nm ($\epsilon = 176$) for the visible spectrum. The infrared spectrum has bands at 3060 cm$^{-1}$ $\nu$(NH); 1660 and 1635 cm$^{-1}$ $\nu$(CO non-bonded); 1250, 810 and 750 cm$^{-1}$ ($\delta$(CO) + $\nu$(CO)) consistent with chelate carbonate.$^{19,20}$ Attempts to synthesise a sample of trans-$[\text{Co(Me}_2\text{cyclam)}(\text{H}_2\text{O})_2]^3+$ for product analysis purposes (see experimental) gave a product whose electronic spectrum had $\lambda_{\text{max}}$ 460nm ($\epsilon = 413$) and 565nm (33), values which indicated a mixture of cis and trans isomers. However, a sample of trans-$[\text{Co(Me}_2\text{cyclam)}(\text{H}_2\text{O})_2]^3+$ was prepared by reacting the trans-$[\text{Co(Me}_2\text{cyclam)}\text{Cl}_2]^+$ with sodium hydroxide followed by addition of a few drops of concentrated perchloric acid.

The visible spectrum of this complex has band maxima at 464 ($\epsilon = 54$) and 620nm ($\epsilon = 40$). In acidic solutions (0.1 - 0.5 mol dm$^{-3}$ $\text{HNO}_3$) the absorbance of the complex cis-$[\text{Co(Me}_2\text{cyclam)}\text{CO}_3]^+$ decreases with time at both wavelengths (530 and 378nm). The resulting spectrum is consistent with the formation of a cis-diaquo complex. Thus cis-$[\text{Co(Me}_2\text{cyclam)}(\text{H}_2\text{O})_2]^3+$ has $\lambda_{\text{max}}$ 526nm ($\epsilon = 98$) and 376nm ($\epsilon = 116$), Fig.5. This rapid reaction is followed by a relatively slow reaction, in which the
Figure 5. Absorbance changes for the acid-catalysed decarboxylation of cis-[Co(Me₂cyclam)CO₃]⁺ in 0.5 mol dm⁻³ HNO₃ at 25°C.
absorbance decreases with time, suggesting isomerization to the trans-diaquo complex. The final product has \( \lambda_{\text{max}} \) 465 nm and 620 nm, Fig.5. This spectrum is identical to that of the trans-[Co(Me\(_2\)cyclam)(H\(_2\)O)\(_2\)]\(^{3+}\) prepared from the trans-dichloro complex. The spectral changes are consistent with the reaction scheme:

\[
\text{cis-[Co(}Me_2\text{cyclam)CO}_3\text{]}^+ + H^+ \rightarrow \text{cis-[Co(}Me_2\text{cyclam)}(OH_2)_2\text{]}^{3+}
\]

\[
\text{cis-[Co(}Me_2\text{cyclam)}(H_2O)_2\text{]}^{3+} \rightarrow \text{trans-[Co(}Me_2\text{cyclam)}(H_2O)_2\text{]}^{3+}
\]

The kinetics of the acid-catalysed ring opening step were monitored spectrophotometrically using the decrease in absorbance at 530 nm, Fig.5. As the isomerisation reaction is relatively slow, it was possible to obtain values of \( A_{\text{max}} \) with little difficulty. The acid-catalysed aquation was studied over the range of nitric acid concentrations 0.1 - 0.5 mol dm\(^{-3}\) at \( I = 0.5 \) mol dm\(^{-3}\), adjusted with potassium nitrate. The complex precipitates as the perchlorate salt in perchloric acid solutions and hence nitric acid was used to prepare the solutions. Values of \( k_{\text{obs}} \) were obtained from plots of \( \log(A_t-A_w) \) which were linear in every case. A representative kinetic plot is shown in Fig.6. The rate constants \( k_{\text{obs}} \) at 35°C are listed in Table 4. Values of \( k_{\text{obs}} \) are almost directly proportional to \([H^+]\) over the acidity range studied, Fig.7. Linear regression analysis gives \( k_1 = 1.58 \times 10^{-3} \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) and \( k_2 = 1.47 \times 10^{-5} \) s\(^{-1}\) at 35°C. As the cis-trans isomerization reaction becomes faster at higher
Figure 6. Kinetic plot for the acid-catalysed decarboxylation of $\text{cis-}[\text{Co(Me}_2\text{cyclam})\text{CO}_2]^+$ in 0.4 mol dm$^{-3}$ HNO$_3$, $I = 0.5$ mol dm$^{-3}$ at 35°C.
**TABLE 4**

Kinetic data for the acid-catalysed aquation of cis-[Co(Me₂cyclam)CO₃]⁺ at I = 0.5 mol dm⁻³ and temperature 35°C.

<table>
<thead>
<tr>
<th>[HNO₃]/mol dm⁻³</th>
<th>10⁴k_{obs}/s⁻¹*</th>
<th>10⁴k_{obs}/[H⁺] dm³ mol⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>1.63</td>
<td>16.25</td>
</tr>
<tr>
<td>0.20</td>
<td>3.1</td>
<td>15.50</td>
</tr>
<tr>
<td>0.294</td>
<td>4.6</td>
<td>15.65</td>
</tr>
<tr>
<td>0.40</td>
<td>6.35</td>
<td>15.87</td>
</tr>
<tr>
<td>0.50</td>
<td>7.92</td>
<td>15.84</td>
</tr>
</tbody>
</table>

Average $k_{1} = 1.58 \times 10^{-3}$ dm³ mol⁻¹ s⁻¹

By linear regression analysis: $k_{1} = 1.58 \times 10^{-3}$ dm³ mol⁻¹ s⁻¹

$k_{o} = 1.47 \times 10^{-6}$ s⁻¹

* Mean of three kinetic measurements.
Figure 7. Plot of $k_{obs}$ versus the nitric acid concentration at 35°C for the acid-catalysed decarboxylation of cis-Co(Me$_2$cyclam)CO$_3$$^+$, $I$ = 0.5 mol dm$^{-3}$. 
temperature, it was not possible to determine the activation parameters, since it becomes difficult to obtain precise values of $A_\text{log}$. At $35^\circ\text{C}$ the rate of the acid-catalysed aquation of the cis-$\text{[Co(Me}_2\text{[14]dieneco}_3\text{]}^+$ is ca 27 times faster than the rate of cis-$\text{[Co(Me}_2\text{cyclamco}_3\text{]}^+$, consistent with the view that the unsaturated ligand could stabilise 5-coordinate intermediates by $d_\pi-p_\pi$ bonding.$^{21,22}$
1.6 The acid-catalysed decarboxylation of cis-carbonato-
(1,4,7,10-tetra-azacyclododecane)cobalt(III);
cis-[Co(cyclen)CO$_3$]$^+$. The ligand cyclen (V) forms only cis-complexes
with cobalt(III) and rhodium(III). This stereochemistry
arises due to the small "hole size" of the 12-membered ring.

Previous studies of the decarboxylation of carbonato
complexes have been limited to macrocycles with 14-membered
rings. Thus it is of interest to study the effect of
ring size on these reactions. The smaller ring might be
expected to lead to a degree of strain in the complex which
could be released on forming dissociative transition state,
and thus lead to more rapid decarboxylation. In addition the
reaction is not complicated by any subsequent isomerization of the cis-diaquo complex to the trans-isomer, which occurs with the 14-membered ring systems,\(^1,^6\) (see the previous examples, 1.4 and 1.5).

**Results**

The complex cis-[Co(cyclen)Cl\(_2\)]Cl was prepared by reacting cyclen.\(4\)HCl with sodium tris(carbonato)cobaltate(III) in methanol-water solution. The spectrum of the product has \(\lambda_{\text{max}}\) at 552 and 385\,nm, identical to that prepared by treating the corresponding dinitro-complex with concentrated HCl.\(^1\)

The reported method is time-consuming, since the dinitro-complex must first be prepared. Cis-[Co(cyclen)\(\text{CO}_3\)]\(^+\) was prepared by two methods, (a) by reacting the cyclen.\(4\)HCl with sodium tris(carbonato)cobaltate(III) and (b) by the published method of Collman and Schneider.\(^1\) Method (a)\(^+\) found to be more convenient and with a better yield (97.5%) while method (b) yields only ca 52%. The spectra of the products obtained by either method are identical, and have \(\lambda_{\text{max}}\) at 530 and 370\,nm.

For the product of method (a) \(\lambda_{\text{max}}\) 370\,nm (\(\varepsilon = 170\)) and 530\,nm (\(\varepsilon = 224\)); lit. \(\lambda_{\text{max}}\) 368 (\(\varepsilon = 210\)) and 530\,nm (\(\varepsilon = 280\)).\(^1\)

The kinetics of the acid-catalysed ring-opening step were monitored spectrophotometrically using the decrease in absorbance at 530\,nm, Fig.8. The reactions were carried out with nitric acid solutions, since the complex precipitates as the perchlorate salt in perchloric acid solutions; nitric acid solutions were adjusted to \(I = 0.5\,\text{mol dm}^{-3}\) with KNO\(_3\). Values
Figure 8. Absorbance changes for the acid-catalysed decarboxylation of
\( \text{cis}-\text{Co(cyclen)CO}_3^+ \) in 0.2 mol dm\(^{-3}\) HNO\(_3\) at 25°C.
of the observed first order rate constants \( k_{\text{obs}} \) at constant hydrogen concentration were obtained from plots of \( \log(A_t - A_\infty) \) versus time, which were linear for at least three half lives. A representative kinetic plot is shown in Fig.9. Values of the observed first order rate constants determined at various hydrogen ion concentrations and temperatures 25°, 35.4° and 45°C are listed in Table 5. Plots of \( k_{\text{obs}} \) versus the concentration of HNO₃ are linear and exhibit small positive intercepts, Fig.10. The rate expression takes the form

\[
k_{\text{obs}} = k_o + k_1[H^+].
\]

The \( k_o \) values are subject to very large errors and are therefore not considered. The \( k_1 \) values (obtained by least squares analysis) are quite precise, and these constants are listed in Table 5 with the appropriate correlation coefficients. The requisite values of \( k_1 \) are 7.03 \( \times \) 10⁻³, 2.68 \( \times \) 10⁻² and 9.69 \( \times \) 10⁻² dm³ mol⁻¹ s⁻¹ at 25°, 35.4° and 45°C respectively. The activation parameters were obtained from the plot of the temperature dependence of \( k_1 \) rate constants, Fig.11, and \( \Delta H^* \) and \( \Delta S^*_{298} \) values are 100.4 kJ mol⁻¹ and +51 JK⁻¹ mol⁻¹ respectively. At 25°C the complex cis-[Co(cyclen)CO₃]⁺ undergoes acid-catalysed ring opening some 5 times faster than cis-[Co(cyclam)CO₃]⁺ where

\[
k_1 = 1.3 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.
\]

Solvent deuterium isotope effect for the acid-catalysed decarboxylation of cis-[Co(cyclen)CO₃]⁺ was studied. For solutions ca 0.5 mol dm⁻³ in hydrogen ion at 25°C, the value of \( k_{D_2O}/k_{H_2O} \) is 2.05, Table 6.
Figure 9. Kinetic plot for the acid-catalysed decarboxylation of cis-[Co(cyclen)CO$_3$]$^+$ in 0.2 mol dm$^{-3}$ HNO$_3$, I = 0.5 mol dm$^{-3}$ at 25°C.
### TABLE 5

Acid-catalysed decarboxylation of cis-[Co(cyclen)CO]⁺
in nitric acid solutions at I = 0.5 mol dm⁻³ (KNO₃)⁺

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25°C</th>
<th>35.4°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HNO₃] mol dm⁻³</td>
<td>10³ kₗ,obs</td>
<td>10³ kₗ,obs</td>
<td>10³ kₗ,obs</td>
</tr>
<tr>
<td>0.10</td>
<td>0.80</td>
<td>0.05</td>
<td>1.42</td>
</tr>
<tr>
<td>0.20</td>
<td>1.67</td>
<td>0.10</td>
<td>3.02</td>
</tr>
<tr>
<td>0.294</td>
<td>2.21</td>
<td>0.15</td>
<td>4.21</td>
</tr>
<tr>
<td>0.40</td>
<td>2.94</td>
<td>0.20</td>
<td>6.24</td>
</tr>
<tr>
<td>0.50</td>
<td>3.68</td>
<td>0.295</td>
<td>8.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[HNO₃] mol dm⁻³</th>
<th>10³ kₗ,obs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.65</td>
</tr>
<tr>
<td>0.03</td>
<td>2.10</td>
</tr>
<tr>
<td>0.05</td>
<td>3.83</td>
</tr>
<tr>
<td>0.10</td>
<td>8.68</td>
</tr>
<tr>
<td>0.15</td>
<td>14.10</td>
</tr>
<tr>
<td>0.40</td>
<td>10.78</td>
</tr>
</tbody>
</table>

kₗ = 7.03x10⁻³ dm³ mol⁻¹ s⁻¹ (corr. coef. = 0.998)
kₗ = 2.68x10⁻² dm³ mol⁻¹ s⁻¹ (corr. coef. = 0.996)
kₗ = 9.69x10⁻² dm³ mol⁻¹ s⁻¹ (corr. coef. = 0.998)

For kₗ, Δ𝐻⁺ = 100.4 kJ mol⁻¹, Δ𝑆⁺₂₉₈ = + 51 JK⁻¹ mol⁻¹,
Δ𝐺₂₉₈ = 85.2 kJ mol⁻¹

* Each kinetic measurement was carried out in duplicate, mean values of the rate constants are quoted.
Figure 10. Plot of $k_{obs}$ versus the nitric acid concentration at the indicated temperatures for the acid-catalysed decarboxylation of Co(II)cyclenCo(III).
Figure 11. Temperature dependence of $k_1$ for the acid-catalysed decarboxylation of cis-$\text{Co}(\text{cyclen})\text{CO}_3^+$.
**TABLE 6**

Solvent deuterium isotope effects for the acid-catalysed decarboxylation of cis-[Co(cyclen)CO$_3$]+.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$[\text{DCl}]$</th>
<th>$k_{\text{obs}}$</th>
<th>$k_{\text{obs}}/[\text{H}^+]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol dm$^{-3}$</td>
<td>s$^{-1}$</td>
<td>dm$^3$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>DC1/D$_2$O solvent at 25°C</td>
<td>0.545</td>
<td>7.33 x 10$^{-3}$</td>
<td>13.45 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$[\text{HCl}]$</th>
<th>$k_{\text{obs}}$</th>
<th>$k_{\text{obs}}/[\text{H}^+]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol dm$^{-3}$</td>
<td>s$^{-1}$</td>
<td>dm$^3$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>HCl/H$_2$O solvent at 25°C</td>
<td>0.500</td>
<td>3.29 x 10$^{-3}$</td>
<td>6.58 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

$k_{\text{D}2\text{O}}/k_{\text{H}2\text{O}} = \frac{13.45 \times 10^{-3}}{6.58 \times 10^{-3}} = 2.05$

*No attempt has been made to correct for the small contribution of $k_o$ to values of $k_{\text{obs}}$. The contribution of the $k_o$ term to $k_{\text{obs}}$ at these acidities is only ca 5%.*
Hydrolysis of cis-[Co(cyclen)CO₃]⁺ in 50/50 (v/v) dioxane-water mixtures were carried out. The study could not be extended to higher dioxane concentrations due to solubility problems. For hydrolysis in 0.2 mol dm⁻³ HNO₃ at 25°C the value of $k_{obs}$ was $(1.43 \pm 0.03) \times 10^{-3}$ s⁻¹, while for the analogous reaction in dioxane-water $k_{obs} = (2.88 \pm 0.05 \times 10^{-3}$ s⁻¹) (average of four kinetic measurements).
1.7 The acid-catalysed decarboxylation of the cisα- and cisβ-
carbonato-(3,6-dimethyl-1,8-diamino-3,6-diazaoctane)-
cobalt(III) cations; cisα- and cisβ-[Co(dmtr)CO₃]⁺.

The cisα-carbonato(3,6-dimethyl-1,8-diamino-3,6-
diazaoctane)cobalt(III) perchlorate (VI) and cisβ-carbonato(3,6-
dimethyl-1,8-diamino-3,6-diazaoctane)cobalt(III) perchlorate
monohydrate (VII) were kindly supplied by Dr. G. H. Searle.
The two complexes were first prepared and characterised by
Francis and Searle,⁵ who also carried out a brief investigation
of the kinetics of the acid-catalysed decarboxylation at 25°C.
In the present study, the reaction has been investigated over
a wider range of perchloric acid concentrations and the
temperature dependence over the range 25, 35 and 45°C. Solvent
deuterium isotope effects and activation parameters for both
complexes have been determined.
Results

The kinetics of decarboxylation were monitored spectrophotometrically by following the decrease in absorbance at 320nm (cisα-isomer) and 370nm (cisβ-isomer), Fig.12(a) and (b). Normally the absorbance change was ca 0.6A for the cisα-isomer and ca 0.4A for the cisβ-isomer. Stable infinity absorbances were obtained from both complexes and there was no evidence for any subsequent isomerisation of the diaquo complexes under the conditions of the experiments. Values of $k_{\text{obs}}$ (the observed rate constant at constant hydrogen ion concentration) were obtained from plots of $\log(A_t-A_0)$ versus time and these plots were linear in all cases. Typical kinetic plots for the cisα- and cisβ-isomers are shown in Fig.13(a) and (b). Values of the observed first order rate constants ($k_{\text{obs}}$) determined at various hydrogen ion concentrations and the temperatures of 25°, 35° and 45°C are listed in Table 7 for the cisα- and cisβ-isomers. Plots of $k_{\text{obs}}$ against the hydrogen ion concentration are linear with small positive intercepts, Fig.14(a) and (b). The rate expression takes the form

$$k_{\text{obs}} = k_0 + k_1[H^+]$$

Least squares analysis of the data gave the values of $k_0$ and $k_1$ listed in Table 7. The $k_0$ values are subject to considerable error, since they make little contribution to $k_{\text{obs}}$, particularly in the higher temperature measurements. At 25°C in 0.5 mol dm$^{-3}$ HClO$_4$, $k_0$ contributes only ca 3% towards $k_{\text{obs}}$. Activation parameters for the acid-catalysed pathway were calculated from the temperature dependence of the $k_1$ rate constants, Fig.15(a) and (b), and these values are listed in
Figure 12. Absorbance changes for the acid-catalysed decarboxylation of cis-[Co(dmtr)CO]⁺ in 0.5 mol dm⁻³ HClO₄ at 25°C.
(a) cisα-isomer
(b) cisβ-isomer
Figure 13(a). Kinetic plot for the acid-catalysed decarboxylation of cis-[Co(dmtp)CO₃]⁺ in 0.5 mol dm⁻³ HClO₄, I = 1.0 mol dm⁻³ at 25°C.
Figure 13(b). Kinetic plot for the acid-catalysed decarboxylation of cis$^8$-[Co(dmtr)$\text{CO}_3]^+$ in 0.5 mol dm$^{-3}$ HClO$_4$, I = 1.0 mol dm$^{-3}$ at 25.4°C.
TABLE 7
Acid-catalysed decarboxylation of cisα- and cisβ-
[Co(dmtr)C03]+ in perchloric acid solutions at I = 1.0 mol dm$^{-3}$
(Na[C10$_4$])

<table>
<thead>
<tr>
<th></th>
<th>25.2°C k$^o$</th>
<th>35.4°C k$^o$</th>
<th>45.0°C k$^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H$^+$]/mol dm$^{-3}$</td>
<td>10$^3$ k$_{obs}$</td>
<td>10$^3$ k$_{obs}$</td>
<td>10$^3$ k$_{obs}$</td>
</tr>
<tr>
<td>mol dm$^{-3}$</td>
<td>s$^{-1}$</td>
<td>mol dm$^{-3}$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>0.049</td>
<td>1.14</td>
<td>0.049</td>
<td>3.83</td>
</tr>
<tr>
<td>0.10</td>
<td>2.27</td>
<td>0.10</td>
<td>6.81</td>
</tr>
<tr>
<td>0.20</td>
<td>4.75</td>
<td>0.20</td>
<td>13.29</td>
</tr>
<tr>
<td>0.29</td>
<td>6.16</td>
<td>0.29</td>
<td>18.96</td>
</tr>
<tr>
<td>0.40</td>
<td>8.44</td>
<td>0.40</td>
<td>27.25</td>
</tr>
<tr>
<td>0.50</td>
<td>10.37</td>
<td>0.50</td>
<td>32.14</td>
</tr>
</tbody>
</table>

$k^o = 3.1 \times 10^{-4}$ s$^{-1}$
$k^1 = 2.03 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$
(correl. coef. = 0.9985)

$k^o = 5.5 \times 10^{-4}$ s$^{-1}$
$k^1 = 6.43 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$
(correl. coef. = 0.9989)

$k^o = 1.6 \times 10^{-3}$ s$^{-1}$
$k^1 = 22.14 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$
(correl. coef. = 0.997)

*Each kinetic measurement was carried out in duplicate,
mean values of the rate constants are quoted.

Table 7 continued:
TABLE 7 (continued)

<table>
<thead>
<tr>
<th>cis 6-isomer</th>
<th>25.4°C</th>
<th>35.4°C</th>
<th>45.6°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H+] (mol dm⁻³)</td>
<td>10⁶ k_obs (s⁻¹)</td>
<td>[H+] (mol dm⁻³)</td>
<td>10³ k_obs (s⁻¹)</td>
</tr>
<tr>
<td>0.50</td>
<td>3.45</td>
<td>0.50</td>
<td>0.93</td>
</tr>
<tr>
<td>0.60</td>
<td>4.10</td>
<td>0.60</td>
<td>1.17</td>
</tr>
<tr>
<td>0.70</td>
<td>4.70</td>
<td>0.7</td>
<td>1.35</td>
</tr>
<tr>
<td>0.80</td>
<td>5.30</td>
<td>0.80</td>
<td>1.45</td>
</tr>
<tr>
<td>0.90</td>
<td>5.60</td>
<td>0.90</td>
<td>1.64</td>
</tr>
</tbody>
</table>

k₀ = 7.8 x 10⁻⁵ s⁻¹  
k₁ = 5.5 x 10⁻⁴ dm³ mol⁻¹ s⁻¹  
(corr. coef. = 0.993)
Figure 14(a). Plot of $k$ versus the perchloric acid concentration at the indicated temperatures for the acid-catalysed decarbonylation of $\text{Co}((\text{dtb})\text{O})_3^+$, $I = 1.0$ mol dm$^{-3}$. 
Figure 14(b). Plot of $k_{obs}$ versus the perchloric acid concentration at the indicated temperatures for the acid-catalysed decarboxylation of $\text{cis-}[\text{Co(dntr)}\text{CO}_3]^+$, $I = 1.0 \text{ mol dm}^{-3}$. 
Figure 15(a). Temperature dependence of $k$, for the acid-catalysed
decarboxylation of cis-[Co(dmtr)CO$_2$]$. 
Figure 15(b). Temperature dependence of $k_1$ for the acid-catalysed decarboxylation of cis-$\{\text{Co(dmtr)CO}_3\}^+$. 
Table 8. The values of $k_1$ are in close agreement with those of Francis and Searle, measured at 25°C and $I = 1.0 \text{ mol dm}^{-3} (\text{Li(ClO}_4))$. Thus for the cis-$\alpha$-isomer, $k_1 = 2.0 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and for the cis-$\beta$-isomer, $k_1 = 5.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The corresponding values obtained by Francis and Searle are $1.8 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $5.6 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

At 25°C the cis-$\alpha$-isomer undergoes acid-catalysed decarboxylation some 37 times faster than the cis-$\beta$-isomer. The activation parameters indicate that the more rapid decarboxylation of the cis-$\alpha$-isomer arises primarily from a more positive entropy of activation, $(\Delta S^*_{\alpha} - \Delta S^*_{\beta}) = +50 \text{ JK}^{-1} \text{ mol}^{-1}$.

The solvent deuterium isotope effects were studied at 25°C in 0.55 mol dm$^{-3}$ DC1 solutions. Under these conditions $k_0$ makes only a very small contribution to $k_{\text{obs}}$, and as a result values of $k_1$ were estimated from the relationship $k_1 = k_{\text{obs}}/[H^+]$. For both isomers, the solvent deuterium isotope effect is ca 2.6, Table 9.
TABLE 8

Activation parameters for the acid-catalysed decarboxylation of cisα- and cisβ-[Co(dmtr)CO$_3$]$^+$ ions.

<table>
<thead>
<tr>
<th>$\theta/°C$</th>
<th>$10^2 k_1$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>$\theta/°C$</th>
<th>$10^3 k_1$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.2</td>
<td>2.03</td>
<td>25.4</td>
<td>0.55</td>
</tr>
<tr>
<td>35.4</td>
<td>6.43</td>
<td>35.4</td>
<td>1.70</td>
</tr>
<tr>
<td>45.0</td>
<td>22.14</td>
<td>45.6</td>
<td>5.41</td>
</tr>
</tbody>
</table>

$\Delta H^\ddagger = 92.9$ kJ mol$^{-1}$  

$\Delta S^\ddagger_{298} = +34.4$ JK$^{-1}$ mol$^{-1}$  

$\Delta G^\ddagger_{298} = 82.6$ kJ mol$^{-1}$

$\Delta H^\ddagger = 86.8$ kJ mol$^{-1}$  

$\Delta S^\ddagger_{298} = -15.9$ JK$^{-1}$ mol$^{-1}$  

$\Delta G^\ddagger_{298} = 91.5$ kJ mol$^{-1}$
TABLE 9

Solvent deuterium isotope effects for the acid-catalysed decarboxylation of cisα- and cisβ-[Co(dmtr)CO₃]⁺ ions at 25°C.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$10^2 k_{obs}/s^{-1}$</th>
<th>$10^2 k_1/dm^3 mol^{-1}s^{-1}$</th>
<th>$k_{D_2O}/k_{H_2O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.49 HCl</td>
<td>0.914</td>
<td>1.86</td>
<td>2.65</td>
</tr>
<tr>
<td>0.55 DCl</td>
<td>2.71</td>
<td>4.93</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Medium</th>
<th>$10^2 k_{obs}/s^{-1}$</th>
<th>$10^2 k_1/dm^3 mol^{-1}s^{-1}$</th>
<th>$k_{D_2O}/k_{H_2O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.49 HCl</td>
<td>2.2</td>
<td>0.45</td>
<td>2.56</td>
</tr>
<tr>
<td>0.55 DCl</td>
<td>6.3</td>
<td>1.15</td>
<td></td>
</tr>
</tbody>
</table>
1.8 Discussion

The kinetics of the acid-catalysed decarboxylation of a number of carbonatotetraminecobalt(III) complexes has been studied. Normally, for these reactions the observed first order rate constant at constant hydrogen ion concentration \( k_{obs} \) conforms to a rate expression of the form \( k_{obs} = k_0 + k_1[H^+] \) where \( k_0 \) relates to the "spontaneous" or water pathway and \( k_1 \) to the acid-catalysed pathway. The \( k_0 \) values are subject to considerable error, since they make little contribution to \( k_{obs} \) especially in the higher temperature measurements. Clean first order dependency of the aquation rates on \([H^+]\) are demonstrated in Figures 3, 7, 10, 14(a) and (b), where the pseudo-first-order rate constants, \( k_{obs} \), are plotted against \([H^+]\) at three different temperatures (except in the case of cis-C-meso-[Co(Me\(_2\)cyclam)CO\(_3\)]\(^+\) where \( k_{obs} \) are plotted against \([H^+]\) only at 35°C). The first order dependence on the hydrogen ion concentration could arise from any one of the three possible mechanisms (discussed earlier in this chapter and summarized in Scheme 2).

The complex cis-[Co(Me\(_2\)cyclam)CO\(_3\)]\(^+\) undergoes the slowest decarboxylation, and the rate is similar to that of cis8-[Co(dmtr)CO\(_3\)]\(^+\), Table 10. The unsaturated complexes derived from Me\(_6\)[\(^{14}\)diene and Me\(_2\)[\(^{14}\)diene decarboxylate 22 to 27 times faster than cis-[Co(Me\(_2\)cyclam)CO\(_3\)]\(^+\). However, the relative rates shown in Table 10 indicate that the effects of methyl substitution and ligand unsaturation are not marked.

Table 11 lists the available rate constants and activation parameters for a large number of carbonato complexes. The
### TABLE 10

Relative rate data for the acid-catalysed aquation of complexes of the type \( \text{cis}-\{\text{CoN}_4\text{CO}_3\}^+ \) at 35°C

<table>
<thead>
<tr>
<th>Complex</th>
<th>(10^3 \text{k}_1/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{cis}-[\text{Co(Me}_2\text{cyclam})\text{CO}_3]^+ )</td>
<td>1.58</td>
<td>1</td>
</tr>
<tr>
<td>( \text{cis}-[\text{Co(cyclam})\text{CO}_3]^+ )</td>
<td>4.33(^a)</td>
<td>2.7</td>
</tr>
<tr>
<td>( \text{cis}-[\text{Co(cyclen})\text{CO}_3]^+ )</td>
<td>26.8</td>
<td>17</td>
</tr>
<tr>
<td>( \text{cis}-[\text{Co(Me}_6[14]\text{ diene})\text{CO}_3]^+ )</td>
<td>35.0(^b)</td>
<td>22</td>
</tr>
<tr>
<td>( \text{cis}-[\text{Co(Me}_2[14]\text{ diene})\text{CO}_3]^+ )</td>
<td>42.5</td>
<td>ca</td>
</tr>
<tr>
<td>( \text{cis}^\alpha-[\text{Co(dmtr})\text{CO}_3]^+ )</td>
<td>64.3</td>
<td>ca</td>
</tr>
<tr>
<td>( \text{cis}^\beta-[\text{Co(dmtr})\text{CO}_3]^+ )</td>
<td>1.70</td>
<td>ca</td>
</tr>
</tbody>
</table>

\(^a\) Value at 35°C calculated by extrapolation of data given in reference 6.

\(^b\) Value at 35°C calculated by extrapolation of data given in reference 1.
### TABLE II

Activation parameters for the acid-catalysed aquation of various \([\text{Co}_4\text{CO}_3]^+\) complexes

<table>
<thead>
<tr>
<th>(N_4)</th>
<th>(k_1/\text{dm}^3\text{mol}^{-1}\text{s}^{-1})</th>
<th>(\Delta H^\dagger/\text{kJ mol}^{-1})</th>
<th>(\Delta S^\dagger/\text{JK}^{-1}\text{mol}^{-1})</th>
<th>(\Delta G^\ddagger/\text{kJ mol}^{-1})</th>
<th>Av. pK(_a) of amine ligand</th>
<th>Reference(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-(en)(NH(_3))(_2)</td>
<td>8.9</td>
<td>41.8</td>
<td>-83.7</td>
<td>66.74</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>tren</td>
<td>2.0</td>
<td>46.4</td>
<td>-83.7</td>
<td>71.34</td>
<td>9.1</td>
<td>-</td>
</tr>
<tr>
<td>(tn)(_2)</td>
<td>0.8</td>
<td>50.2</td>
<td>-79.5</td>
<td>73.89</td>
<td>9.7</td>
<td>-</td>
</tr>
<tr>
<td>(pn)(_2)</td>
<td>0.5</td>
<td>58.6</td>
<td>-54.4</td>
<td>74.8</td>
<td>8.5</td>
<td>-</td>
</tr>
<tr>
<td>(en)(_2)</td>
<td>0.6</td>
<td>57.7</td>
<td>-31.0</td>
<td>66.94</td>
<td>8.6</td>
<td>-</td>
</tr>
<tr>
<td>(NH(_3))(_4)</td>
<td>1.5</td>
<td>64.0</td>
<td>-26.33</td>
<td>71.85</td>
<td>9.3</td>
<td>-</td>
</tr>
<tr>
<td>cis-(en)(NH(_3))(_2)</td>
<td>0.9</td>
<td>67.0</td>
<td>-16.7</td>
<td>71.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(a)-trien</td>
<td>5.2</td>
<td>62.8</td>
<td>-20.9</td>
<td>69.0</td>
<td>7.3</td>
<td>-</td>
</tr>
<tr>
<td>(s)-trien</td>
<td>0.2</td>
<td>71.1</td>
<td>-20.9</td>
<td>77.33</td>
<td>7.3</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Me}_2[14]) diene</td>
<td>(1.5\times10^{-2})</td>
<td>82.9</td>
<td>-0.4</td>
<td>83.0</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>(\text{Me}_6[14]) diene</td>
<td>(8.0\times10^{-3})</td>
<td>(88.6)(^c)</td>
<td>(+3.8)(^c)</td>
<td>(87.5)(^c)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) \(N_4\) = \text{amino acid or amine}.

\(^b\) Reference for the values of \(k_1\), \(\Delta H^\dagger\), \(\Delta S^\dagger\), and \(\Delta G^\ddagger\) is not specified in the table.

**Note:** This work refers to the author's recent research or the current study.
TABLE 11 (continued)

<table>
<thead>
<tr>
<th>N₄</th>
<th>k₁/dm³mol⁻¹s⁻¹</th>
<th>ΔH⁺/kJ mol⁻¹</th>
<th>ΔS⁺/JK⁻¹ mol⁻¹</th>
<th>ΔG⁺/kJ mol⁻¹</th>
<th>Av. pKₐ of amine ligand</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclen</td>
<td>7.6x10⁻³</td>
<td>100.4</td>
<td>+51</td>
<td>85.2</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>cyclam</td>
<td>1.3x10⁻³</td>
<td>86.11</td>
<td>-10.9</td>
<td>89.4</td>
<td>6.7</td>
<td>This work</td>
</tr>
<tr>
<td>α-dmtr</td>
<td>2.0x10⁻²</td>
<td>92.9</td>
<td>+34.4</td>
<td>82.6</td>
<td>6.4</td>
<td>This work</td>
</tr>
<tr>
<td>β-dmtr</td>
<td>5.5x10⁻⁴</td>
<td>86.8</td>
<td>-15.9</td>
<td>91.5</td>
<td>6.4</td>
<td>This work</td>
</tr>
<tr>
<td>phen</td>
<td>1.5x10⁻⁴</td>
<td>85.4</td>
<td>-36.0</td>
<td>96.13</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>bipy</td>
<td>2.2x10⁻⁴</td>
<td>93.3</td>
<td>-8.4</td>
<td>95.8</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>py</td>
<td>8.9x10⁻⁶</td>
<td>100.3</td>
<td>-4.2</td>
<td>101.6</td>
<td>5.3</td>
<td></td>
</tr>
</tbody>
</table>

a. Values of k₁ at 25°C
b. The quoted values in this table are reproduced from reference 6 unless otherwise stated,
   ΔG⁺ values are calculated from reference 6 unless otherwise stated.
c. Calculated from reference 1.
macrocycles fall into an intermediate area between the very rapid and very slow decarboxylations. In Table 11 the rates of acid decarboxylation vary by a factor of \(10^6\).

In the case of the cyclen complex, the release of steric strain engendered in the 12-membered ring could favour a dissociative reaction pathway, and the value of \(\Delta S^+\) is indeed more positive, consistent with this view. However, the existence of steric strain in the complex would be expected to lower the value of \(\Delta H^+\) compared with cyclam derivative, but this is not observed. The more favourable \(\Delta S^+\) is counterbalanced by a somewhat higher \(\Delta H^+\), so that values of \(\Delta G^+\) are quite similar for all four macrocyclic complexes, Table 11.

**Solvent deuterium isotope effects** - The solvent deuterium isotope effects were studied at 25°C in \(0.5\) mol dm\(^{-3}\) DCl. Under these conditions \(k_0\) makes only a very small contribution to \(k_{\text{obs}}\), and as a result values of \(k_1\) were estimated from the relationship \(k_1 = k_{\text{obs}}/[H^+]\). For all complexes studied, the solvent deuterium isotope effects were in the range of 2.05-2.65, Table 12, fully consistent with a rapid pre-equilibrium protonation. Very similar values have been reported for the specific acid-catalysed hydrolysis of ethyl orthoformate \((k_{D_2O}/k_{H_2O} = 2.35)^{23,24}\) and the hydrolysis of acetal \((k_{D_2O}/k_{H_2O})^{25,26} = 2.68\). The solvent deuterium isotope effects exclude mechanism A since in this case \(k_{D_2O}/k_{H_2O} < 1\). As mentioned earlier the magnitude of the solvent isotope is in the range \((1.9-2.6)\) considered typical\(^{27,28,10}\) for A-1
TABLE 12
Solvent isotope effects for the acid-catalysed aquation of various \([\text{CoN}_4\text{CO}_3]^+\) complexes in acid solutions.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(k_{\text{D}<em>2\text{O}}/k</em>{\text{H}_2\text{O}})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Co(Me(_2)([\text{14}]) diene)\text{CO}_3]^+</td>
<td>2.60</td>
<td>This work</td>
</tr>
<tr>
<td>cis-[Co(cyclen)\text{CO}_3]^+</td>
<td>2.05</td>
<td>This work</td>
</tr>
<tr>
<td>cis-[Co(dmtr)\text{CO}_3]^+</td>
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<td>This work</td>
</tr>
<tr>
<td>cis(_\beta)-[Co(dmtr)\text{CO}_3]^+</td>
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<td>This work</td>
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<tr>
<td>cis-[Co(en)(_2)\text{CO}_3]^+</td>
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<td>12</td>
</tr>
<tr>
<td>cis-[Co(py)(_4)\text{CO}_3]^+</td>
<td>1.8</td>
<td>7</td>
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</tbody>
</table>
reactions (Mechanism C, Scheme 2) and is much larger than the values of 1.3-1.4 which have been observed for A-2 reactions, in addition the values of $\Delta S^+$ are more consistent with unimolecular A-1 processes.\textsuperscript{10} Table 12 summarises the available values of $k_{D_2O}/k_{H_2O}$ for the acid-catalysed decarboxylation of $[\text{CoN}_4\text{CO}_3]^+$ complexes. The solvent isotope effects all fall within the expected range for A-1 reactions, and in addition the values of $\Delta S^+$ are also more typical of A-1 processes.\textsuperscript{11} Harris and Hyde\textsuperscript{12} in a recent paper have not considered the possibility of an A-1 process and have only discussed mechanisms A and B, Scheme 2. Most substitution reactions at octahedral cobalt(III) centres occur by essentially dissociative mechanisms; thus on these grounds an A-1 process involving a five coordinate intermediate appears to be mechanistically reasonable.

An inspection of the available literature values of $\Delta S^+$ for the acid-catalysed decarboxylation of $[\text{CoN}_4\text{CO}_3]^+$ complexes, Table 11, indicates that the majority of these reactions have values of $\Delta S^+$ which fall within the range -4 to -24 JK$^{-1}$ mol$^{-1}$, values which are consistent with A-1 processes.\textsuperscript{11} However, there are a group of complexes ($N_4 = (1,2$-diamino-propane)$_2$, (1,3-diaminopropane)$_2$, 2,2',2"-triaminotriethylamine), and trans-(en)(NH$_3$)$_2$) which have values of $\Delta S^+$ of ca -80 JK$^{-1}$ mol$^{-1}$, and these reactions may possibly correspond to genuine A-2 processes where water is involved. It would be of interest to study the solvent deuterium isotope effects for some of these complexes.
reactions (Mechanism C, Scheme 2) and is much larger than
the values of 1.3-1.4 which have been observed for A-2 reactions, in addition the values of $\Delta S^*$ are more consistent with uni-
molecular A-1 processes. Table 12 summarises the available values of $k_{D_2O}/k_{H_2O}$ for the acid-catalysed decarboxyl-
ation of [CoN$_4$CO$_3$]$^+$ complexes. The solvent isotope effects all fall within the expected range for A-1 reactions, and in addition the values of $\Delta S^*$ are also more typical of A-1 processes. Harris and Hyde in a recent paper have not considered the possibility of an A-1 process and have only discussed mechanisms A and B, Scheme 2. Most substitution reactions at octahedral cobalt(III) centres occur by essentially dissociative mechanisms; thus on these grounds an A-1 process involving a five coordinate intermediate appears to be mechanistically reasonable.

An inspection of the available literature values of $\Delta S^*$ for the acid-catalysed decarboxylation of [CoN$_4$CO$_3$]$^+$ complexes, Table 11, indicates that the majority of these reactions have values of $\Delta S^*$ which fall within the range -4 to -24 JK$^{-1}$ mol$^{-1}$, values which are consistent with A-1 processes. However, there are a group of complexes ($N_4 = (1,2$-diamino-
propane)$_2$, (1,3-diaminopropane)$_2$; 2,2',2"-triaminotriethylamine), and trans-(en)(NH$_3$)$_2$) which have values of $\Delta S^*$ of ca 80 JK$^{-1}$ mol$^{-1}$, and these reactions may possibly correspond to genuine A-2 processes where water is involved. It would be of interest to study the solvent deuterium isotope effects for some of these complexes.
Effect of Dioxane Content - A variety of mechanistic probes have been proposed to differentiate between A-1 and A-2 reactions. Typical examples are Hammett-Zucker\textsuperscript{29} and Bunnett-Olsen\textsuperscript{30} plots. Kice and Anderson\textsuperscript{10} have used the effect of dioxane content on the rate of hydrolysis in dioxane-water mixtures. The dissociation constant ($K_a$) of any neutral acid HA decreases markedly with increasing dioxane content in 40-80\% dioxane-water mixtures, and of course, the free water concentration is also decreased. In some cases these effects may be used to differentiate between A-1 and A-2 mechanisms.

For a metal complex of the type $[\text{CoN}_4\text{CO}_3]^+$ it would be expected that protonation to give the dipositive cation $[\text{CoN}_4\text{CO}_3\text{H}]^{2+}$ would not be favoured as the dioxane content was increased. A marked rate decrease would probably therefore be expected for an A-2 reaction, since the water concentration would also be reduced. For A-1 reactions the effect would be less marked since any effect would be essentially limited to the pre-equilibrium step. For this reason we have studied the hydrolysis of cis-$[\text{Co(cyclen)CO}_3]^+$ in 50/50 (v/v) dioxane-water mixtures. The study could not be extended to higher dioxane concentrations due to solubility problems. For hydrolysis in 0.2 mol dm$^{-3}$ HNO$_3$ at 25\textdegree C the value of $k_{\text{obs}}$ was $(1.43 \pm 0.03) \times 10^{-3}$ s$^{-1}$, while for the analogous reaction in dioxane-water $k_{\text{obs}} = (2.88 \pm 0.05) \times 10^{-3}$ s$^{-1}$ (average of four kinetic measurements). The two-fold increase in rate in dioxane-water lends further support to the view that the reaction occurs by an A-1 mechanism involving a five-coordinate intermediate. The observed rate increase may be due to a medium
effect, since the value of $k_{Cl}$ may be somewhat increased in
dioxane-water mixtures, thus counterbalancing the decrease
in the value of the protonation constant $K$.

The available evidence (solvent deuterium isotope
effect, entropy of activation and the effect of dioxane content
on the reaction rate) support the view that these acid-catalysed
decarboxylations occur by an essentially A-1 process (i.e.
mechanism C, Scheme 2), however for some decarboxylations having
$\Delta S^+ \sim -80 \text{ JK}^{-1} \text{ mol}^{-1}$ an A-2 process cannot be excluded. The
work definitely confirms that the previously assumed mechanism
(mechanism A) must be discarded.
CHAPTER 2

Kinetics of Aquation of cis-Dichloro(C-meso-5,12-Dimethyl-1,4,8,11-tetra-azacyclotetradecane)Chromium(III); cis-[Cr(Me₂ cyclam)Cl₂]⁺.

2.1 Introduction

At the present time very little synthetic or mechanistic work has been carried out on chromium(III) complexes of macrocyclic ligands. Ferguson and Tobe⁴¹ have described the preparation of a number of cis- and trans-complexes of the type [Cr(cyclam)X₂]⁺ where X = Cl, Br, NCS, ONO and N₃. Sperati⁴² has also reported the preparation of a number of chromium(III) complexes of macrocyclic tetra-aza ligands by oxidation of the appropriate chromium(II) complexes.

Campi et al⁴³ have studied the kinetics and the steric course of aquation and base hydrolysis of the cis and trans-dichloro(1,4,8,11-tetra-azacyclotetradecane)chromium(III) cations. Base hydrolysis occurred with a second order rate law and values of kₒ₃ were reported to be very much less than those of the corresponding cobalt(III) complexes. All of the substitution reactions proceeded with complete retention of configuration and there was no evidence for any displacement of the amine ligand.

In the present work the kinetics of acid hydrolysis of cis-[Cr(Me₂ cyclam)Cl₂]⁺ have been studied as a function of temperature (in 0.01 mol dm⁻³ nitric acid as reaction medium) to extend the measurements to substituted cyclams. The difficulty of removing such a macrocyclic ligand from the complex makes it ideal for the study of the aquation of the
acido groups. It has been reported\textsuperscript{34,35} that, in the aquation of \textit{trans-}[\text{Cr(en)}\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{+} two parallel reactions occur, one leading to the displacement of the chloride and the other leading to displacement of ethylenediamine.
2.2 Experimental

Cis-dichloro(C-meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III)Chloride; cis-[Cr(Me₂cyclam)Cl₂]Cl.

The ligand C-meso-Me₂cyclam was prepared as previously described (Chapter 1, page 16). The complex was prepared as follows; chromium(III)chloride hexahydrate (0.22g, 0.82 mmole) was dissolved in dry dimethylformamide (previously distilled over BaO). The solution was then distilled to remove the water, i.e. until the distillate boiled between 152-153°C. The solution was then reduced in volume (ca. 15 cm³) and the ligand (0.19g, 0.82 mmole) added. The reaction mixture was then heated for ca. 15 minutes, during which time the complex precipitated. The product was filtered off and washed with dry DMF then dry ether and dried in vacuo (Yield 0.2g, 54%). The product was suspended in boiling methanol (70 cm³) for 5 minutes and the insoluble violet-purple cis-isomer filtered off from the methanol solution of the trans-complex. (Calc. for the cis-isomer C₁₂H₂₈N₄Cl₃Cr: C, 37.26; H, 7.30; N, 14.5%. Found: C, 37.20; H, 7.20; N, 14.3%). The i.r. spectrum of this complex has vNH bands at 3160 and 3060 cm⁻¹. The methanolic solution from the above reaction was evaporated to a small volume and cooled in a refrigerator. The grey-green product which precipitated was filtered off (0.02g, ca. 10% of the total yield). The i.r. spectrum of this complex has a single vNH band at 3200 cm⁻¹.
Dichloro(C-rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)chromium(III)Chloride; 
[Cr(Me₆cyclam)Cl₂].Cl.

The ligand C-rac-Me₆cyclam(tet b) was prepared as previously described by Hay and Lawrance²⁶ (m.p. 110°, 
lit. 109-110°C). The complex [Cr(Me₆cyclam)Cl₂]⁺ was prepared as follows; a solution of CrCl₃.6H₂O (2.7g, 0.01 mole) in 
dimethyl sulphoxide (30 cm³) was boiled for ca. 0.5 hr. to expel the water and give CrCl₃(DMSO)₃. The ligand (2.8g, 
0.01 mole) dissolved in dimethyl sulphoxide (15 cm³) was added to the deep violet solution, and the mixture was boiled 
for 20 minutes. The greyish-green product which precipitated on standing at room temperature was filtered off and washed with 
acetone. Calc. for CrC₁₆H₃₆N₄Cl₂: C, 43.40; H, 8.20; N, 12.65; 
Found: C, 43.50; H, 8.1; N, 12.83%. The i.r. spectrum displays 
two νNH bands and there is obviously some cis-isomer present. 
Separation of the isomers (which are insoluble in methanol and 
concentrated hydrochloric acid) was not attempted.
Kinetics

The kinetics of acid hydrolysis of cis-[Cr(Me₂cyclam)-Cl₂]⁺ were monitored spectrophotometrically by following the increase in absorbance at 514nm which is an isosbestic point for the hydrolysis of the second chloride ligand. The first hydrolysis step could thus be studied in isolation. The acid hydrolysis of cis-[Cr(Me₂cyclam)Cl(H₂O)]²⁺ was studied using the decrease in absorbance at 544nm which is an isosbestic point for the loss of the first halide ligand. The reactions were initiated by the addition of the appropriate amount of the solid complex to the equilibrated nitric acid solution. The solutions were filtered before transfer to the cell. Normally 4 runs were carried out at each temperature.

Plots of log (Aᵦ - Aₜ) or (Aₜ - Aᵦ) against time were linear for at least three half lives. The concentration of HNO₃ in the runs was 0.01 mol dm⁻³. The nitric acid solutions were prepared by dilution of commercially available C.V.S. ampoules.

The kinetic measurements were carried out using the instrumentation previously described (Chapter 1).
2.3 Results and discussion

The reaction of trichlorotris(N,N-dimethylformamide)chromium(III) (produced by dehydration of CrCl$_3$·6H$_2$O in DMF) with C-meso-Me$_2$cyclam in DMF solution gives predominantly the cis-isomer of [Cr(Me$_2$cyclam)Cl$_2$]Cl although small quantities of the trans-isomer are also formed in the reaction. The isomers are readily separated as the cis-isomer is essentially insoluble in methanol while the trans-isomer is quite soluble. The two isomers are readily distinguished by their i.r. spectra. The cis-isomer has two vNH bands at 3160 and 3060 cm$^{-1}$, while the trans-isomer has a single vNH band at 3200 cm$^{-1}$, Figure 16.

The preference for chromium(III) to form cis-complexes is in marked contrast to the behaviour observed with cobalt(III) where the trans-complexes with 14-membered macrocyclic tetra-aza ligands are generally favoured and cis $\rightarrow$ trans isomerisation occurs under the appropriate conditions. This apparent preference for the chromium(III) complexes to adopt a cis-configuration is also observed with 1,4,8,11-tetra-azacyclotetradecane(cyclam). The assignment of geometric configuration is confirmed by d-d spectra, the more symmetrical trans-isomers of [CrN$_4$Cl$_2$]$^+$ complexes normally have extinction coefficients of <30 and the lowest energy d-d band occurs in the range 570-580nm, Table 13. The less symmetrical cis-isomers have much higher extinction coefficients (ca. 70-120) and the lowest energy d-d band occurs in the region 530-560nm. Thus the cis-[Cr(Me$_2$cyclam)Cl$_2$]$^+$ has $\lambda_{max}$ 559nm ($\epsilon$ = 123) and 412nm ($\epsilon$ = 97) in DMSO solution. Aqueous solution spectra are suspect since loss of the first chloride ligand occurs quite
Figure 16. The I.R. Spectra of [Cr(Me₂Cyclam)Cl]Cl.

1. mixture of cis and trans isomers before separation by dissolving in methanol.
2. the cis-isomer (insoluble in methanol).
3. the trans-isomer (soluble in methanol).

TRANSMITTANCE
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\max}$ (in nm)</th>
<th>Reference</th>
</tr>
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<td>trans-[Cr(en)$_2$Cl$_2$]$^+$</td>
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<td>34</td>
</tr>
<tr>
<td></td>
<td>453 (23)</td>
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</tr>
<tr>
<td></td>
<td>396 (34)</td>
<td></td>
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<tr>
<td>trans-[Cr(cyclam)Cl$_2$]$^+$</td>
<td>572 (19.9)</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>407 sh (35)$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>365 (41)</td>
<td></td>
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<tr>
<td>trans-[Cr(Me$_2$cyclam)Cl$_2$]$^+$</td>
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</tr>
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<td>386 (31)</td>
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<td>34</td>
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<tr>
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<td>402 (69)</td>
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<td>529 (111)</td>
<td>31</td>
</tr>
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<td>404 (106)</td>
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<tr>
<td>cis-[Cr(Me$_2$cyclam)Cl$_2$]$^+$</td>
<td>559 (123)</td>
<td>This work</td>
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<td></td>
<td>412 (97)</td>
<td></td>
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<td>cis-[Cr(en)$_2$(H$_2$O)$_2$]$^{3+}$</td>
<td>484 (67)</td>
<td>42</td>
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<td>366 (43)</td>
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<tr>
<td>cis-[Cr(cyclam)(H$_2$O)$_2$]$^{3+}$</td>
<td>483 (126)</td>
<td>31</td>
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<tr>
<td></td>
<td>370 (38)</td>
<td></td>
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<tr>
<td>cis-[Cr(Me$_2$cyclam)(H$_2$O)$_2$]$^{3+}$</td>
<td>506 (75.4)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>380 (53)</td>
<td></td>
</tr>
</tbody>
</table>

a. Values in parentheses are extinction coefficients ($\text{dm}^3 \text{mol} \text{cm}^{-1}$)
b. sh = shoulder
c. Measured in DMSO solvent
d. Measured in DMSO solvent, in water immediately after dissolution, $\lambda_{\max} = 536(100)$ and 408nm (100).
rapidly in aqueous solution (see later). The corresponding trans-isomer has $\lambda_{\text{max}}$ 571 ($\epsilon = 20$) and 386 nm ($\epsilon = 31$).

Poon\textsuperscript{38} has shown that the number and position of the infrared bands in the CH\textsubscript{2} rocking region (800-910 cm\textsuperscript{-1}) can be used to distinguish between cis and trans-isomers in the case of [Co(cyclam)X\textsubscript{2}]\textsuperscript{+}. In general, the cis-isomers exhibit five or more bands between 800 and 910 cm\textsuperscript{-1}, while the trans-isomers have two bands close to 900 cm\textsuperscript{-1} and one close to 800 cm\textsuperscript{-1}, the intensities being somewhat weaker in the case of the cis-complexes. The differences in this region for the cis and trans chromium(III) complexes of Me\textsubscript{2} cyclam is not significant. However, the i.r. spectra of these two isomers differ significantly in the vNH absorption region. The cis-isomer exhibits two vNH bands at 3160 and 3060 cm\textsuperscript{-1}, possibly due to the low (maximum C\textsubscript{2v}) symmetry of the molecule, while the trans-isomer displays only one vNH band. Figure 16 shows the i.r. spectra of the cis and the trans-isomer in the vNH region together with the spectrum of the crude product.

The reaction of CrCl\textsubscript{3}(DMSO)\textsubscript{3} with C-rac-Me\textsubscript{6} cyclam (tet b) in DMSO solution gives a greyish-green product of [Cr(Me\textsubscript{6}cyclam)Cl\textsubscript{2}]Cl. The complex has a limited solubility in methanol, DMSO or 6M HCl, so that the extinction coefficients were difficult to determine with accuracy. The visible spectrum of a dilute solution of the complex in DMSO has bands at 425 and 590 nm, comparable with those reported for the trans-[Cr(tet a)Cl\textsubscript{2}]Cl. The spectrum of the tet a complex has bands at 384.6, 578 nm and a shoulder at 420 nm.\textsuperscript{32} The i.r. spectrum of [Cr(tet b)Cl\textsubscript{2}]\textsuperscript{+} shows two vNH bands at 3150 and 3050 cm\textsuperscript{-1},
Figure 17, while the tet a complex shows only one $\nu$NH band, thus the i.r. spectrum of tet b complex probably indicates a mixture of cis and trans-isomers.

The complex $[\text{Cr(tet b)Cl}_2]^+$ is highly reactive in 0.01 mol dm$^{-3}$ HNO$_3$, the visible spectrum does not change with time which is suggestive of rapid aquation during the mixing time. This observation was confirmed by conductivity measurements. Thus the complex is 3:1 electrolyte immediately on dissolution in water ($\Lambda_M = 380$ ohm$^{-1}$ cm$^2$ mol$^{-1}$). Stop-flow techniques would be required to study the kinetics of acid aquation. Separation of the isomers must be done before kinetic work can be carried out.

The spectrum of a solution of cis-$[\text{Cr(Me}_2\text{cyclam)Cl}_2]^+$ in 0.01 mol dm$^{-3}$ HNO$_3$ changes with time in a way that is consistent with a two-stage reaction. The first stage is characterised by three clean isosbestic points at 544, 458 and 398nm, Figure 18(a), and proceeds at a rate 76 times faster than the second stage (with isosbestic points at 514, 445 and 336nm), Figure 18(b). The visible spectrum of the final product is consistent with a cis-diaquo species with two d-d bands at 506 ($\varepsilon = 75.4$) and 380 ($\varepsilon = 53$), Table 13, thus, the reaction proceeds with complete retention of configuration. Independent conductivity measurements on aqueous solution of the complex confirm a two stage reaction,

$$
cis-[\text{Cr(Me}_2\text{cyclam)Cl}_2]^++\text{H}_2\text{O} \overset{k_1}{\longrightarrow} \text{cis-[Cr(Me}_2\text{cyclam)Cl(H}_2\text{O)]]}^{2+}+\text{Cl}^- \quad cis-[\text{Cr(Me}_2\text{cyclam)Cl(H}_2\text{O)]]}^{2+}+\text{H}_2\text{O} \overset{k_2}{\longrightarrow} \text{cis-[Cr(Me}_2\text{cyclam)H}_2\text{O)]]}^{3+}+\text{Cl}^-
$$
Figure 18. Absorbance changes for the aquation of \( \text{cis-}[\text{Cr}(\text{Me}_2\text{cyclam})\text{Cl}_2]^{2+} \) in 0.01 HNO\(_3\):  

(a) First stage \( \text{cis-}[\text{Cr}(\text{Me}_2\text{cyclam})\text{Cl}_2]^{2+} + \text{H}_2\text{O} \rightarrow \text{cis-}[\text{Cr}(\text{Me}_2\text{cyclam})\text{Cl}(\text{H}_2\text{O})]^{2+} + \text{Cl}^{-} \).  

(b) Second stage \( \text{cis-}[\text{Cr}(\text{Me}_2\text{cyclam})\text{Cl}(\text{H}_2\text{O})]^{2+} + \text{H}_2\text{O} \rightarrow \text{cis-}[\text{Cr}(\text{Me}_2\text{cyclam})(\text{H}_2\text{O})_2]^{3+} + \text{Cl}^{-} \)
Thus the complex cis-[Cr(Me₂cyclam)Cl₂]⁺ (1 x 10⁻³ mol dm⁻³) is 1:1 electrolyte immediately on dissolution in water ($\Lambda_M = 128$ ohm⁻¹ cm² mol⁻¹ at 25°C). The conductivity rises to 226 ohm⁻¹ cm² mol⁻¹ after 70 minutes consistent with the value for a 2:1 electrolyte and over a period of 8 hours it rises to 480 ohm⁻¹ cm² mol⁻¹ a value which is consistent with a 3:1 electrolyte, Figure 19.

Acid hydrolysis of cis-[Cr(Me₂cyclam)Cl₂]⁺

Figure 18(a) shows the spectral changes observed in the early stages of the reaction. Three clean isosbestic points are seen at 544, 458 and 398 nm consistent with only two absorbing species and hence the reaction

\[
\text{cis-[Cr(Me₂cyclam)Cl₂]}^+ + \text{H}_2\text{O} \rightarrow \text{cis-[Cr(Me₂cyclam)Cl(H₂O)}^+ \text{Cl}^-
\]

The kinetics were monitored at 514 nm, plots of log ($A_\infty - A_t$) versus time are linear. Figure 20 shows a representative kinetic plot. Values of $k_{\text{obs}}$ were obtained from these plots. Table 14 lists the values of $k_{\text{obs}}$ at the temperatures 25, 30.2, 35.2 and 40.2°C. A plot of log $k_{\text{obs}}$ versus 1/T is linear, Figure 21, and the value of the activation energy $E_a = 69.7$ kJ mol⁻¹. The requisite values of $\Delta H^\ddagger = 67.2$ kJ mol⁻¹ and $\Delta S^\ddagger = -87$ JK⁻¹.

For the acid hydrolysis of cis-[Cr(cyclam)Cl₂]⁺, $k_{\text{aq}} = 2.5 \times 10^{-5}$ s⁻¹ at 25°C, while for the present complex $k_{\text{aq}} = 3.0 \times 10^{-4}$ s⁻¹. Thus substitution by the two methyl substituents leads to a rate acceleration of ca 12 times. For cis-[Cr(en)₂Cl₂]⁺, the reported aquation rate is
Figure 19. Changes in conductivity with time for the complex \( \text{cis-}[\text{Cr(Me}_2\text{cyclam)}\text{Cl}_2] \text{Cl} \) at 25°C in aqueous solution.
Figure 20. Kinetic plot for the acid hydrolysis of the cis-[Cr(Me₂cyclam)Cl₂]⁺ in 0.01 mol dm⁻³ HNO₃ at 33°C.
TABLE 14

Rate constants for acid hydrolysis of cis-\([\text{Cr(Me}_2\text{cyclam})\text{Cl}_2]^+\) in nitric acid solutions 0.01 mol dm\(^{-3}\).

<table>
<thead>
<tr>
<th>(0°C)</th>
<th>(10^4k_{\text{obs}}/s^{-1})</th>
<th>(10^4\text{Aver. }k_{\text{obs}}/s^{-1})</th>
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<tr>
<td>25</td>
<td>2.9</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>30.2</td>
<td>4.64</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>4.60</td>
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</tr>
<tr>
<td></td>
<td>4.50</td>
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</tr>
<tr>
<td>35.2</td>
<td>7.74</td>
<td>7.54</td>
</tr>
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<td>7.50</td>
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<tr>
<td>40.2</td>
<td>12.30</td>
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</tr>
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<td></td>
<td>11.70</td>
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<td></td>
<td>12.00</td>
<td></td>
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<td></td>
<td>12.00</td>
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</tr>
</tbody>
</table>

\(E_a = 69.7\text{ kJ mol}^{-1}\)

\(\Delta H^+ = 67.2\text{ kJ mol}^{-1}\)

\(\Delta S^+_{298} = -87\text{ JK}^{-1}\)

(Corr. coef.) = 0.997
Figure 21. Temperature dependence of $k_{obs}$ for the acid hydrolysis of the complex cis-$\text{[Cr(Me}_2\text{-cyclam)}\text{Cl}_2]^{+}$. 
This is similar to the complex studied in this work, though the activation parameters differ significantly. Table 15 lists the rate constants and values for the activation parameters for the aquation of a number of cis-dichloro complexes of chromium(III) and cobalt(III).

The large negative value of the entropy for the reaction studied is suggestive of a SN2 type of mechanism leading to a 7-coordinate intermediate or transition state. The reaction appears to be predominantly associative in character, in which both bond making and bond breaking are important.

Acid hydrolysis of cis-[Cr(Me₂cyclam)Cl(H₂O)]²⁺

The kinetics of acid hydrolysis of this species were studied at 544nm (where the first reaction does not interfere), Figure 18(b). Plots of log⁡(A_0 - A_t) versus time are linear. Values of k_{obs} were obtained from these plots. Table 16 lists the values of k_{obs} at the temperatures 54.5, 59.8, 65 and 70.8°C. A plot of log k_{obs} versus 1/T is linear, Figure 22, and the value of the activation energy E_a = 102.3 kJ mol⁻¹. The requisite values of ΔH^+ and ΔS^+ are 99.8 kJ mol⁻¹ and -13.0 JK⁻¹ respectively. At 25°C k_{aq} = 3.97 x 10⁻⁶ s⁻¹, thus the rate of aquation is 76 times slower than the loss of the first halide ligand.

The relatively small negative value of ΔS_{298}^+ = -13 JK⁻¹ mol⁻¹ is consistent with a unimolecular process where the entropy of activation would be expected to be close to zero.
TABLE 15

Rate constants and activation parameters for the aquation of cis dichloro-amine complexes of cobalt(III) and chromium(III).

<table>
<thead>
<tr>
<th>Complex</th>
<th>k at 25°C</th>
<th>$\Delta H^+$ kJ mol$^{-1}$</th>
<th>$\Delta S^+$ JK$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-$\left[\text{Co(en)}_2\text{Cl}_2\right]^+$</td>
<td>$2.4 \times 10^{-4}$</td>
<td>89.9</td>
<td>-20.9</td>
<td>39</td>
</tr>
<tr>
<td>cis-$\left[\text{Cr(en)}_2\text{Cl}_2\right]^+$</td>
<td>$3.3 \times 10^{-4}$</td>
<td>85.69</td>
<td>-25.10</td>
<td>40</td>
</tr>
<tr>
<td>cis-$\left[\text{Co(cyclam)}\text{Cl}_2\right]^+$</td>
<td>$1.6 \times 10^{-2}$</td>
<td>76.50</td>
<td>-25.10</td>
<td>41</td>
</tr>
<tr>
<td>cis-$\left[\text{Cr(cyclam)}\text{Cl}_2\right]^+$</td>
<td>$2.5 \times 10^{-5}$</td>
<td>93.63</td>
<td>-20.9</td>
<td>33</td>
</tr>
<tr>
<td>cis-$\left[\text{Cr(Me}_2\text{cyclam)}\text{Cl}_2\right]^+$</td>
<td>$3.0 \times 10^{-4}$</td>
<td>67.2</td>
<td>-87</td>
<td>This work</td>
</tr>
</tbody>
</table>
TABLE 16

Rate constants for acid hydrolysis of cis-[Cr(Me₂cyclam)Cl(H₂O)]²⁺ in 0.01 mol dm⁻³ HNO₃.

<table>
<thead>
<tr>
<th>O°C</th>
<th>10⁴ kₐₚₑₕ/s⁻¹</th>
<th>10⁴ Aver. kₐₚₑₕ/s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.5</td>
<td>1.73</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td>59.8</td>
<td>2.9</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>65.0</td>
<td>6.0</td>
<td>5.27</td>
</tr>
<tr>
<td></td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.45</td>
<td></td>
</tr>
<tr>
<td>70.8</td>
<td>9.50</td>
<td>9.95</td>
</tr>
<tr>
<td></td>
<td>9.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.23</td>
<td></td>
</tr>
</tbody>
</table>

Eₐ = 102.3 kJ mol⁻¹
ΔH⁺ = 99.8 kJ mol⁻¹
ΔS₂⁰⁸ = -13.0 J K⁻¹ mol⁻¹
(Corr. coef.) = 0.998

* Value for kₐₚₑₕ at 25°C was obtained by extrapolation of data given in this Table (kₐₚₑₕ = 3.97 x 10⁻⁶ s⁻¹).
Figure 22. Temperature dependence of $k_{obs}$ for the acid hydrolysis of $\text{cis-}[\text{Cr}(\text{Me}_2\text{cyclam})(\text{H}_2\text{O})\text{Cl}]^{2+}$. 
Bimolecular \((SN_2)\) type processes normally have values of \(\Delta S^\ddagger\) of \textit{ca.} -60 to -70 JK\(^{-1}\) mol\(^{-1}\). It thus appears that the second hydrolysis step is primarily dissociative in character. One possible explanation for a dissociative type of second step could be hydrogen bonding between the leaving \(\text{Cl}^-\) ligand and the \textit{cis}-water molecule which aids the departure of the \(\text{Cl}^-\) ligand.
REFERENCES

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SYNTHETIC AND STEREOCHEMICAL STUDIES
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(2) The crude complex in $d_6$-DMSO solvent

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CHAPTER 1

Introduction

1.1 General Considerations

Macrocyclic ligands are large rings so constituted as to bring three or more donor atoms into contact with one metal ion. The donor atoms are most commonly nitrogen atoms, though oxygen or sulfur atoms, or a mixed set, also occur (I - V)\(^1\)\(^-3\). Although metal complexes of the naturally-occurring macrocyclic ligands have been known for more than

![Diagram of ligand structures]

(I) Oxygen donor atoms

(II) Nitrogen donor atoms

(III) Sulfur-nitrogen donor atoms

(IV) Sulfur donor atoms
half a century, e.g. metal porphyrins and metal corrins, (VI) and (VID, it is only during the past eighteen years that a large number of macrocyclic ligands have been synthesized and their metal complexes extensively studied. In 1960 the nickel(II) complex (VIII) was prepared by Curtis \(^4,5\) by the

(Sulfur-oxygen donor atoms)

(VI)

Metal Porphyrin

(VII)

Metal Corrin
reaction of Ni(en)$_3^{+2}$ with acetone. The corresponding isomer (IX) with the cis-imine stereochemistry is also formed in the reaction.

\[
\begin{align*}
\text{trans-Me}_6[14] \text{diene} N_4 & & \text{cis-Me}_6[14] \text{diene} N_4 \\
\end{align*}
\]

Subsequently, a large number of other synthetic macrocycles have been investigated and aspects of the transition-metal chemistry of such macrocyclic systems have been discussed.\textsuperscript{2,5,6-12} Cyclic polyethers of the "crown" types of which (I) is a typical example,\textsuperscript{1} have received much recent attention because of their unusual behaviour towards a range of non-transition metal ions.\textsuperscript{13} Few studies involving transition metal ions have been reported,\textsuperscript{2} it is evident that the majority of such polyether macrocyclic ligands show a limited tendency to form stable complexes with
these ions. A series of cage-like macrocycles containing both nitrogen and oxygen atoms has been reported. A typical example is (X). Complexes formed by this ligand are called "cryptates" (Gk. kryptus = hidden), because the metal ion is effectively hidden from the solvent by the ligand which encloses it.

![Diagram of a cryptand]

(X)

Cryptand

This thesis is mainly concerned with tetra-aza-ligands, e.g. 1,4,8,11-tetra-azacyclotetradeca-4,11-dienes and 1,4,8,11-tetra-azacyclotetradecanes in which the basic ring system is 1,4,8,11-tetra-azacyclotetradecane, "cyclam" (II).

The majority of all nitrogen-donor macrocycles that have been studied are quadridentate, e.g. ligands (II) and (XI). These four functional groups are more or less evenly spaced in a ring containing 12 to 16 atoms, (II) and Fig. 1a, b, c and d. To fully encircle a first row
transition metal ion a macrocyclic-ring size of between 13 and 16 members is required. The twelve-membered ring macrocycle (cyclen, Fig. 1a) gives with cobalt(III) and rhodium(III), complexes which, as a result of the small "hole size", have a cis-configuration. Busch et al have studied macrocycles such as (II) and Fig. 1a,b,c,d and their cobalt(III) and nickel(II) complexes to demonstrate that there is an ideal ring size for any metal ion with a specific metal-donor atom distance. Ring sizes slightly smaller (0.1 - 0.2 Å in terms of M-N distance) than the best fit ring show abnormally strong metal-donor bonds while rings which are slightly oversize show substantially decreased metal-donor interactions. It has previously been realised that in cases where the mismatch in size is more extreme, distortions from the square planar coordination occur, common distortions
Macrocyclic ligands with different ring sizes being ring folding to form cis-octahedral or trigonal bipyramidal structures, and extrusion of the metal ion from the donor atom plane to form a tetragonal pyramidal
structure. Metal complexes of macrocyclic ligands often possess considerably greater thermodynamic and kinetic stability (with respect to ligand dissociation) than their open chain analogues, these effects have collectively been referred to as the "macrocyclic effect" or "multiple juxtapositional fixedness".

1.2 Synthesis of Macrocyclic Ligands

Cyclic polyamines have been prepared by conventional organic routes and by metal template procedures involving cyclization in the presence of a metal ion. In the former reactions cyclization is performed under conditions of moderate to high dilution in order to minimize competing linear polymerization reactions. In 1937 Van Alphen synthesized the saturated amine 1,4,8,11-tetra-azacyclotetradecane (cyalam), (II), by high dilution techniques. A large number of cyclic ligands can be prepared by metal template reactions. For example, Barefield et al have prepared cyclam, (II), by using a linear tetramine, glyoxal, and nickel(II), Fig. 2. It is believed that the metal ion serves as a template to organize the course of the complex multistep reactions. This route has been extended to many cyclizations using propylene-diamine and linear quadridentate amines with nickel(II), cobalt(II) and copper(II) salts. As examples, both nickel(II) and copper(II)-triethylenetetramine complexes react with acetone to give complexes of Me₃[13]ene N₄, (XII) and, in presence of a suitable acid, methanolic solutions of nickel(II) and cobalt(II) salts condense with stoichiometric amounts of
Figure 2. Nickel ion assisted cyclization.

biacetyl and 1,3-diaminopropane or biacetyl and 4,7-diaza-1,10-decanediamine to yield macrocyclic nickel(II) and cobalt(III) complexes containing α-diimine groupings. These are
illustrated in (XIII) and (XIV).

M = Ni or Cu

M = Ni or Co

Cis and trans complexes of [14]-ane N₄(cyclam) with nickel(II), cobalt(III) and rhodium(III) have been prepared. Complexes of Mn(III), Ni(III), Cu(III), Ag(II), Ag(III) and Cr(III) with cyclam have also been prepared.

A number of non-template reactions have recently been
developed. Curtis and Hay have shown that the monohydroperrchlorate salt of ethylenediamine reacts with acetone or mesityl oxide to yield \([\text{Me}_6[14]\text{diene}]\) as its dihydroperchlorate salt. The reaction appears to be stereospecific, thus, the transoid isomer is formed exclusively. These authors postulated the initial occurrence of a Michael addition of the non-protonated amine of ethylenediamine across the double bond of mesityl oxide to yield the \(\beta\)-aminoketone, Fig. 3. The protonation of the second amine group is assumed to block its participation in a similar reaction effectively. It was suggested that condensation of two molecules of \(\beta\)-aminoketone gives the ligand \([\text{Me}_6[14]\text{diene}]\) as its dihydroperchlorate salt, and its complexes with nickel(II) and metals other than nickel(II) have been prepared. Kolinski, Hay and co-workers have used this route to prepare a number of alkyl substituted macrocyclic dienes by the reaction of \(\alpha,\beta\)-unsaturated ketones with ethylenediamine monohydroperrchlorate to give dihydroperchlorates of polyalkyl-1,4,8,11-tetra-aza-cyclotetradeca-4,11-dienes, (XV), (XVI), (XVII), (XVIII) and (XIX). Nickel(II) complexes of these macrocycles have been studied. Complexes of the ligand (XIX) with zinc(II), copper(II) and cobalt(III) have been studied. Hay and Lawrance have prepared a number of metal(II) and cobalt(III) complexes of the ligand (XV).

Hideg and Lloyd isolated 5,12-dimethyl-7,14-diphenyl-tetra-azacyclotetradeca-4,11-diene, by the reaction of 1,2-diaminoethane with benzylideneacetone (PhCH:CHCOMe).
These workers provisionally assigned the cis-diimine structure (XX), to the macrocycle and subsequently provided mass-spectral evidence to support this structure.\(^{56}\) Cook et al.\(^{57}\) prepared a variety of nickel(II) and copper(II) complexes of this ligand, and on the basis of n.m.r. work and comparisons with other macrocyclic ligands a known structure suggested that the ligand was the trans-C-meso-diimine, (XXI), in which the two carbon centres have different chiralities (R and S) (where R and S represent the absolute configuration of the chiral centres). Cobalt(III) and rhodium(III) complexes of (XXI) have been studied.\(^{58,59}\) Reduction of the diimine, (XXI), with NaBH\(_4\) in methanol gives only three tetra-amines (L\(_a\), L\(_b\), L\(_c\)) establishing that the diimine (XXI) is a pure diastereoisomer. A recent crystal-structure determination\(^{60}\)
\[ [14]-4,11\text{-diene} \]

(XV) \( R_1 = R_2 = H \)
(XVI) \( R_1 = H; \ R_2 = CH_3 \)
(XVII) \( R_1 = H; \ R_2 = C_2H_5 \)
(XVIII) \( R_1 = H; \ R_2 = 1-C_3H_7 \)

(XIX)

(XX)
trans-C-meso-Ph$_2$Me$_2$[14]-diene

on [CuLa][NO$_3$]$_2$ showed that the complex has the C-meso-C-meso-N-meso-N-meso configuration, (XXII), providing almost unequivocal evidence for the trans-C-meso structure, (XXI).

Cobalt(III) and rhodium(III) complexes of La have been studied.\textsuperscript{59}
A new direct synthesis of cyclic amines in usually high yields (40-90%) has been recently developed. This route can be used to prepare 9 to 21-membered rings macrocycles containing three to seven donor atoms and does not require either high dilution techniques or template effects in the cyclization step. A typical reaction is the condensation of the tosylated reactants a and b in Fig. 4, by heating in DMF at 100°C for one hour. The tetra-tosyl derivative C in Fig. 4, was obtained in 80% yield. The tosyl groups are readily removed by heating with concentrated sulphuric acid, Fig. 4.

Fig. 4 Synthesis of cyclen by the Richman and Atkins procedure.

Ts = C₇H₇SO₂
In addition to the abovementioned methods for synthesizing macrocyclic ligands and macrocyclic complexes, there exist systematic transformations that permit the generation of a variety of products by reactions of a single condensation product. Two processes, hydrogenation and dehydrogenation, have been used in the synthesis of many of these new complexes.  \(^5,62-65\) Dehydrogenation reactions involve the conversion of secondary amine groups into azomethine linkages through the abstraction of one mole of hydrogen. Such linkages have been introduced into five- and six-membered chelate rings.  \(^66\) Goedkin \(^67\) has shown that simple bidentate ligands, e.g. ethylenediamine, can be oxidatively dehydrogenated to \(\alpha\)-diimines while remaining coordinated. Also, the early work of Vassian and Murmann \(^68\) showed that, when two \(\alpha\)-diimine linkages are produced in one chelate ring-ionization of a proton may occur, producing a \(\beta\)-diketonate-like chelate structure.

The converse process, hydrogenation of coordinated imine groups is well documented among complexes containing macrocyclic ligands.  \(^5,62,64\) Such processes have been observed both chemically \(^5,64,69\) and electrochemically.  \(^52,70\) Fig. 5 shows hydrogenation-dehydrogenation sequences in macrocycles as produced by Curtis.  \(^5\)

1.3 Stereochemistry

Metal complexes of macrocyclic ligands usually have two or more chiral carbon and chiral nitrogen centres leading to a large number of stereoisomers. Two chiral nitrogen centres are present in metal complexes of ligand (XV), (N-1 and N-8), and this gives rise to \(N\)-meso and \(N\)-racemic
Hydrogenation-dehydrogenation sequences in nickel(II) complexes of macrocyclic tetra-aza ligands.

Figure 5.
diastereoisomers, (XXIII) and (XXIV). Kolinski and Korybut-Daszkiewicz isolated two labile inter-convertible diastereoisomers by fractional crystallisation of the nickel(II) complex of the ligand (XV), and on the basis of molar extinction coefficients assigned the N-meso and N-rac configurations. The least symmetric diastereoisomer will have the higher extinction coefficient. Thus the complex (ε = 87) was assigned the N-rac configuration and the complex (ε = 81) the N-meso configuration on this basis. Sledziewska has confirmed this assignment by resolving the N-rac nickel(II)
complex (XXIV) on a potato starch column. Hay and Lawrance have identified the two diastereoisomers of trans-[Co(Me₂[14]-
diene][Cl₂][ClO₄], (XXIII) and (XXIV); [M = Cobalt(III)]. These diastereoisomers designated as isomer (a) and (b). They assigned the N-meso and N-rac configurations to isomer (a) and (b) respectively (XXIII) and (XXIV). A recent crystallographic work has confirmed the N-rac configuration for the isomer [Co[XV](SCN)₂][SCN]·H₂O. This isomer was prepared by anion metathesis from the parent [Co[XV][Cl₂][ClO₄] (isomer (b)), thus the X-ray work confirms the initial assignments. Analogously in metal complexes of ligand (XI) two chiral nitrogen centres are present. Two isomers have been reported for both the nickel(II) and cobalt(III) complexes of Meg[14]diene, (XI). These isomers have been shown to correspond to the two possible orientations of N-H bonds (racemic or meso) of the secondary nitrogen donors.

Reduction of 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydroperchlorate, (XV) gives rise to two carbon chiral centres, thus, forming the C-meso and the C-rac diastereoisomers, (XXV) and (XXVI). Metal complexes of the C-meso and the C-rac ligands (XXV) and (XXVI) contain six chiral centres (two carbon and four nitrogen) so that 20 diastereoisomers (16 racemates and 4 meso forms) are theoretically possible. In the C-meso series there are six racemates and four meso forms, while in the C-rac series there are ten racemates. The various stereoisomers of the C-meso series are shown in Fig. 6. Similarly, reduction of the imine functions in the ligand [Me₆[14]diene], (XI) forms two
Figure 6.
Possible stereoisomers of the C-meso series of Me₂-cyclam complexes.
isomeric ligands C-meso and C-rac \([\text{Me}_6[14]-\text{ane N}_4]\). Metal complexes of each form contains four chiral nitrogen and two chiral carbons, giving rise to the same number of diastereoisomers as in metal complexes of (XXV) and (XXVI). A complete study on these complexes by n.m.r. has been carried out \(^{76,77}\) and some structures have been confirmed by X-ray studies. \(^5\)
CHAPTER 2

Square Planar vs Octahedral Equilibria in Nickel(II) Complexes of C-meso-C-meso-5,7,12,14-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane.

The reaction of the monohydropseudonolate salt of 1,2-diaminoethane with pent-3-ene-2-one in methanol solution gives the dihydropseudonolate salt of 5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene-[Me₄(S)[¹⁴]diene].2HClO₄ (XVI). The ligand contains two chiral carbon centres at C-7 and C-14 so that C-rac (XXVII) and C-meso (XXVIII) diastereoisomers can occur. Kolinski and Korybut-Daszkiewicz studied the square planar nickel(II) complexes of the ligands in detail. Fractional crystallisation of the crude [Ni(Me₄(S)[¹⁴]diene)][ClO₄]₂ complex from 90% methanol gave two isomers A (orange crystals, least soluble)
and B (yellow needles). The ratio of isomer A to B was ca 5:1. X-ray crystallography has confirmed that isomer A is the C-meso compound and that B is the C-rac compound.78,79

The nickel(II) complex of isomer A is readily reduced with sodium borohydride or nickel-aluminium alloy in basic solution. Reduction of the C-meso complex could give the nickel(II) complexes of the three diastereoisomeric amines (XXIX-XXXI). However, the nickel(II) complex of amine (XXX) is formed preferentially (ca 70%) and is readily obtained isomerically pure. The preferred stereochemistry for metal complexes of (XXX) is shown in (XXXII) in which the thermodynamically favoured N-meso-N-meso configuration of the chiral N-centres occurs leading to four equatorial methyl groups.

\[\text{(XXIX)} \quad \text{C-meso-C-rac} \quad \text{(XXX)} \quad \text{C-meso-C-meso} \quad \text{(XXXI)} \quad \text{C-meso-C-meso}\]
The axial coordination sites on nickel(II) are readily accessible to monodentate ligands. In the present work a number of octahedral nickel(II) complexes of the ligand (XXX) are prepared and characterised. The square planar \* octahedral equilibrium of such complexes has been studied in detail.
2.1 Experimental

5,7,12,14-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene Dihydroperchlorate; Me₄(S)\[14\]diene.2HClO₄.

The ligand was prepared as follows:⁴⁶,⁵¹

Perchloric acid (83 cm³ of 72%, 1 mole) was added dropwise with continuous stirring to a cooled (ice-salt bath) solution of 1,2-diamino-ethane (67 cm³, 1 mole) dissolved in methanol (600 cm³). On completion of the addition the reaction mixture was cooled to -5°C. Pent-3-ene-2-one (81 cm³, 1 mole) diluted with an equal volume of methanol was then added dropwise with continuous stirring, the temperature being maintained below 5°C. On completion of the addition the mixture was stirred for four hours during which time the temperature was allowed to rise to ambient. The resulting suspension was stored overnight in a refrigerator. The white product was filtered off, washed thoroughly with methanol, then ether and dried in a vacuum desiccator. Yield 120g, m.p. 120-123°C.

(Calc. for C₁₄H₂₈N₄.2HClO₄: C, 37.1; H, 6.7; N, 12.35%. Found: C, 37.4; H, 6.7; N, 12.2%).

5,7,12,14-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene nickel(II)Perchlorate; [Ni(Me₄(S)[14]diene)]ClO₄₂⁻.

A suspension of powdered nickel(II) carbonate (basic) (50g, 0.134 mole) in water (200 cm³) was heated to boiling and a suspension of the ligand dihydroperchlorate (60g, 0.13 mole) in water (100 cm³) added dropwise. The reaction mixture was
boiled until evolution of carbon dioxide ceased (0.5 hours). The unreacted nickel(II) carbonate was filtered off and the filtrate reduced to half volume on a rotary evaporator. Cooling in an ice-bath gave a yellow-orange product, which was filtered off, and the filtrate reduced to half volume and cooled. A second crop of yellow crystals was obtained. The two crops were combined and the mixture of diastereoisomers fractionally crystallised from hot water. The first fractions gave the "orange" isomer \( A_\alpha = \text{N-rac-C-meso} \) (a-e). The \(^1\text{H} \) n.m.r. spectrum of the \( A_\alpha \) isomer was identical to that reported in the literature,\(^5\) however column chromatography on Sephadex C-25 indicated ca 80% \( A_\alpha \) and ca 15% \( B \) and ca 5% of a third component which has subsequently been identified (see Appendix II).

The subsequent fractions gave small amounts of the "yellow" isomer (B). (Calc. for \( \text{C}_{14}\text{H}_{28}\text{Cl}_{2}\text{N}_{4}\text{O}_{8}\text{Ni.F}_{2}\text{O} \) (orange isomer): C, 31.95; H, 5.4; N, 10.65%. Found: C, 31.8; H, 5.7; N, 10.4%. Calc. for \( \text{C}_{14}\text{H}_{28}\text{Cl}_{2}\text{N}_{4}\text{O}_{8}\text{Ni} \) (yellow isomer); C, 32.95; H, 5.6; N, 11.0%. Found: C, 33.2; H, 5.7; N, 10.85%).

Reduction of \( \text{N-rac-C-meso-5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene nickel(II)Perchlorate.} \)

The orange isomer (64.77g, 0.127 mole) was dissolved in hot water (750 cm\(^3\)), then allowed to cool to room temperature. The pH of the solution was adjusted to about 9 (by adding 2M NaOH). Sodium borohydride (slight excess > 0.25 mole) was added to the solution proportionwise with
vigorously stirred and the temperature maintained at 60°C. On completion of the addition the solution was heated for
a further 0.5 hours and filtered. The volume of the filtrate
was reduced to about half and left to stand at room temperature.
On standing overnight a crop of violet crystals was obtained
(15g, 23%). The mother liquor was left for further crystallisation
(24 hours), a second crop of orange-red crystals (5g, 7.5%) was obtained.
Further standing at room temperature ca 2 days, gave a third
crop of orange-red crystals (5g, 7.5%). Total yield 25g, 38%.
Recrystallisation of the first crop (violet) from water gave
a mixture of red and violet crystals which arises due to a
square planar → octahedral equilibrium. This mixture
recrystallised from 6M NaClO₄ to give a homogeneous reddish-orange product. The second and the third crops were also
recrystallised from water and reddish orange crystals were
obtained from each crop. From this point the product of the
first crop will be called NiLₐ²⁺, the product of the second
crop NiLₐ²⁺ and the product of the third NiLₐ²⁺.
(Calc. for [NiLₐ][ClO₄]₂·1.5H₂O (NiCl₄N₄Cl₂O₈H₃O·1.5H₂O):
C, 31.1; H, 6.5; N, 10.35%. Found: C, 31.22; H, 6.0; N, 10.50%.
Calc. for [NiLₐ][ClO₄]₂ 0.5 H₂O: C, 32.15; H, 6.36; N, 10.70%.
Found: C, 32.24; H, 6.13; N, 10.61%. Calc. for
[NiLₐ][ClO₄]₂: C, 32.70; H, 6.30; N, 10.9%.
Found: C, 32.90; H, 6.30; N, 10.80%).

Decomposition of the [NiLₐ][ClO₄]₂.
The red complex [NiLₐ][ClO₄]₂ (1g, 0.002 mole)
was dissolved in hot water and solid sodium cyanide (0.5g, 0.01 mole)
added. The red solution turned violet in colour (axial addition of cyanide). The reaction mixture was heated under reflux for 2 hours. The reaction mixture allowed to cool, and then evaporated to dryness on a rotary evaporator. The solid residue was extracted with hot chloroform. The chloroform evaporated to leave the macrocyclic amine which was recrystallised from xylene, m.p. 169-172°C. (Calc. for \(\text{L}_a\) \(\text{C}_{14}\text{N}_4\text{H}_{32} \): C, 65.6; H, 12.6; N, 21.9%. Found: C, 65.3; H, 12.4; N, 22.0%).

In the same manner the complexes \([\text{NiL}_b]\)\(\text{ClO}_4\)_2 and \([\text{NiL}_c]\)\(\text{ClO}_4\)_2 were decomposed. The macrocyclic amines (\(\text{L}_b\) and \(\text{L}_c\)) obtained have melting points 150-155°C and 70-72°C respectively (further work will be required to purify and fully characterise these amines). The amine \(\text{L}_a\) is the least soluble in xylene and \(\text{L}_c\) is the most soluble. The i.r. spectra of the three amines lack the band at 1660 cm\(^{-1}\) due to \(\nu\text{C} : \text{N}\), indicating that complete reduction has occurred. Calc. for \((\text{L}_b)\) \(\text{C}_{14}\text{N}_4\text{H}_{32}\text{.5H}_2\text{O} \): C, 59.32; H, 12.45; N, 19.77%. Found: C, 59.0; H, 12.5; N, 19.44%. Calc. for \((\text{L}_c)\) \(\text{C}_{14}\text{N}_4\text{H}_{32}\text{2H}_2\text{O} \): C, 57.5; H, 12.4; N, 19.16%. Found: 57.26; H, 12.25; N, 19.1%.

The nickel(II) complex \([\text{NiL}_a]\)\(\text{ClO}_4\)_2 was used for the following preparations.

**Trans-dichloro(5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II);**

\[\text{trans-[NiL}_a\text{Cl}_2]\].

To a hot solution of the complex \([\text{NiL}_a]\)\(\text{ClO}_4\)_2 (0.5g, 0.9 mmole) in methanol-water (25 cm\(^3\)), sodium chloride
(0.1g, 1.9 mmole) was added. The solution heated on a water bath, during which time the colour of the solution turned violet. On cooling the solution in an ice-bath violet crystals formed, these were filtered off, washed with ethanol then ether and finally dried in a vacuum desiccator. (Calc. for NiC_{14}H_{32}N_{4}Cl_{2}: C, 43.56; H, 8.36; N, 14.5; Cl, 18.37%. Found: C, 43.3; H, 8.31; N, 13.84; Cl, 18.12%).

Trans-dibromo(5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Dihydrate; trans-[NiL_{a}Br_{2}] \cdot 2H_{2}O.

To a hot solution of [NiL\_a][ClO\_4] \_2 (0.5g, 0.9 mmole) in methanol-water (25 cm\(^3\) 1:1 v/v), sodium bromide (0.2g, 1.9 mmole) was added and the solution heated on a water bath. On cooling the solution, violet crystals of the product were obtained, these were filtered off, washed with ethanol, then ether and dried in a vacuum desiccator. (Calc. for NiC_{14}N_{4}H_{32}Br\_2 \cdot 2H_{2}O: C, 32.9; H, 7.1; N, 10.96%. Found: C, 32.6; H, 7.15; N, 10.61%).

Trans-diiodo(5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Dihydrate; trans-[NiL\_aI\_2].

To a hot solution of [NiL\_a][ClO\_4] \_2 (0.3g, 0.58 mmole) in methanol-water (25 cm\(^3\)), sodium iodide (0.17g, 1.1 mmole) was added. The reaction mixture was heated on a water bath for 0.5 hours, then cooled in an ice-bath. The violet product was collected by filtration, washed with ethanol then ether and dried in a vacuum desiccator. (Calc. for NiC_{14}N_{4}H_{32}I\_2 \cdot 2H_{2}O; C, 27.8; H, 5.99; N, 9.26%. Found: C, 27.54; H, 5.9; N, 8.93%).
Trans-dinitro(5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Hemihydrate; trans-[NiLa(NO$_2$)$_2$]•0.5H$_2$O

To a hot solution of [NiLa][ClO$_4$]$_2$ (0.5, 0.9 mmole) in water (30 cm$^3$), sodium nitrite (0.13g, 1.9 mmole) was added. The solution was heated on a water bath for 0.5 hours. On cooling in an ice-bath the pale pink product precipitated. This was filtered off, washed with ethanol, then ether and dried in a vacuum desiccator. (Calc. for NiC$_{14}$H$_{32}$N$_6$O$_4$.0.5 H$_2$O: C, 40.4; H, 7.9; N, 20.2%. Found: C, 40.7; H, 6.9; N, 20.5%).

Trans-diisothiocyanato(5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II); trans-[NiLa(SCN)$_2$].

To a hot solution of [NiLa][ClO$_4$]$_2$ (0.3g, 0.58 mmole) in water (30 cm$^3$), potassium thiocyanate (0.11g, 1.16 mmole) was added and the reaction mixture heated on a water bath for 0.5 hours. The product which precipitated on heating was filtered off and washed with ethanol and ether and dried in a vacuum desiccator. (Calc. for NiC$_{16}$N$_6$S$_2$H$_{32}$; C, 44.55; H, 7.5; N, 19.49%. Found: C, 44.8; H, 7.4; N, 19.0%).

Trans-diammine(5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Perchlorate; trans-[NiLa(NH$_3$)$_2$][ClO$_4$]$_2$.

The nickel complex [NiLa][ClO$_4$]$_2$ (0.3g) was dissolved in water (25 cm$^3$). Ammonia (0.88 solution, 5 cm$^3$) was added, the solution gently warmed on a water bath for 10 minutes, and the solution cooled in an ice-bath for 2 hours.
The violet product which precipitated was filtered off and air dried (on long standing in the air the product loses the ammine ligands and turns red in colour). (Calc. for NiC_{14}N_{6}H_{38}Cl_{2}O_{8}: C, 30.7; H, 7.0; N, 15.34%. Found: C, 30.8; H, 6.9; N, 14.9%).

Trans-bis(dimethylsulphoxide)(5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)-nickel(II) Perchlorate; trans-[Ni(L_{a})(DMSO)_{2}[ClO_{4}].

A solution of [NiL_{a}]ClO_{4} (0.3g, 0.58 mmole) in DMSO (20 cm³) was heated on a water bath for one hour. On long standing in a refrigerator (2 days) the crystalline product was obtained, this was filtered off, and air dried. (Calc. for NiC_{18}H_{41}N_{4}S_{2}Cl_{2}O_{10}: C, 32.25; H, 6.62; N, 8.4%. Found: C, 31.9; H, 6.44; N, 8.10%).

Trans-Cyano-perchlorato(5,7,12,14-tetramethyl-1,4,8,11-azacyclotetradecane)nickel(II) Hemihydrate; trans-[NiL_{a}(ClO_{4})(CN)]0.5H_{2}O.

To a solution of [NiL_{a}]ClO_{4} (0.3g, 0.58 mmole) in water (25 cm³) sodium cyanide (0.06g, 1.16 mmole) was added. The solution heated on a water bath for half an hour. On cooling the violet product precipitated, this was filtered off and dried. (Calc. for NiC_{15}H_{32}N_{5}ClO_{4}.0.5H_{2}O: C, 40.1; H, 7.4; N, 15.6%. Found: C, 40.1; H, 7.0; N, 15.2%).

Trans-Acetato-aquo(5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Perchlorate; trans-[NiL_{a}(H_{2}O)(OAc)][ClO_{4}].

To a solution of [NiL_{a}]ClO_{4} (0.3g, 0.58 mmole)
in water (25 cm$^3$) sodium acetate (0.096g, 1.16 mmole) was added. The solution then heated on a water bath for 0.5 hours, the product which precipitated during heating was filtered off and dried in a vacuum desiccator.

(Calc. for NiC$_{16}$H$_{37}$N$_4$ClO$_7$: C, 39.1; H, 7.6; N, 11.4%  
Found: C, 39.3; H, 7.4; N, 11.3%).
2.2 Results and discussion

The reaction of the nickel(II) complex of C-meso-5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene with sodium borohydride would be expected to give three diastereoisomeric nickel(II) complexes, which would be obtained from the amines (XXIX-XXXI). If the complexes are assumed to have the most stable cyclam or trans(III) configuration (chair six-membered rings and gauche five-membered rings) the complexes will be as represented in (XXXII-XXXIV).

![Chemical Structures](XXXIII)(XXXIV)

C-meso-C-rac  
C-meso-C-meso

The first fraction \([\text{NiLa}]^{2+}\) obtained on sodium borohydride reduction consisted of violet crystals indicating
octahedral nickel(II) rather than square planar nickel(II) which was observed in the subsequent fractions ([NiL_b]^2+ and [NiL_c]^2+).

The visible spectrum of the violet complex in water displays bands characteristic of both square planar nickel(II) and octahedral nickel(II) complexes.

Recrystallisation of the violet complex from 6M NaClO_4 gave a homogeneous red-orange complex. The function of the NaClO_4 is to decrease the "free" water concentration and so drive the equilibrium

\[
\text{square planar } + 2\text{H}_2\text{O} \rightleftharpoons \text{octahedral}
\]

to the left. The planar form in CH_3NO_2 as solvent has a single d-d band at 21,053 cm\(^{-1}\) (\(\varepsilon = 51\)), Figure 7. A solution of the planar form in water gives the spectrum shown in Figure 8 with d-d bands at:

<table>
<thead>
<tr>
<th>Octahedral</th>
<th>Planar</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_3) 29,200 cm(^{-1})</td>
<td>21,053 cm(^{-1})</td>
</tr>
<tr>
<td>(v_2) 18,900; 14,300 cm(^{-1})</td>
<td>8,700</td>
</tr>
<tr>
<td>(v_1) 9,100</td>
<td>8.8</td>
</tr>
<tr>
<td>(\varepsilon_{\text{obs}} = 10.4)</td>
<td>(\varepsilon_{\text{obs}} = 5.8) (\varepsilon_{\text{obs}} = 2.9)</td>
</tr>
</tbody>
</table>

Treatment of the square planar complex [NiL_a]^2+ with sodium cyanide (to remove the nickel(II)) gave initially the violet trans-dicyano derivative which decomposed on heating to give the free ligand (m.p. 172°C) and Ni(CN)_4\(^{2-}\). The tetra-amine can be recrystallised from hot xylene. The same
Figure 7: The visible spectrum of the planar complex [NiL₄][ClO₄]₂ in nitromethane.
Figure 8: The visible spectrum of \([\text{NiLa}]\)[ClO₄]₂ in water showing
\[ v_3 \quad 29,200 \]
\[ v_2 \quad 18,900 \]
\[ v_1 \quad 14,300 \]
procedure with \([\text{NiL}_b]^2+\) and \([\text{NiL}_c]^2+\) gave amines m.p. 150°-155°C and 69°-70°C respectively, however, the complexes of these amines were not studied in detail.

Since \([\text{NiL}_a]^2+\) is the only nickel(II) complex to undergo axial additions it is assumed to be (XXXII) in which all the methyl groups are equatorial. Molecular models indicate that the axial sites are quite open, and accessible to monodentate ligands. A crystal structure will be required to confirm this point, but n.m.r. measurements (CD$_3$NO$_2$) solution display a single methyl doublet at 1.156 (J = 6Hz) consistent with four equatorial methyl groups (equatorial methyl groups normally occur near 1.28 and axial methyl groups near 1.96 in nickel(II) complexes).

A number of complexes of \([\text{NiL}_a]^2+\) with a variety of axial ligands (X)

\[ [\text{NiL}_a]^2+ + 2X \rightarrow [\text{NiL}_aX_2]^n^+ \]

have been prepared and characterised (X = Cl, Br, I, NO$_2$, NH$_3$, SCN, DMSO and also CN, ClO$_4^-$, OAc, OH$_2$). The reactions are summarised in Figure 9.

The reaction of two equivalents of NaCN with \([\text{NiL}_a][\text{ClO}_4]\) in aqueous solution gave \([\text{NiL}_a(\text{CN})(\text{ClO}_4)]\) containing coordinated perchlorate. The i.r. spectrum has bands at 1100 cm$^{-1}$ (split), 940 cm$^{-1}$ and 620 cm$^{-1}$. The complex has $\Lambda_M = 73$ ohm$^{-1}$ cm$^2$ mol$^{-1}$ in water, suggesting that the coordinated perchlorate is displaced by water to give the cyano-aquo derivative.

* A crystal structure determination is currently being carried out.
Figure 9: Summary of the reactions of \([\text{Ni}_\text{L}_\text{a}]\text{[ClO}_4\text{]}_2\)
The reaction of two equivalents of NaOAc with 
[\text{NiLa}][\text{ClO}_4]_2 gives the acetato-aquo species \([\text{NiLa}(\text{OAc})(\text{OH}_2)]^-\)
[\text{ClO}_4], which has \(\Lambda_M = 173 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\) in water, a value intermediate between a 1:1 and a 1:2 electrolyte presumably as a result of the equilibrium,

\[
[\text{NiLa}(\text{OAc})(\text{OH}_2)]^+ + \text{H}_2\text{O} \rightarrow [\text{NiLa}(\text{OH}_2)_2]^2+ + \text{OAc}^-
\]

In acetonitrile the complex is a 1:1 electrolyte 
\((\Lambda_M = 144 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1})\). Typical values in acetonitrile as solvent are 1:1 \(\sim 150 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\) and for a 1:2 \(\sim 290 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\).

d-d-Spectra

The solid state spectra of the various complexes with axial ligands display the expected three bands for nickel(II) in \(O_h\). For nickel(II) in \(D_{4h}\) six bands are theoretically possible, and these can be seen in figure 10. In cases where the ligand field strength of the axial ligands differs markedly from that of the equatorial macrocycle as in \([\text{NiLa}I_2]\) five bands are in fact observed. Thus for \([\text{NiLa}I_2]\)
the \(3\text{A}_{2g} \rightarrow 3\text{T}_{2g}\) \((\nu_1)\) occurs as two bands which can be assigned to \(3\text{B}_{1g} \rightarrow 3\text{E}_g^a (7,800 \text{ cm}^{-1})\) and \(3\text{B}_{1g} \rightarrow 3\text{B}_{2g} (9,000 \text{ cm}^{-1})\) in \(D_{4h}\) symmetry while for the \(3\text{A}_{2g} \rightarrow 3\text{T}_{1g}\) \((\nu_2)\) two bands are also observed \(3\text{B}_{1g} \rightarrow 3\text{A}_{2g} (14,700 \text{ cm}^{-1})\) and \(3\text{B}_{1g} \rightarrow 3\text{E}_g (18,900 \text{ cm}^{-1})\).

In \([\text{NiLa}(\text{NO}_2)_2]\) which approximates more closely to \(O_h\) only three bands are clearly seen \(\nu_3 29,000; \nu_2 20,000\) (some splitting can be detected) and \(\nu_1\) at 11,100 cm\(^{-1}\).
Figure 10: Energy level diagram for nickel(II) in $O_h$ and $D_{4h}$ symmetry-weak field model (reproduced from reference 80)
Figure 10: Energy level diagram for nickel(II) in $O_h$ and $D_{4h}$ symmetry-weak field model (reproduced from reference 80)
spectra are very similar to those observed by Cummings et al. for the axial coordination derivatives of the nickel complexes of the ligand 12,14-dimethyl-1,4,8,11-tetra-azacyclotetradecane-(Me₂cyclam). Thus for [Ni(Me₂cyclam)(SCN)₂] bands were observed at 10,929; 12,461; 19,608 and 30,769 cm⁻¹ (solution spectra) while in [NiLa(SCN)₂] bands were observed at 10,900 (v₁); 13,500, 18,900 (v₂) and 29,400 cm⁻¹ (v₃) in the solid state. The spectra are fully consistent with high spin tetragonal nickel(II) (D₄h). Table 1 summarises d-d bands observed for the various high spin nickel(II) complexes studied.

Infrared Spectra

The prominent i.r. absorption bands in the various complexes are listed in Table 2. The i.r. spectra are consistent with the formulations discussed. For [NiLa(SCN)₂] the i.r. data is consistent with N-bonded isothiocyanato structure, with a strong and broad band at 2080 cm⁻¹ characteristic of M-N bonding.

The complex [NiLa₂(OAc)(H₂O)][ClO₄] has vOH at 3440 cm⁻¹ and ClO₄⁻ bands at 1165 cm⁻¹ (v O=Cl assymm.) and 625 cm⁻¹ (δ ClO₄⁻) consistent with ionic perchlorate. However, in trans-[NiLa(CN)(ClO₄)]0.5H₂O there is strong evidence for coordinated ClO₄⁻ (monodentate) since the 1100 cm⁻¹ band is split and in addition to the band at 625 cm⁻¹ the 940 cm⁻¹ band is present which can be assigned to a coordinated perchlorate.
**TABLE 1**

d-d Spectra for the various nickel(II) complexes of the type $[\text{NiL}_aX_2]^{n+}$ ($n = 0, 1$ or 2).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_3$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans- $[\text{NiL}_a\text{Cl}_2]$</td>
<td>27,800</td>
<td>18,500; 14,300</td>
<td>8,900</td>
</tr>
<tr>
<td>trans- $[\text{NiL}_a\text{Br}_2]$</td>
<td>29,000</td>
<td>18,900; 14,700</td>
<td>9,000</td>
</tr>
<tr>
<td>trans- $[\text{NiL}_a\text{I}_2]$</td>
<td>29,000</td>
<td>18,900; 14,700</td>
<td>9,000; 7,800</td>
</tr>
<tr>
<td>trans- $[\text{NiL}_a\text{(NO}_2)_2]$</td>
<td>29,000</td>
<td>20,000$^a$</td>
<td>11,100</td>
</tr>
<tr>
<td>trans- $[\text{NiL}_a\text{(SCN)}_2]$</td>
<td>29,400</td>
<td>18,900; 13,500</td>
<td>10,900</td>
</tr>
<tr>
<td>trans- $[\text{NiL}_a\text{(CN)}(\text{ClO}_4)]$</td>
<td>30,300</td>
<td>19,400</td>
<td>12,350</td>
</tr>
<tr>
<td>trans- $[\text{NiL}_a\text{(OAc)}-(\text{H}_2\text{O})][\text{ClO}_4]$</td>
<td>29,000</td>
<td>18,900; 14,100</td>
<td>9,500</td>
</tr>
</tbody>
</table>

**Solid State ($\lambda_{max}$ in cm$^{-1}$).**

**Solution Spectra**

- trans- $[\text{NiL}_a\text{(DMSO)}_2][\text{ClO}_4]_2$ $^b$
  - 28,600 | 18,350; 14,100 | - |
- trans- $[\text{NiL}_a\text{(NH}_3)_2][\text{ClO}_4]_2$ $^c$
  - 29,400 | 19,050 | - |

*a* = Some splitting of this band is observable and the band position is only approximate

*b* = In DMSO solution

*c* = In ammonia solution
**TABLE 2**

Prominent i.r. absorption bands * (cm$^{-1}$) of complexes of the type $[\text{NiL}_a \text{XY}]^{n+}$, $\text{X=Cl}^-, \text{Br}^-, \text{I}^-, \text{NH}_3, \text{NO}_2^-, \text{SCN}^-$ and DMSO; $\text{X} \neq \text{Y}$, $\text{X=OAc}$ or CN and $\text{Y} = \text{ClO}_4^-$ or $\text{H}_2\text{O}$; $n = 0, 1$ or $2^+$ and $Z = \text{ClO}_4^-$.  

<table>
<thead>
<tr>
<th>Compound</th>
<th>vNH</th>
<th>vClO$_4^-$</th>
<th>Other ligand bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}$</td>
<td>3250vs</td>
<td></td>
<td>2900 v(CH)bs</td>
</tr>
<tr>
<td>$[\text{NiLa}[\text{ClO}_4]_2\text{.5H}_2\text{O}]$</td>
<td>3190vs</td>
<td>1100b, vs</td>
<td>2950 v(CH) vs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta625$vs</td>
<td></td>
</tr>
<tr>
<td>trans-$\text{[NiLaCl}_2]$</td>
<td>3200s</td>
<td></td>
<td>2920 v(CH) vs</td>
</tr>
<tr>
<td>trans-$\text{[NiLaBr}_2$2\text{H}_2\text{O}$</td>
<td>3170s</td>
<td></td>
<td>2940 v(CH), 1650s(H$_2$O) 3300 v(H$_2$O)</td>
</tr>
<tr>
<td>trans-$\text{[NiLaI}_2$2\text{H}_2\text{O}$</td>
<td>3170s</td>
<td></td>
<td>3300, 1630 v and $\delta$(H$_2$O) 2900 v(CH)</td>
</tr>
<tr>
<td>trans-$\text{[NiLa(NO}_2]_2$-$0.5$\text{H}_2\text{O}$</td>
<td>3200vs</td>
<td></td>
<td>2940 v(CH)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>815 $\delta$(NO$_2$)</td>
</tr>
<tr>
<td>trans-$\text{[NiLa(SCN)}_2$</td>
<td>3230vs</td>
<td></td>
<td>2950 vs v(CH) 2080 vs, b v(Coord.C:N)</td>
</tr>
<tr>
<td>trans-$\text{[NiLa(DMSO)}_2$-$\text{ClO}_4]$</td>
<td>3210m</td>
<td>1120b, vs</td>
<td>2950s v(CH) 940 v(SO)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta625$s vs</td>
<td></td>
</tr>
<tr>
<td>trans-$\text{[NiLa(NH}_3]_2$-$\text{ClO}_4]$</td>
<td>3180s</td>
<td>1100b, vs</td>
<td>2980 v(CH)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta620$s vs</td>
<td></td>
</tr>
<tr>
<td>trans-$\text{[NiLa(OAc)}-\text{(H}_2\text{O})\text{ClO}_4]$</td>
<td>3260m</td>
<td>1165b, vs</td>
<td>3440 v(H$_2$O) 2980 v(CH) 1565 v(COO)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta625$s vs</td>
<td></td>
</tr>
<tr>
<td>trans-$\text{[NiLa(CN)}-\text{(ClO}_4)$0.5\text{H}_2\text{O}$</td>
<td>3270vs</td>
<td>1100(split)</td>
<td>2960 v(CH)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta625$ vs</td>
<td></td>
</tr>
</tbody>
</table>

* Spectra recorded as KBr discs.
Equilibrium studies

The equilibrium,

\[ [\text{NiLa}]^{2+} + 2\text{H}_2\text{O} \rightarrow [\text{NiLa(OH}_2]^2+ \]

was studied in detail as a function of temperature. As discussed previously the addition of 6M NaClO₄ to a solution of the planar \* octahedral mixture of the diaquo derivative leads to the immediate precipitation of the planar orange isomer (since the sodium perchlorate decreases the effective water concentration). The planar isomer in nitromethane as solvent has a single d-d band at 475nm (21,053 cm⁻¹) (ε = 51). This value may be compared with [Ni(cyclam)]²⁺ at 22,470 cm⁻¹ and [Ni(2,3,2-tet)]²⁺ at 22,420 cm⁻¹.²³

The absorbance at 475nm is due exclusively to the square planar isomer, and the proportion of the square planar isomer increases with increasing temperature, Figure 11. Table 3 lists values of the absorbance at 475nm as a function of temperature. Values of the % planar isomer were obtained from the expression

\[
\% \text{Planar isomer} = \frac{\epsilon_{\text{obs}}}{51} \times 100
\]

where 51 is the extinction coefficient obtained in nitromethane.

The equilibrium constant K is defined as

\[ K = \frac{[\text{Octahedral}]}{[\text{Planar}]} \]

A plot of log K versus 1/T is linear, Figure 12. The value of ΔH° obtained from the least square slope (correlation
Figure 11: Spectral changes for the complex $[\text{Ni}_2\text{AlCl}_4]_2^-$ as a function of temperature in aqueous solution.
### TABLE 3

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$A_{475}$</th>
<th>$\epsilon_{obs}$</th>
<th>% Planar</th>
<th>% Oct</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.42</td>
<td>8.4</td>
<td>16.5</td>
<td>83.5</td>
<td>5.06</td>
</tr>
<tr>
<td>33</td>
<td>0.50</td>
<td>10.0</td>
<td>19.6</td>
<td>80.4</td>
<td>4.10</td>
</tr>
<tr>
<td>45</td>
<td>0.64</td>
<td>12.8</td>
<td>25.1</td>
<td>74.9</td>
<td>2.98</td>
</tr>
<tr>
<td>60</td>
<td>0.87</td>
<td>17.4</td>
<td>34.1</td>
<td>65.9</td>
<td>1.93</td>
</tr>
<tr>
<td>70</td>
<td>0.97</td>
<td>19.4</td>
<td>38.0</td>
<td>62.0</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Initial conc. of $\text{[NiLa]}\text{[ClO}_4\text{]}_2 = 0.0499 \text{ mol dm}^{-3}$

* The value of $\epsilon_{obs}$ is obtained from the stoichiometric concentration of the complex

\[
\% \text{ planar} = \frac{\epsilon_{obs}}{51} \times 100
\]
Figure 12:
Temperature dependence of \( \log K \) for the planar octahedral equilibrium of \([\text{NiL}_a]^{2+}\) in water.
coefficient 0.9992) is -5.3 kcal mol$^{-1}$. Values of $\Delta S^\circ$ were calculated at each temperature from the expression $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The value of $\Delta S^\circ$ is -14.6 cal K$^{-1}$ mol$^{-1}$, Table 4 lists the thermodynamic parameters for the planar $\rightarrow$ octahedral equilibrium.

The values of $\Delta H^\circ$ and $\Delta S^\circ$ obtained are quite similar to those recently reported for cyclam and for open chain ligands such as 2,3,2-tet and 3,2,3-tet$^{83}$, Table 5.

For the equilibrium

$$[\text{NiL}]^{2+} + 2\text{H}_2\text{O} \rightarrow [\text{NiL(OH}_2)\text{]}^{2+}$$

the value of $\Delta S^\circ$ is as expected negative, since two water molecules are constricted.

The conversion of the planar to the octahedral species is an exothermic reaction. Formation of the octahedral species involves the formation of the two axial Ni-OH$_2$ bonds and heat is released as a result. It has been suggested that stronger Ni-N bonds are involved in the square planar species (Ni-N = 1.90 to 1.91\AA)$^{84,85}$ versus ca 2.06\AA which occurs in Ni(cyclam)Cl$_2$. $^{86}$ This effect which is endothermic will be overridden by the formation of the two axial Ni-OH$_2$ bonds which is exothermic.

The importance of steric interactions between the coordinated water molecules and the ligand is also observed in bis complexes of nickel(II) with ethylenediamine and substituted ethylenediamines. Thus Ni(en)$_2^{2+}$ is blue(octahedral), Ni(C,C-dimethyl-ethylenediamine)$_2^{2+}$ is a 50% blue-yellow mixture$^{87}$.
# TABLE 4

Thermodynamic Parameters for Planar → Octahedral

<table>
<thead>
<tr>
<th>Temp/°K</th>
<th>K (^a)</th>
<th>(\log K (^a)</th>
<th>(\Delta G/\text{kcal mol}^{-1})</th>
<th>(\Delta H/\text{kcal mol}^{-1})</th>
<th>(\Delta S/\text{e.u.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>5.06</td>
<td>0.7042</td>
<td>-0.96</td>
<td>-5.3</td>
<td>-14.6</td>
</tr>
<tr>
<td>306</td>
<td>4.10</td>
<td>0.6128</td>
<td>-0.86</td>
<td>-5.3</td>
<td>-14.5</td>
</tr>
<tr>
<td>318</td>
<td>2.98</td>
<td>0.4742</td>
<td>-0.69</td>
<td>-5.3</td>
<td>-14.5</td>
</tr>
<tr>
<td>333</td>
<td>1.93</td>
<td>0.2856</td>
<td>-0.43</td>
<td>-5.3</td>
<td>-14.6</td>
</tr>
<tr>
<td>342</td>
<td>1.63</td>
<td>0.2122</td>
<td>-0.33</td>
<td>-5.3</td>
<td>-14.5</td>
</tr>
</tbody>
</table>

\(\Delta H = -5.3 \text{ kcal mol}^{-1} = -22.1 \text{ kJ mol}^{-1}\)

\(\Delta S = -14.6 \text{ cal K}^{-1} \text{ mol}^{-1} = -60.6 \text{ JK}^{-1} \text{ mol}^{-1}\)

\(^a\) \(K = [\text{Oct}] / [\text{Planar}]\)
TABLE 5

Thermodynamic parameters for planar * octahedral equilibria for various nickel(II) complexes

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\Delta H^\circ$/kcal mol$^{-1}$</th>
<th>$\Delta S^\circ$/e.u.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclam</td>
<td>-5.4</td>
<td>-20</td>
<td>83</td>
</tr>
<tr>
<td>$L'_a$</td>
<td>-5.3</td>
<td>-14.5</td>
<td>This work</td>
</tr>
<tr>
<td>2,3,2-tet</td>
<td>-3.4</td>
<td>-9</td>
<td>83</td>
</tr>
<tr>
<td>3,2,3-tet</td>
<td>-4.4</td>
<td>-15</td>
<td>83</td>
</tr>
</tbody>
</table>
and Ni(C,C',C'-tetramethylethylene diamine)²⁺ exists only in the planar yellow form.⁸⁸

Only in the nickel(II) complexes of Lₐ where all four methyl groups can be placed in equatorial positions does axial addition occur. The ligands L₉ and L₃ give only square planar species, since with these ligands at least one methyl group must be in the axial position, thus blocking the axial sites.
CHAPTER 3

Separation of Stereoisomers of the Nickel(II) Complex of the Ligand 5,6,12,13-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene.

The reaction of isopropenyl methyl ketone with the monohydroperchlorate salt of 1,2-diaminoethane in methanol solution gives the dihydroperchlorate salt of 5,6,12,13-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene(XIX)\(^52\). The ligand contains two chiral carbon centres at C-6 and C-13 so that C-meso (XXXV) and C-racemic (XXXVI) diastereoisomers of the ligand can occur. The reaction gives the trans-diiimine and ca 70:30 mixture of the two diastereoisomers.\(^52\)

![Diagrams of C-meso and C-racemic isomers]

In the present work fractional crystallisation
of the \([\text{Ni(Me}_4[14] \text{diene})][\text{ClO}_4]_2\) complex from aqueous solution was carried out and led to characterization of three isomers (a, b and c), identified by \(^1\text{H} \text{n.m.r.}\). Equilibration of a and b in DMSO/KOH gives isomer d. N.m.r. studies confirm that the reaction proceeds via the steps, b + a + d (see Figure 17, page 167).
3.1 Experimental

5,6,12,13-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene Dihydroperchlorate; Me₄[14]diene.2HClO₄.

The ligand was prepared as described by Hay and Piplani as follows:

Aqueous perchloric acid (165 cm³ (72%), 2 mol) was added dropwise with continuous stirring to a cooled (ice-salt bath) solution of 1,2-diaminoethane (134 cm³, 2 mol) in methanol (1200 cm³). After completion of the addition, methyl isopropenyl ketone (196 cm³, 2 mol, Fluka) diluted with an equal volume of methanol was added slowly over a period of 2 hours with the temperature being maintained between 0-5°C. The resulting mixture was then stirred for 4 hours, the temperature being slowly allowed to rise to ambient. The resulting suspension was stored overnight in a refrigerator. The white product was filtered off, washed several times with methanol, then ether, and dried in a vacuum desiccator. Yield 310g, m.p. 132-134°C, v(C = N) 1669, vNH 3170 cm⁻¹. (Calc. for C₁₄H₃₀N₄Cl₂O₈: C, 37.1; H, 6.7; N, 12.35%. Found: C, 36.9; H, 6.5; N, 12.35%).


An excess of basic nickel(II) carbonate (30g, 81 mmoles) and the ligand dihydroperchlorate (30g, 66 mmoles)
were slurried in water and heated on a water bath until
evolution of carbon dioxide ceased (ca one hour). The
solution was filtered hot and the filtrate reduced in
volume. Cooling in an ice-bath gave orange needles
(isomers a and b). Isomer c is very soluble in both
cold water and cold methanol and was recovered from the
filtrates. The mixture of isomers a and b was recrystallised
from hot water. Various fractions were monitored by $^1$H
n.m.r. using d$_6$-DMSO as solvent. The complexes were dried
in a vacuum desiccator. (Calc. for $C_{14}H_{28}O_8N_4Cl_2$Ni:
C, 32.95; H, 5.5; N, 11.0%. Found isomer b: C, 32.85;
H, 5.6; N, 10.85%. Found isomer c: C, 32.7; H, 5.55;
N, 10.80%). Isomer b is partially paramagnetic in d$_6$-DMSO
solution with broad signals at 1.26 and 1.66 Figure 13(2).
Isomer c has a doublet at 1.266 (J = 7.2 Hz) due to the
ring methyls and the imine methyls occur as a singlet at
2.026. Isomer a which occurs with isomer b is readily
identified by two imine methyl singlets at 2.036 and 2.206.
3.2 Results and discussion

Fractional crystallisation of [Ni(Me$_4$[14]diene)]-\([\text{ClO}_4]\)_2 from water led to the characterisation of three isomers (a, b and c). Isomer b is partially paramagnetic in DMSO solution and diamagnetic in the non-coordinating solvent nitromethane. Isomer a is diamagnetic in DMSO, as is isomer c. The three isomers are readily characterised by their n.m.r. spectra, Figures 13 and 14. Metal complexes of the ligand Me$_4$[14]diene contain two chiral carbon centres and two chiral nitrogen centres. There is therefore the possibility of ten stereoisomers; two all meso forms and four racemic mixtures. The various stereoisomers belong to two sets, one derived from the C-racemic ligand and the other from the C-meso ligand. The possible stereoisomers are shown in Figure 15. The stereoisomers (1) and (2) have a C$_2$ axis, while (3) and (4) have no elements of symmetry. Stereoisomers (5) and (6) have centres of symmetry. The complexes of one C-configuration are not readily convertible into complexes of the other C-configuration, whereas base should isomerise the N-configurations within each set. In the C-meso series only the N-rac-C-meso diastereoisomer (4) can be resolved, since the other two diastereoisomers are all meso forms.

X-ray crystallography has been carried out on isomer b$^{89}$ and isomer c.$^{90}$ Isomer b is the N-meso-C-meso diastereoisomer (6) with both methyl groups axial, while isomer c is the N-rac-C-rac diastereoisomer (1), which also
Figure 13

$^1$H n.m.r. spectra of $[\text{Ni(Me}_4\text{[14]dienen}))-\text{[ClO}_4\text{]}_2$

1. Isomer b in $\text{CD}_3\text{NO}_2$

2. Isomer b in $d_6\text{-DMSO}$
Figure 14: \textsuperscript{1}H n.m.r. spectra of [Ni(Me\textsubscript{4}1,1-diene)]ClO\textsubscript{4}\textsubscript{2} in d\textsubscript{6}-DMSO:

1. Mixture of isomers a and b
2. Isomer c in d\textsubscript{6}-DMSO
Figure 15
Stereoisomers of metal complexes of 5,6,12,13-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. The symbols (a) and (e) refer to the substituents being axial or equatorial respectively.
has both methyl groups axial. The $^1$H n.m.r. spectrum of isomer $a$ (which has not been obtained isomerically pure) has two singlets at 2.03$\delta$ and 2.20$\delta$, Table 6, which can be assigned to imine methyl groups in different environments. Isomer $a$ must therefore be (3) or (4) since only in these two isomers are the imine methyls non-equivalent. Isomer $a$ is always found in association with isomer $b$. Treatment of a mixture of isomer $a$ and $b$ dissolved in $d_6$-DMSO with a trace of solid potassium hydroxide leads to significant changes in the $^1$H n.m.r. spectrum, Figure 16. The signals due to isomer $b$ decrease, while initially, the signals of isomer $a$ increase with time; in addition new signals due to a further isomer $d$ appear. Subsequently $a$ and $b$ are completely converted to isomer $d$, which must therefore be the other member of the C-meso series, i.e. isomer (5). Thus $b$ isomerises via $a$ to give $d$, Figure 17. The n.m.r. data for $c$ and $d$ are quite similar, so that treatment of a mixture of $a$ and $b$ with base could possibly lead to isomerisation to isomer $c$. The hydrogens at C-6 and C-13 are quite acidic as they lie a to the imine bond. However, equilibration at carbon centres would probably give the C-meso rather than the C-racemic diastereoisomer as the former is expected to be the most thermodynamically stable. Therefore the discussion given above provides the best explanation for the experimental observations. The n.m.r. results confirm that the diequatorial N-meso derivative is the most thermodynamically stable diastereoisomer in the C-meso series of complexes.
TABLE 6

'H nmr data for the various isomers of [Ni(Me$_4$14diene)][ClO$_4$]$_2$ in d$_6$-DMSO solution.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Ring Methyls</th>
<th>Imine Methyls</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.166 (doublet, $J=7.2$ Hz)</td>
<td>2.035 (singlet)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.206 (singlet)</td>
</tr>
<tr>
<td>b</td>
<td>1.26 (singlet, broad)</td>
<td>1.66 (singlet, broad)</td>
</tr>
<tr>
<td>c</td>
<td>1.26 (doublet, $J=7.2$ Hz)</td>
<td>2.026 (singlet)</td>
</tr>
<tr>
<td>(at 60MHz)</td>
<td>1.256 (doublet, $J=6$ Hz)</td>
<td>1.986 (singlet)</td>
</tr>
</tbody>
</table>

a  At 90 MHz with T.M.S. as internal reference.

b  Partially paramagnetic in d$_6$-DMSO. In CD$_3$NO$_2$, the complex is diamagnetic, ring methyls 1.326 (doublet, $J=7.2$ Hz), imine methyls 2.286 (singlet).
Figure 16

(1) Mixture of isomers a and b isomerising to isomer $\text{d}^1$ in $d_6$-DMSO/KOH (60 MHz)

(2) Isomer $\text{d}^1$ in $d_6$-DMSO at 60 MHz
Figure 17
Interconversions in the C-meso series of $\text{[Ni(Me}_4\text{[14]diene)]}^2^+$ $\text{[ClO}_4\text{]}^2$
Attempts to isomerise isomer c of the C-rac series by the same technique were unsuccessful, therefore isomer c is the most thermodynamically stable member of this series of complexes. There is little difference between the d-d spectra of the various isomers. Isomer b has $\lambda_{\text{max}}$ 446 nm ($\varepsilon = 90 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and isomer c $\lambda_{\text{max}}$ 446 nm ($\varepsilon = 86 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$). Such a band is characteristic of square planar nickel(II) complexes with four nitrogen donors and can be assigned to the $^1B_{1g} \rightarrow ^1A_{1g}$ transition of square planar nickel(II). Isomers b and c behave as 2:1 electrolytes in aqueous solution, with conductivities 234 and 201 ohm$^{-1}$ cm$^3$ mol$^{-1}$ respectively, consistent with four coordinate structures and ionic perchlorate. Isomer b has a tendency to accept axial ligands and paramagnetic line-broadening in the $^1H$ n.m.r. spectrum ($d_6$-DMSO solution) can be attributed to the equilibrium (b) $[\text{NiMe}_4(14\text{ diene})]^{2+} + 2\text{DMSO} \leftrightarrow (b) [\text{NiMe}_4(14\text{ diene})(\text{DMSO})_2]^{2+}$. Paramagnetic line-broadening is not observed in DMSO solution with isomers a, c or d or with isomer b in nitromethane, Figures 13, 14 and 16.
CHAPTER 9

Synthesis and Characterization of Cobalt(III), Copper(II) and Nickel(II) Complexes of 1,4,7,10,13,16-Hexa-Aza-octadecane (Hexacyclen)

4.1 Introduction

The ligand 1,4,7,10,13,16-hexa-aza-octadecane (hexacyclen) (XXXVII), the nitrogen analogue of 18-Crown-6, is now readily available due to the synthetic procedures of Richman and Atkins. Other than a brief report of cobalt(III) complex of hexacyclam(XXXVIII) and a preliminary report on the cobalt(III) complex of hexacyclen, which appeared when the present work was completed, little has been published on the structure and stereochemistry of these nitrogen analogues of the crown ethers.

In the present study the cobalt(III), copper(II) and nickel(II) complexes of hexacyclen have been prepared and characterized and the stereochemistry of the cobalt(III) complex discussed.

If hexacyclen acts as a hexadentate ligand two gross geometrical structures are possible which may be designated symm(XXXIX) and unsym(XXXX). In the single symm isomer (XXXIX) the coupled rings give "angular" or facial arrangements at all six coordinated secondary amine nitrogens and the dispositions of the six NH hydrogen are thus fixed. The point group is D\textsubscript{3d}. The six NH groups are stereochemically equivalent and the twelve methylene carbons are also all equivalent.

In the unsym arrangement the point group is D\textsubscript{2}
Possible geometric isomers of [Co(hexacyclen)]^{3+} and their designations. Point groups are in parentheses.
if the chelate rings are considered to be coplanar. The structure is thus dissymmetric due to a configurational effect, and structures XXXX and XXXX) show the absolute configuration A only.94

The unsym-[Co(hexacyclen)]^{3+} arrangement contains two trans "planar" or meridionally coordinated secondary amine nitrogens at each of which alternative dispositions of the NH bonds are possible. These dispositions which are fixed by the conformations σ or λ of the mer rings introduce further isomerism and another source of dissymmetry to the molecule which is analogous to the isomerism and dissymmetry of the optical isomers of mer-[Co(dien)]^{3+}.95 This NH effect gives rise to two geometric isomers for unsym-[Co(hexacyclen)]^{3+} and reduces the molecular symmetry from D_{2} (coplanar meridional rings) to C_{2}. These geometric isomers of unsym-[Co(hexacyclen)]^{3+} are in fact internal diastereoisomers and they correspond to the optical isomers of mer-[Co(dien)]^{3+}. The two unsym geometric isomers should be differentiated by their optical rotatory properties after their optical resolutions. As a result of their C_{2} symmetry each isomer should have three stereochemically different NH hydrogens (two facial or angular and one meridional or planar) and six stereochemically different methylene carbon atoms.

The two unsym-[Co(hexacyclen)]^{3+} geometric isomers differ only in the orientation of one sec-NH hydrogen at a "planar" sec-amine site. Such NH protons exchange under basic conditions so that in the presence of base each
separate isomer would be expected to isomerise to an
equilibrium mixture of the two, in the same manner as
mer-[Co(dien)]^{3+} racemises.\textsuperscript{96}
4.2 Experimental

Unsymm-1,4,7,10,13,16-hexa-azaoctadecanecobalt(III) Perchlorate Dihydrate; [Co(hexacyclen)]\([\text{ClO}_4]\)_3\cdot2\text{H}_2\text{O}.

Hexacyclen \(3\text{H}_2\text{SO}_4\) (1.10g) was stirred into a slurry of Na\(_3\)[Co(CO\(_3\))]\(_3\)\cdot3\text{H}_2\text{O} (1.0g, excess) in cold water (30 cm\(^3\)). Reaction occurred in the cold to give an orange solution, and was completed by warming on a steam bath (30 min.). The solution was filtered and a small portion removed for Sephadex chromatography. The diluted solution was passed through a column (1.2 x 7 cm) of Biorex-70 weak-acid cation-exchange resin (50-100 mesh) in the Li\(^+\) form when the orange complex was absorbed. It was eluted off with 0.1M HClO\(_4\), and the effluent concentrated to a sludge on a rotary evaporator. Ethanol was added, and the crude product was filtered, washed with ethanol, and dried at 50\(^\circ\)C. The complex did not crystallise readily and was obtained as a fine orange powder, yield 1.2g (98%). The complex was dissolved in hot water and some rather insoluble pinkish-orange material was filtered off. The solution was readsorbed on a column of Biorex-70 cation-exchange resin and eluted with 0.1M HClO\(_4\). The effluent was concentrated on a rotary evaporator when more pinkish-orange material separated, and was filtered off. The filtrate was allowed to evaporate slowly in a vacuum desiccator. The orange crystals were filtered, washed with ethanol and dried in a vacuum desiccator.

Calc. for Co(C\(_{12}\text{H}_{30}\text{N}_6\))(ClO\(_4\))\(_3\).2H\(_2\)O: C, 22.1; H, 5.25; N, 12.9%.

Found: C, 22.0; H, 5.0; N, 12.9%. The complex was also
prepared from \(\text{[Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) as follows: A mixture of
\(\text{[Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) (0.27g), hexacyclen.\(3\text{H}_2\text{SO}_4\) (0.62g),
\(\text{LiOH.H}_2\text{O}\) (0.28g) and activated charcoal (0.4g) in water
was heated on a steam bath for 4 hours. The charcoal was
filtered off, and a portion of the solution was removed
for Sephadex chromatography. The orange complex was isolated
using the ion-exchange technique described above. Crude
yield 0.43g (65%).

\[1,4,7,10,13,16-\text{Hexa-azaoctadecanenickel(II)}\]
\[\text{Perchlorate Dihydrate; [Ni(hexacyclen)][ClO}_4^\text{-2}\text{.2H}_2\text{O}}.\]

Hexacyclen \(3\text{H}_2\text{SO}_4\) (1g, 1.8 mmole) was suspended in
water (30 cm\(^2\)) and \(\text{BaCO}_3\) (1.2g (excess) 6 mmoles) added.
The mixture was heated with continuous stirring on a water
bath for ca 30 minutes. The solution was allowed to cool
and the pH of the mixture was determined. When the pH of
the reaction mixture was >10 the solution was filtered to
remove the precipitated \(\text{BaSO}_4\) (it was found from pH-titration
that the ligand is completely neutralised at pH ca 11). To
the filtrate \(\text{Ni(ClO}_4\text{)}_2\text{.6H}_2\text{O}\) (0.66g, 1.8 mmole) was added.
The solution heated on a water bath for ca 30 min. On
standing and cooling in an ice-bath a lavender product
crystallised, this was filtered off and dried in a vacuum
desiccator.

Calc. for \(\text{Ni(C}_{12}\text{H}_{30}\text{N}_6)(\text{ClO}_4\text{)}_2\text{.2H}_2\text{O}\): C, 26.1; H, 6.2;
N, 15.2%. Found: C, 26.0; H, 5.7; N, 15.2%.
1,4,7,10,13,16-Hexa-azaoctadecane copper(II) Perchlorate Sesquihydrate; \([\text{Cu(hexacyclen)}] - [\text{ClO}_4^-]_2 \cdot 1.5\text{H}_2\text{O}\).

Hexacyclen $3\text{H}_2\text{SO}_4$ (1g, 1.8 mmole) was suspended in water (30 cm$^3$) and BaCO$_3$ (1.2g (excess) 6 mmoles) added. The mixture was then heated with stirring on a water bath for ca 30 minutes. The solution was allowed to cool and the pH of solution determined. When the pH was >10 the solution filtered. To the filtrate Cu(ClO$_4$)$_2 \cdot 6\text{H}_2\text{O}$ (0.66g, 1.8 mmole) was added. The reaction mixture heated on a water bath for half-an-hour. On standing and cooling in an ice-bath a deep blue product crystallised, this was filtered off and dried in a vacuum desiccator. Calc. for Cu(C$_{12}$H$_{30}$N$_6$)(ClO$_4$)$_2 \cdot 1.5\text{H}_2\text{O}$: C, 26.3; H, 6.1; N, 15.3%. Found: C, 26.0; H, 5.8; N, 15.3%.

The complexes \([\text{Ni(dien)}]_2[\text{ClO}_4^-]_2\) and \([\text{Cu(dien)}]_2[\text{ClO}_4^-]_2\) were prepared by adding an aqueous solution of the appropriate metal perchlorate to a slight excess of the ligand in aqueous solution. Calc. for Ni(C$_8$H$_{26}$N$_6$)(ClO$_4$)$_2$: C, 20.71; H, 5.65; N, 18.12; Cl, 15.3%. Found: C, 20.6; H, 5.7; N, 17.9; Cl, 15.3%.

Calc. for Cu(C$_8$H$_{26}$N$_6$)(ClO$_4$)$_2$: C, 20.5; H, 5.6; N, 17.93; Cl, 15.13%. Found: C, 20.4; H, 5.7; N, 17.9; Cl, 15.0%.
4.3 Results and discussion

The cobalt(III) complex was prepared by two methods, reaction of hexacyclen \(3H_2SO_4\) with \(Na_3[Co(CO_3)_3]3H_2O\) in an aqueous slurry and by reaction of hexacyclen \(3H_2SO_4\) with \([Co(NH_3)_5Cl]Cl_2\) in the presence of activated charcoal in aqueous solution. The later route is an equilibrium method and would be expected to give any possible isomers. Portions of the total solution from each preparation were chromatographed on columns (1.2 x 40 cm) of SP-Sephadex C-25 using 0.1M sodium orthophosphate and 0.3M Sodium(+)−tartrate as eluants. For each eluent a single orange band was observed. The relative \(R_X\) (relative \(R_F\)) values for the complex versus the standard complex \(s-fac-[Co(\text{Medien})_2]^3+\) are shown in Table 7. The similar elution rates of \([Co(\text{hexacyclen})]^3+\) and \(\text{mer-[Co(dien)}_2]^{2+}\) are strongly suggestive of the unsym topology for the hexacyclen complex. The electronic spectrum has the \(1A_{1g} + 1T_{1g}\) transition at 20,576 cm\(^{-1}\) consistent with a CoN\(_6\) chromophore.

The copper(II) and nickel(II) complexes were prepared from the "free" ligand and the appropriate metal perchlorate. Both complexes are 2:1 electrolytes in aqueous solution \(A_M = 220 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\) for the nickel(II) complex and 226 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) for the copper(II) complex at 25°C. The nickel complex has the \(3A_{2g} + 3T_{1g}\) transition at 18,315 cm\(^{-1}\) (\(\varepsilon = 10\)) and the \(3A_{2g} + 3T_{1g}(P)\) transition at 28,570 cm\(^{-1}\) (\(\varepsilon = 18\)). For \([\text{Ni(dien)}_2][\text{ClO}_4]\)\(_2\) these transitions occur at 18,450 cm\(^{-1}\) (\(\varepsilon = 7.8\)) and 28,730 cm\(^{-1}\) (\(\varepsilon = 10.4\)). The
TABLE 7

$R_x$ (relative $R_p$) values for cobalt(III) complexes, relative to the standard complex $s$-fac-$\{\text{Co(Medien)}_2\}^{3+}$.  

<table>
<thead>
<tr>
<th>Complex</th>
<th>Eluent 0.1M $\text{Na}_3\text{PO}_4$</th>
<th>Eluent $\text{Na}_2(\pm)$-tartrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$-fac-${\text{Co(dien)}_2}^{3+}$</td>
<td>12</td>
<td>2.3</td>
</tr>
<tr>
<td>$u$-fac-${\text{Co(dien)}_2}^{3+}$</td>
<td>3.7</td>
<td>1.5</td>
</tr>
<tr>
<td>mer-${\text{Co(dien)}_2}^{3+}$</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>unsymm-${\text{Co(hexacyclicen)}}^{3+}$</td>
<td>2.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

a = A detailed discussion of the chromatographic separations is given in reference 67.
corresponding values for Ni(en)$_3^{3+}$ are 18,500 cm$^{-1}$ and 30,000 cm$^{-1}$. The nickel(II) complex is quite labile to acid and is rapidly destroyed. This behaviour is in marked contrast to the observations made with 14-membered macrocycles where the nickel(II) complexes are not acid labile. The i.r. spectrum of the perchlorate salt has $\nu$(NH) at 3318 and 3280 cm$^{-1}$ and the characteristic bands due to ionic perchlorate at 1100 cm$^{-1}$ (broad) and 628 cm$^{-1}$.

Very similar considerations apply to [Cu(hexacyclen)]$_2^{2+}$ which has a broad absorption at 15,150 cm$^{-1}$ ($\varepsilon = 80$), cf. [Cu(dien)$_2$]$_2^{2+}$ at 15,625 cm$^{-1}$ ($\varepsilon = 100$). This complex is also acid labile. The i.r. spectrum has $\nu$(NH) at 3260, 3300 and 3344 cm$^{-1}$ and bands due to ionic perchlorate at 1100 cm$^{-1}$ and 628 cm$^{-1}$.

$^1$H and $^{13}$C n.m.r. of Cobalt(III) complex

The 60 MHz $^1$H n.m.r. spectrum of [Co(hexacyclen)]$_3^{3+}$ (from both preparative routes) in d$_6$-DMSO solution displays three broad overlapping NH signals in the ratio 1:1:1 ($\delta = 6.21$, 6.47 and 6.73 from SiMe$_4$) and a complex CH$_2$ resonance consistent with the unsymm topology. This assignment is fully confirmed by the $^{13}$C n.m.r. spectrum of [Co(hexacyclen)]$_3^{3+}$ (from [Co(NH$_3$)$_5$Cl]$^{2+}$ + charcoal) in D$_2$O solution, Figure 18, which displays ten separate signals. Two of these ($\delta$ 61.1, 56.2) have ca twice the intensity of the other eight which are of approximately equal intensity, thus accounting for twelve carbon atoms. The $^{13}$C n.m.r. spectrum unequivocally establishes
unsym-[Co(hexacyclen)](ClO₄)₃ (top), with the spectra of
mer-[Co(dien)₂](ClO₄)₃ (centre) and u-fac-[Co(dien)₂](ClO₄)₃ for
comparison.
FIGURE 18. 22.6-31\textsuperscript{m}C n.m.r. spectrum in D\textsubscript{2}O of unsymmetric-Co(hexacycleten)(ClO\textsubscript{4})\textsubscript{3} (top), with the spectra of meso-Co(\textsubscript{2}dien\textsubscript{2})(ClO\textsubscript{4})\textsubscript{3} (centre) and \textsubscript{2}faco-Co(\textsubscript{2}dien\textsubscript{2})(ClO\textsubscript{4})\textsubscript{3} for comparison.
that the product consists of the two NH geometrical isomers of the **unsymm** topology which are present in roughly equal amounts. The signals at 61.1 and 56.2 can be assigned to C-NH-C methylene carbons in rings coupled meridionally, as a similar magnetic equivalence has been observed with mer-[Co(dien)₂]^{3+} and mer-[Co(dien)(Medien)]^{3+} despite (in principle) stereochemical non-equivalence.

It is noteworthy that the **unsymm** topology is observed preferentially for [Co(hexacyclen)]^{3+} (Yoshikawa has observed <1% of the **symm**-isomer), while the **symm** topology is apparently favoured in [Co(hexacyclam)]^{3+}. This result may occur due to the relief of the large non-bonded hydrogen-hydrogen interactions present in **symm**-[Co(hexacyclen)]^{3+} when three of the 5-membered rings are replaced by the more flexible six-membered rings. It is probable that the **unsymm** topology also occurs preferentially in the paramagnetic copper(II) and nickel(II) complexes of hexacyclen, thus the mer-configuration has been established by X-ray structure analysis for [Cu(dien)₂]Br₂ 0.5H₂O.
CHAPTER 5

Transition Metal Complexes of the Macrocyclic Ligand 5,12-Dimethyl-7,14-di(2-thienyl)-1,4,8,11-tetra-azacyclotetradeca-4,11-diene.

At the present time there are relatively few examples of tetra-azamacrocycles with substituents other than alkyl groups. The present chapter describes the coordination chemistry of some metal complexes of a thienyl substituted macrocyclic ligand.

The reaction of 4-(2-thienyl)-3-butene-2-one with 1,2-diaminoethane in ether solution in the presence of potassium carbonate gives high yields (ca 70%) of the macrocyclic ligand 5,12-dimethyl-7,14-di(2-thienyl)-1,4,8,11-tetra-azacyclotetradeca-4,11-diene\(^{100}\), (XXXII=L). The macrocycle is more stable than meso-6,17-diphenyl-2,5,13,16-tetra-aza-bicyclo(16,4,6,0,7,12)docosa-1,12-diene(XXXIII) thus the uv spectrum in 50% methanol-water solvent at 25°C is not time
dependent indicating that a retro-Michael reaction does not occur under these conditions. A retro-Michael reaction occurs with the ligand (XXXXIII)\textsuperscript{101,102} in methanol-water solvent as the uv spectrum is time-dependent, a marked increase in absorption occurring at 246nm due to the release of the α,β-unsaturated carbonyl chromophore. The ligand L (XXXXII) is expected to have the transoid diimine stereochemistry with a C-meso-arrangement of the chiral carbon centres since this seems to be the preferred stereochemistry for ligands of this type.
5.1 Experimental

The ligand L used for the following preparations was kindly supplied by Dr. K. Hideg of the University of Pecs, Hungary. Calc. for \( \text{C}_{20}\text{H}_{28}\text{N}_{4}\text{S}_{2} \): C, 61.8; H, 7.2; N, 14.4%. Found: C, 61.5; H, 7.1; N, 14.6%.

\[ 5,12-\text{Dimethyl}-7,14-\text{di}(2\text{-thienyl})-1,4,8,11\text{-tetraazacyclotetradeca}-4,11\text{-dienenickel(II) Diperchlorate}; [\text{NiL}]\left[\text{ClO}_{4}\right]_{2}. \]

Nickel(II) acetate tetrahydrate (0.3g) dissolved in methanol-water (300 cm\(^3\), 1:1 v/v) was heated on a water-bath with a slight excess of the ligand (0.4g) for ca 30 minutes. The solution was filtered hot and the filtrate reduced in volume to ca 2 cm\(^3\). Addition of methanol (15 cm\(^3\)) followed by saturated sodium perchlorate solution and cooling in an ice-bath gave the yellow complex which was washed with ice cold methanol then ether and dried in a vacuum desiccator.

Calc. for \( \text{NiC}_{20}\text{H}_{28}\text{N}_{4}\text{S}_{2}\text{Cl}_{2}\text{O}_{8} \): C, 37.2; H, 4.4; N, 8.7%. Found: C, 37.3; H, 4.4; N, 8.7%.

\[ 5,12-\text{Dimethyl}-7,14-\text{di}(2\text{-thienyl})-1,4,8,11\text{-tetraazacyclotetradeca}-4,11\text{-dienecopper(II) Diperchlorate}; [\text{CuL}]\left[\text{ClO}_{4}\right]_{2}. \]

Copper(II) perchlorate hexahydrate (0.05g) was dissolved in methanol (30 cm\(^3\)) and a slight excess of the ligand (0.1g) added. The mixture was heated on a water-bath for 30 minutes. The red-purple complex crystallised on concentrating the solution, and was recrystallised from methanol and dried in a vacuum desiccator. Calc. for \( \text{CuC}_{20}\text{H}_{28}\text{N}_{4}\text{Cl}_{2}\text{O}_{8}\text{S}_{2} \): C, 36.9; H, 4.3; N, 8.6%. Found: C, 36.7; H, 4.3; N, 8.3%. 
Trans-dichloro(5,12-dimethyl-7,14-di(2-thienyl)-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) cobalt(III) Perchlorate; trans-[CoCl₂][ClO₄].

The ligand (0.8 g) was added to a hot solution of cobalt(II) acetate tetrahydrate (0.6 g) in methanol (50 cm³) and the mixture heated on a water-bath for 30 minutes, filtered, then cooled. To the filtrate was added methanol-water (50 cm³ 1:1 v/v) and the solution aerated for 20 hours. The methanol was removed on a rotary evaporator and concentrated hydrochloric acid (4 cm³, 11.6 M) added to the dull-red solution. Addition of concentrated sodium perchlorate solution followed by cooling in ice gave green crystals which were recrystallised from methanol. Calc. for CoC₂₀H₂₈N₄S₂O₄Cl₃: C, 38.8; H, 4.6; N, 9.1; Cl, 17.2%. Found: C, 38.7; H, 4.6; H, 9.3; Cl, 17.4%.

Trans-dibromo(5,12-dimethyl-7,14-di(2-thienyl)-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) cobalt(III) Perchlorate 2.5H₂O; trans-[CoBr₂][ClO₄] 2.5H₂O.

A solution of trans-[CoCl₂][ClO₄] (0.2 g) in a 10% methanolic solution of hydrobromic acid (20 cm³) was evaporated to small volume (ca 3 cm³) on a water-bath. The bright green complex was isolated by cooling in an ice-bath and was recrystallised from hot methanol. Calc. for CoC₂₀H₂₈N₄Br₂ClO₄S₂·2.5H₂O: C, 31.9; H, 4.4; N, 7.45%. Found: C, 31.7; H, 4.0; N, 7.3%.
Trans-(5,12-dimethyl-7,14-di(2-thienyl)-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)dinitrocobalt(III) Perchlorate Monohydrate; 
trans-[CoL(NO₂)₂][ClO₄]H₂O.

A solution of trans-[CoLCl₂][ClO₄] (0.3g) in methanol (40 cm³) was heated with a slight excess of sodium nitrite (0.06g) on a water bath for 20 minutes. The brown solution was filtered hot and the filtrate cooled in an ice-bath. The product crystallised as orange crystals, these were filtered off, washed with ice-cold methanol, then ether and dried in a vacuum desiccator. Calc. for CoC₂₀H₂₈N₆O₆S₂Cl.H₂O: C, 36.6; H, 4.6; N, 12.9%. Found: C, 37.0; H, 4.3; N, 13.1%. In a similar manner the diazido-complex was prepared by heating one mole of trans-[CoLCl₂][ClO₄] with two moles of sodium azide in methanol, however, the analytical data on this complex is not satisfactory for the nitrogen. Calc. for CoC₂₀H₂₈N₁₀O₄S₂Cl.H₂O: C, 37.0; H, 4.4; N, 21.6%. Found: C, 36.8; H, 4.6; N, 23.7%.
5.2 Results and discussion

Metal(II) complexes

The metal(II) complexes \([\text{ML}[\text{ClO}_4]^2\] (\(M = \text{Cu(II)}\) and \(\text{Ni(II)}\)) were readily prepared and isolated. At 25°C the nickel complex has a conductivity of 205 ohm\(^{-1}\) cm\(^2\) (water solvent) while the copper complex has a conductivity of 270 ohm\(^{-1}\) cm\(^2\) (acetonitrile solvent). These values are consistent with 2:1 electrolytes confirming that the complexes are four-coordinate. The i.r. spectra of the complexes, Table 8, are also consistent with ionic perchlorate. The nickel complex has bands at 625 cm\(^{-1}\) and 1090 cm\(^{-1}\) due to the asymmetric stretching and asymmetric bending vibrations of \(\text{ClO}_4^-\). These bands occur at 620 and 1100 cm\(^{-1}\) in the copper complex. The non-degenerate frequency \(v_1\) which is theoretically forbidden in the i.r. occurs as weak absorption at 930 cm\(^{-1}\) (nickel complex) and at 927 cm\(^{-1}\) in the copper complex, presumably as a result of distortion of the \(\text{ClO}_4^-\) ion in the crystal lattice. The characteristic band due to the thiophene ring at ca 725 cm\(^{-1}\) occurs at 732 cm\(^{-1}\) in the nickel complex and 725 cm\(^{-1}\) in the copper complex. The constancy of the band position lends strong support to the view that the sulphur atoms of the thiophene rings do not act as donors.

Metal complexes of the ligand have two chiral nitrogen centres so that \(\text{N-meso}\) and \(\text{N-racemic}\) diastereoisomers are possible. Molecular models indicate that the centro-symmetric \(\text{C-meso-N-meso}\) arrangement (XXXIV) is preferred, since both thiophene rings are equatorial and do not interfere with
TABLE 8

Prominent infrared absorption bands (in cm\(^{-1}\)) of metal(II) and cobalt(III) complexes of the ligand (L)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_{\text{NH}})</th>
<th>(\nu_{\text{C}:\text{N}})</th>
<th>(\nu_{\text{ClO}_4^-})</th>
<th>Thiophene</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{NiL}][\text{ClO}_4])_2</td>
<td>3180s</td>
<td>1650s</td>
<td>1090br</td>
<td>732s</td>
</tr>
<tr>
<td>([\text{CuL}][\text{ClO}_4])_2</td>
<td>3200m</td>
<td>1655s</td>
<td>1100br</td>
<td>725s</td>
</tr>
<tr>
<td>trans-([\text{CoLCl}_2][\text{ClO}_4]]</td>
<td>3160s</td>
<td>1655s</td>
<td>1095br</td>
<td>720s</td>
</tr>
<tr>
<td>trans-([\text{CoBr}_2][\text{ClO}_4]] (2.5\text{H}_2\text{O})^a</td>
<td>3185m</td>
<td>1650s</td>
<td>1095br</td>
<td>710s</td>
</tr>
<tr>
<td>trans-([\text{Co}(\text{NO}_2)_2][\text{ClO}_4]]^b</td>
<td>3180</td>
<td>1640s</td>
<td>1090br</td>
<td>720</td>
</tr>
<tr>
<td>trans-([\text{Co}(\text{N}_3)_2][\text{ClO}_4]] (\text{H}_2\text{O})^c</td>
<td>masked</td>
<td>1640s</td>
<td>1090br</td>
<td>620s</td>
</tr>
</tbody>
</table>

\(a = \nu_{\text{OH}} 3400\text{br}\)

\(b = \text{vasy. NO}_2 1390\text{m,sh}; 0-\text{N-O def. 816}\)

\(c = \nu_{\text{N}_3} (\text{coord.}) 2000\)
the axial ligand positions which are occupied in the six-coordinate cobalt(III) complexes. This arrangement has been confirmed by X-ray crystallography of the analogous copper(II) complex (XXXV).\textsuperscript{103} The n.m.r. spectrum of the nickel(II) complex in d\textsubscript{6}-DMSO is suggestive of a centrosymmetric structure for the complex.

The nickel(II) complex has a d-d band at 440nm

\[(\text{XXXIV})\]

\textit{C-meso-N-meso}

\(\varepsilon = 90\). Such a band is characteristic of square planar nickel(II) complexes with four nitrogen donor atoms and can be assigned to the \(1\text{A}_{1g} + 1\text{B}_{1g}\) transition.\textsuperscript{91} The d-d band of the copper(II) complex occurs at 515nm \((\varepsilon = 112)\). The wavelength and intensity of this band is comparable to values
reported for related tetra-aza-macrocycle which normally have a band in the region of 510nm within the range 90-110 M⁻¹ cm⁻¹. The observed transition bands are summarised in Table 9.

**Cobalt(III) complexes**

Reaction of the ligand with cobalt(II) acetate in methanol followed by aerial oxidation and treatment with hydrochloric acid gave the green trans-[CoLCl₂]⁺ cation, readily isolated as the perchlorate salt. The trans configuration is consistent with the d-d spectrum with bands at 615nm (ε = 46) and 460nm (shoulder, ε = 57).

Metathesis reactions in methanol or aqueous solution give the bright green trans-[CoBr₂L]⁺, orange trans-[CoL(NO₂)₂]⁺ and trans-[CoL(N₃)₂]⁺. The i.r. spectra and the d-d spectra for these complexes are summarised in Tables 8 and 9. The n.m.r. spectrum of trans-[CoLCl₂]²⁺[ClO₄] in d₆-DMSO has a single N-H signal consistent with a centrosymmetric N-meso-C-meso configuration.
## Table 9

Electronic Spectra for complexes of the ligand (L) (in nm)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}(\epsilon)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{NiL}][\text{ClO}_4]_2$</td>
<td>440(90)</td>
</tr>
<tr>
<td>$[\text{CuL}][\text{ClO}_4]_2$</td>
<td>515(112)</td>
</tr>
<tr>
<td>trans-$[\text{CoLCl}_2][\text{ClO}_4]$</td>
<td>615(46)</td>
</tr>
<tr>
<td></td>
<td>460sh(57)</td>
</tr>
<tr>
<td></td>
<td>345sh($3.2 \times 10^3$)</td>
</tr>
<tr>
<td>trans-$[\text{CoLBr}_2][\text{ClO}_4]$</td>
<td>650(60)</td>
</tr>
<tr>
<td></td>
<td>385sh($3.6 \times 10^3$)</td>
</tr>
<tr>
<td></td>
<td>313($2.2 \times 10^4$)</td>
</tr>
<tr>
<td>trans-$[\text{CoL(NO}_2)_2][\text{ClO}_4]$</td>
<td>455(360)</td>
</tr>
<tr>
<td></td>
<td>465($9 \times 10^3$)</td>
</tr>
<tr>
<td>trans-$[\text{CoL(N}_3)_2][\text{ClO}_4]$</td>
<td>564</td>
</tr>
<tr>
<td></td>
<td>360</td>
</tr>
</tbody>
</table>

a = In all cases the solvent was acetonitrile unless otherwise stated

b = Spectrum determined using water as solvent
APPENDIX I

Macrocycle Synthesis

The main aim of this work was to synthesise the ligand \([12]\)-aneN\(_4\)(cyclen). This material was used to prepare \(\text{cis-}[\text{Co(cyclen)CO}_2]^+\) for kinetic studies, but some material was also used to prepare the nickel(II) complex. The procedure employed for synthesising this ligand is essentially as described by Richman and Atkins\(^6\) and outlined in Figure 4 of the Introduction.

The ligand \([13]\)-aneN\(_4\) was also synthesised by a modified route summarised below,
This method provides a simple straightforward method for the preparation of the ligand (Busch has recently described a similar synthesis). The route requires only one tosylated linear amine as a starting reagent. Ring closure occurs quite readily with 1,3-dibromopropane, but does not occur with 1,2-dibromoethane, so that this method cannot be used for the synthesis of cyclen. The nickel(II) complex of this ligand was also prepared.

Experimental

The tosylates of triethylenetetramine, diethanolamine and diethylenetriamine were prepared as previously described by Tajik.104

Tetratosyl-1,4,7,10-tetra-azacyclododecane

The tritosylate of diethylenetriamine (28g, 0.05 mol) was dissolved in dry dimethylformamide (500 cm³). Sodium hydride (80% in paraffin oil, 12.5g, 0.42 mol) was added in small portions and when effervescence ceased the solution was warmed on a water bath for ca 0.5 hour. The solution was cooled to room temperature and the excess sodium hydride filtered off. The filtrate was transferred to a flask equipped with a thermometer, double surface condenser and magnetic stirrer. The tritosylate of diethanolamine (28g, 0.05 mol) dissolved in dimethylformamide (200 cm³) was added and the mixture heated on an oil-bath for ca 2 hours at 110-120°C with continuous stirring. The solution was cooled to room temperature and water (1 dm³) added slowly with vigorous stirring.
The solid product was filtered off and washed thoroughly with water and dried in vacuum oven at 60°C (yield 32g). The tosylate can be recrystallised from formic acid if required, mp 268-271 (lit. 273°C and 292°C). (Calc. for C₃₆H₄₄N₄O₈S₂; C, 54.8; H, 5.6; N, 7.1%. Found: C, 54.7; H, 5.4; N, 7.1%).

**Tetratosyl-1,4,7,10-tetra-azacyclotridecane**

The tetratosylate of triethylenetetramine (15.2g, 0.02 mol) was dissolved in dry dimethylformamide (200 cm³). Sodium hydride (4g, 0.16 mol) was added proportion-wise, and when effervescence ceased the solution was warmed on a water bath for one hour. The solution was cooled and the excess NaH filtered off. The filtrate was transferred to a flask equipped with a thermometer, condenser and magnetic stirrer. To the filtrate 1,3-dibromopropane (4.1g, 0.02 mol) was added and the solution heated under reflux maintaining the temperature at 130°C for six hours. The reaction mixture was cooled and transferred to a large beaker. Water (250 cm³) added and the product precipitated immediately. (Yield 12.5g, 75%, m.p. 205-208°C). The product can be recrystallised from hot formic acid.

The above procedure was repeated using 1,2-dibromoethane (3.76g, 0.02 mol), but the attempt was unsuccessful.

**Hydrolysis of the tetratosylates of the macrocyclic ligands [12]-aneN₄**

The tetratosylate of this ligand was hydrolysed as follows: the tetratosylate (32g crude product) was dissolved
in concentrated sulphuric acid (150 cm$^3$), in a long-necked flask, and the solution heated on an oil bath with continuous stirring at 110-120°C for 48 hours. The black solution was cooled to room temperature. The reaction mixture was then added slowly with stirring to sodium hydroxide solution (1 dm$^3$, 8 mol dm$^{-3}$) cooled in an ice bath. On completion of the addition the pH was checked to ensure that pH > 14 (the pK$_a$ values of cyclen are pK$_1$ < 1; pK$_2$ = 1.15; pK$_3$ = 9.6 and pK$_4$ 10.53). The mixture was allowed to stand at room temperature for ca 24 hours to complete the precipitation of sodium sulphate, which was then filtered off. The filtrate was extracted with 4 x 200 cm$^3$ portions of chloroform and the chloroform removed on a rotary evaporator. The oily product was dissolved in methanol (20 cm$^3$) and concentrated hydrochloric acid (2.5 cm$^3$) added. The precipitated tetrahydrochloride was filtered off and recrystallised from 50% hydrochloric acid. Yield 6g (46.5%), m.p. 185-187°C. (Calc. for C$_8$H$_{24}$N$_4$Cl$_4$; C, 30.2; H, 17.6; N, 7.6%. Found: C, 30.2; H, 17.5; N, 7.6%). The $^1$H n.m.r. spectrum of the amine tetrahydrochloride (D$_2$O solution) showed the complete absence of tosyl groups and a single signal at 3.346 due to the CH$_2$ groups (in d$_6$-DMSO the signal occurs at 3.416).

In the same manner the tetratosylate of [13]-aneN$_4$ was hydrolysed (12g) using the appropriate amount of concentrated H$_2$SO$_4$, then neutralised with the appropriate amount of NaOH. The free ligand was obtained as an oil. This oily material was dissolved in methanol and concentrated
HC1 added. The ligand, 4HCl was recrystallised from 50% HCl. Yield (3g), m.p. 285-287°C. (Calc. for C9H26N4Cl4: C, 32.54; H, 7.9; N, 16.9%. Found: C, 32.3; H, 7.74; N, 16.82%). The 1H n.m.r. spectrum of the ligand showed the complete absence of tosyl groups.

The detosylation may also be carried out electrochemically as described in the literature.108,109

**Nickel(II) complexes**

**Cis-chloro-aquo(1,4,7,10-tetraazacyclododecane)nickel(II) Perchlorate; cis-[Ni(cyclen)Cl(H2O)][ClO4].**

A suspension of nickel(II) carbonate (0.99g) in water (50 cm³) was heated on a water bath. To the hot suspension the ligand cyclen.4HCl (0.8g) was added. The mixture was heated for ca one hour and filtered. The filtrate was reduced in volume to ca 15 cm³, and a saturated solution of sodium perchlorate then added. The blue product which precipitated immediately, was filtered off washed with cold water then ethanol and finally dried in vacuum dessicator. Yield 0.93g (95%). (Calc. for NiN4Cl2O5C8H22: C, 25.0; H, 5.78; N, 14.6%. Found: C, 24.74; H, 5.34; N, 14.33%).

**1,4,7,10-Tetra-azacyclotridecane nickel(II)Perchlorate; [Ni[13]-aneN4][ClO4].**

A solution of nickel(II) carbonate (0.94g) in water (50 cm³) was heated on a water bath and then [13]-aneN4 4HCl (0.8g) added to the hot solution. The reaction mixture was heated for ca one hour and filtered. The filtrate was
reduced in volume to ca 15 cm³ and saturated sodium perchlorate added. Cooling in an ice bath gave a yellow product which was filtered off and recrystallised from water. The filtrate was reduced in volume and left for further crystallisation. A mixture of blue and yellow crystals was obtained. The mixture was dissolved in methanol, the blue material which is insoluble in methanol was separated by filtration. The filtrate was evaporated and a second fraction of the yellow product obtained. Yield (yellow product) 0.2g (37%), the blue material 0.02g (3.7%). (Calc. for NiN₄Cl₂O₈C₉H₂₂ (yellow compound):
C, 24.35; H, 5.0; N, 12.62%. Found: C, 24.0; H, 5.1; N, 12.33%).
The analytical data on the blue compound was not satisfactory for the cis-[Ni([13]-aneN₄)(H₂O)₂][ClO₄]₂. However, the i.r. spectrum of this compound is similar to that of cis-[Ni(cyclen)-(H₂O)Cl][ClO₄] and exhibits two vNH bands at 3270 and 3325 cm⁻¹. The blue compound could be the cis-isomer of the nickel(II) complex of the[13]-aneN₄ ligand and may be contaminated with some inorganic salt. Further investigation was not attempted due to the very small quantity of complex available which did not allow further attempts of purification.

The i.r. spectrum of the complex cis-[Ni(cyclen)Cl-(H₂O)][ClO₄] has bands at 1100 and 620 cm⁻¹. These are typical of ionic perchlorate. The complex is a 2:1 electrolyte in water (A_M = 235 ohm⁻¹ cm² mol⁻¹) and is insoluble in DMSO, MeCN, Me₂CO and CH₃NO₂. The behaviour of the complex as a 2:1 electrolyte is consistent with the reaction

\[
\text{cis-[Ni(cyclen)Cl(H₂O)]}^+ + \text{cis-[Ni(cyclen)(H₂O)₂]}^{2+} + \text{Cl}^-
\]

occurring in the ionising solvent.
The visible spectrum of the complex in water (presumably the diaquo species) has bands at 380, 575 and 800 nm(sh) consistent with a cis-configuration.\textsuperscript{110}

The i.r. spectrum of the complex [Ni(13)-aneN\textsubscript{4}][ClO\textsubscript{4}]\textsubscript{2} (yellow complex) has bands at 3220 cm\textsuperscript{-1} (vNH) and 1100 and 620 cm\textsuperscript{-1} (ionic ClO\textsubscript{4}\textsuperscript{-}). The complex is a 2:1 electrolyte in water (\(\Lambda_M = 255 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\)). The visible spectrum of the complex has a single band at 426 nm (\(\epsilon = 107.5\)) consistent with a square planar complex. The addition of LiCl leads to no change in the visible spectrum in aqueous solution, however, addition of concentrated ammonia gives a lavender-violet colour indicating axial addition. It is likely that octahedral species can be prepared in non-aqueous solvents such as methanol.

Although a number of cobalt(III) complexes of [13]-aneN\textsubscript{4} have been described (both cis and trans derivatives\textsuperscript{111,112}) no nickel(II) derivatives have so far been described. This work should therefore be continued.
APPENDIX II

Preparation and Characterisation of 5,7,7,12,14-Pentamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and its metal complexes.

Dr. G. H. Searle during attempts to separate the two carbon diastereoisomers of the nickel(II) complexes of (XXVII) and (XXVIII) by column chromatography detected small quantities (ca 5% of the total complex) of another macrocycle which n.m.r. data suggested was the nickel(II) complex of (L5).

\[
\begin{align*}
\text{Me}_4[14]\text{diene} \\
\text{Me}_5-[14]\text{diane}
\end{align*}
\]

The Me₄[14]diene macrocycle was prepared by the reaction of 3-pentene-2-one (I) with 1,2-diaminoethane mono-
hydroperchlorate. The 3-pentene-2-one is prepared by the reaction of CH₃CHO with acetone under basic conditions.

\[
\begin{align*}
\text{CH}_3\text{C}=\text{O} + \text{CH}_3\text{C}=\text{O} + \text{OH}^{-} & \rightarrow \text{CH}_3\text{C}=\text{C} - \text{CH}_3
\end{align*}
\]

Some self-condensation of acetone could also occur under these conditions to give mesityl oxide,

\[
\begin{align*}
\text{CH}_3\text{C}=\text{O} + \text{CH}_3 - \text{C} - \text{CH}_3 & \rightarrow \text{CH} - \text{C} - \text{CH}_3
\end{align*}
\]

and it is probable that the commercial 3-pentene-2-one contained some mesityl oxide (the b.p. of mesityl oxide is 130-1°C and the b.p. of 3-pentene-2-one is 122°C). The isolation of the Me₅[14] diene could result from a "mixed" reaction between 1,2-diaminoethane monohydroperchlorate and both mesityl oxide and 3-pentene-2-one. For this reason the reaction of 1,2-diaminoethane with a 1:1 mixture of mesityl oxide and 3-pentene-2-one was studied in an attempt to prepare new macrocycles by this type of "mixed" reaction.

**Experimental**

"5,7,7,12,14-Pentamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene Dihydroperchlorate"; Me₅[14]diene.2HClO₄(L₅).

Perchloric acid (41.5 cm³ of 72% 0.5 mole) was added dropwise with continuous stirring to a cooled (ice-salt
bath) solution of 1,2-diaminoethane (33.5 cm$^3$, 0.5 mole) dissolved in methanol (350 cm$^3$). On completion of the addition the reaction mixture was cooled to -5°C. A mixture of 3-pentene-2-one (21g, 0.25 mole) and mesityl oxide (24.5g, 0.25 mole) in methanol (60 cm$^3$) was then added dropwise with continuous stirring, during the addition the temperature was maintained between -5 0°C. On completion of the addition the mixture was stirred for a further four hours, during which time the temperature was allowed to rise to ambient. The white product precipitated as the temperature increased. The resulting suspension was stored overnight in refrigerator. The product was filtered off, washed thoroughly with methanol then ether and dried in vacuum desiccator. Yield 60g, m.p. 120-128°C (decomposition). (Calc. for C$_{15}$N$_4$H$_{32}$O$_8$Cl$_2$: C, 38.55; H, 6.9; N, 12.0%. Found: C, 38.4; H, 6.8; N, 11.9%).

5,7,7,12,14-Pentamethyl-1,4,8,11-tetra-azacyclo-tetradeca-4,11-diene nickel(II) Perchlorate; [Ni(L$_5$)][CIO$_4$]$_2$.

A suspension of nickel(II) carbonate (10g, 0.027 mole) in water (100 cm$^3$) was heated. To the hot solution a slurry of the ligand L$_5$.2HClO$_4$ (10g, 0.02 mole) in water (50 cm$^3$) was added portionwise. The reaction mixture was heated for ca one hour, then filtered. The volume of the filtrate was reduced to ca 50 cm$^3$ and left to crystallise. The first fraction of orange crystals was filtered off. Further crystallisation gave a second and third fraction. The n.m.r.
spectra for all fraction were identical, and they exhibit signals (DMSO solvent) at 1.146 singlet (CMe2), 1.98 singlet and a doublet at 1.756. (Calc. for NiC15H30N4O8Cl2:
C, 34.4; H, 5.8; N, 10.7%. Found: C, 34.2; H, 5.9; N, 10.6%).

5,7,7,12,14-Pentamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene copper(II) Perchlorate;  
[CuL5][ClO4]2.

Equimolar amounts of the ligand L5·2HClO4 (2g, 4 mmoles) and copper(II) perchlorate hexahydrate (1.6g, 4 mmoles) were mixed in methanol-water (60 cm³) and heated on water bath for 0.5 hour. The purple solution was filtered hot. Cooling in an ice-bath gave the purple crystals, these were filtered off and dried in vacuum dessicator.
(Calc. for CuC15H30N4O8Cl2: C, 34.1; H, 5.72; N, 10.6%. Found: C, 33.9; H, 5.95; N, 10.7%).

Trans-dichloro(5,7,7,12,14-pentamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Perchlorate;  
trans-[CoL5Cl2][ClO4].

To a hot solution of cobalt(II) acetate tetrahydrate (2.7g, 0.01 mole) in methanol-water (100 cm³ 1:1 v/v) the ligand L5·2HClO4 (5g, 0.01 mole) was added. The solution was heated on a water bath for ca one hour, filtered while hot, and then cooled. The filtrate was diluted with methanol-water (100 cm³, 1:1 v/v) and air passed through the dull red solution for ca 20 hours. The methanol was removed on rotary evaporator and concentrated hydrochloric acid (40 cm³) added. The green product was isolated by slow evaporation on a steam-bath followed by cooling in an ice-bath, and was recrystallised from hot methanol. (Calc. for CoC15H30N4O8Cl3: H, 6.1; N, 11.3%. Found: C, 36.2; H, 6.2; N, 11.3%).
spectra for all fraction were identical, and they exhibit signals (DMSO solvent) at 1.146 singlet (CMe₂), 1.96 singlet and a doublet at 1.756. (Calc. for NiC₁₅H₃₀N₄₀₈Cl₂:
C, 34.4; H, 5.8; N, 10.7%. Found: C, 34.2; H, 5.9; N, 10.6%).

5,7,7,12,14-Pentamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene copper(II) Perchlorate;
[CuL₅][ClO₄]₂.

Equimolar amounts of the ligand L₅·2HClO₄ (2g, 4 mmoles) and copper(II) perchlorate hexahydrate (1.6g, 4 mmoles) were mixed in methanol-water (60 cm³) and heated on water bath for 0.5 hour. The purple solution was filtered hot. Cooling in an ice-bath gave the purple crystals, these were filtered off and dried in vacuum dessicator.
(Calc. for CuC₁₅H₃₀N₄₀₈Cl₂: C, 34.1; H, 5.72; N, 10.6%. Found: C, 33.9; H, 5.95; N, 10.7%).

Trans-dichloro(5,7,7,12,14-pentamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate;
trans-[CoL₅Cl₂][ClO₄].

To a hot solution of cobalt(II) acetate tetrahydrate (2.7g, 0.01 mole) in methanol-water (100 cm³ 1:1 v/v) the ligand L₅·2HClO₄ (5g, 0.01 mole) was added. The solution was heated on a water bath for ca one hour, filtered while hot, and then cooled. The filtrate was diluted with methanol-water (100 cm³, 1:1 v/v) and air passed through the dull red solution for ca 20 hours. The methanol was removed on rotary evaporator and concentrated hydrochloric acid (40 cm³) added. The green product was isolated by slow evaporation on a steam-bath followed by cooling in an ice-bath, and was recrystallised from hot methanol. (Calc. for CoC₁₅H₃₀N₄₀₈Cl₃:
H, 6.1; N, 11.3%. Found: C, 36.2; H, 6.2; N, 11.3%).
A further number of cobalt(III) complexes of the type $\text{trans-}[\text{CoL}_5X_2]^+$, $X=\text{N}_3$, CN or NO$_2$ were also prepared by metathetical reactions of the $\text{trans-}[\text{CoL}_5\text{Cl}_2]^+$ with the appropriate sodium salt in methanol or methanol-water as solvent.

$\text{trans-}[\text{CoL}_5(\text{N}_3)_2][\text{ClO}_4]0.5\text{H}_2\text{O}$.
Found: C, 34.5; H, 6.1; N, 27%. CoC$_{15}$H$_{30}$N$_{10}$ClO$_4$, requires C, 34.8; H, 6.0; N, 27%.

$\text{trans-}[\text{CoL}_5(\text{NO}_2)_2][\text{ClO}_4]\text{H}_2\text{O}$.
Found: C, 34.1; H, 6.2; N, 15.9%. CoC$_{15}$H$_{32}$N$_6$O$_9$Cl, requires C, 33.7; H, 6.0; N, 15.7%.

$\text{trans-}[\text{CoL}_5(\text{CN})_2][\text{ClO}_4]\text{H}_2\text{O}$.
Found: C, 41.5; H, 6.14; N, 17.34%. CoC$_{17}$H$_{32}$N$_6$O$_5$Cl, requires C, 41.3; H, 6.5; N, 17.0%.
Discussion

The reaction of ethylenediamine monohydroperchlorate with an equimolar mixture of 3-pentene-2-one and mesityl oxide could give the four macrocycles shown below.

\[ \text{C-meso-Me}_4^{[14]} \text{ diene} \quad \text{C-rac-Me}_4^{[14]} \text{ diene} \]

\[ \text{Me}_5^{[14]} \text{ diene} \quad \text{Me}_6^{[14]} \text{ diene} \]
The reaction of the crude ligand mixture with \( \text{NiCO}_3 \) followed by direct column chromatography on SP-Sephadex C-25 indicates ca 70\% [\( \text{Ni(Me}_{14}\text{diene}) \)]^{2+}, ca 15\% of [\( \text{Ni(C-rac-Me}_4{14}\text{diene}) \)]^{2+} and ca 15\% of [\( \text{Ni(C-meso-Me}_4{14}\text{-diene}) \)]^{2+}. Using the chromatographic technique it is possible to obtain pure [\( \text{Ni(Me}_5{14}\text{diene})][\text{ClO}_4]_2 \) and \(^1\text{H} \) n.m.r. spectra of the purified complex (in TFA solvent) and the crude complex (in DMSO solvent) are shown in Figure 19. The chromatographic work of this system was carried out by Dr. G. H. Searle of the University of Adelaide.

The "mixed" \( \alpha,\beta \)-unsaturated ketone reaction does give high yields of the previously unknown macrocycle \( \text{Me}_5{14}\text{diene} \) plus other macrocycles.

The ligand hydroperchlorates are difficult to purify by fractional crystallisation due to the hydrolysis of the ligand. For this reason the various metal complexes were prepared. These complexes can be readily purified by column chromatography or by fractional crystallisation.

**N.m.r. studies**

The n.m.r. spectrum of the nickel(II) complex, Figure 19(1), is consistent with the configuration shown below. The methyl doublet due to the methyl group at C-14 occurs at 2.036 which is the normal position for axial methyl groups in nickel(II) complexes of tetra-aza macrocycles.

The n.m.r. spectrum of [\( \text{Co(Me}_5{14}\text{diene})\text{Cl}_2][\text{ClO}_4] \) is shown in Figure 20(2). It shows the axial methyl singlet \( \text{(CMe}_2 \) at 1.56 is imposed upon one arm of the doublet (centred
Figure 19

$^1$H nmr spectra of $[\text{Ni(Me$_5$[14]dienel][ClO$_4$]}_2$

(1) The purified complex in TFA solvent and TMS as standard reference

(2) The crude complex in d$_6$-DMSO solvent and TMS as reference
Figure 20

(1) $^1$H nmr spectrum of
$\text{Ni(Me}_6\text{l}_4\text{dienel}_2\text{[ClO}_4]_2$ in TFA/TMS

(2) $^1$H nmr spectrum of
$\text{[Co(Me)}_6\text{l}_4\text{dienel}_2\text{[ClO}_4]_2$ in
$\text{d}_6\text{-DMSO/TMS}$
at 1.45) of the C-14 methyl group. This methyl doublet is at the normal position for axial methyl groups in cobalt(III) complexes of macrocyclic ligands. Thus the configuration of methyl substituents for this complex is identical to that of the nickel(II) complex.

The n.m.r. spectrum of \( \text{[Ni(Me}_6[14] \text{diene}]^2+ \), Figure 20(1), shows clearly the position of the axial and equatorial methyl groups. The recent work of Kolinski et al.\(^{51}\) on the Ni(II) complexes of Me\(_6[14]\)diene allow the assignments of high field signals to equatorial methyls and low field signals to axial methyls. The order of assignment of methyl resonances of cobalt(III) complexes relative to nickel(II) complexes is reversed, with the axial substituent at higher field.\(^{114,115}\) Table 10 summarises the n.m.r. data for the complexes discussed.
TABLE 10

$^1$H n.m.r. spectra of the nickel(II) and cobalt(III) complexes of Meg$_6$[14]diene and Meg$_6$[14]diene.

1. $[\text{Ni(Me}_5[14]\text{diene})][\text{ClO}_4]$ in TFA solvent$^a$
   
   1.406 3H(singlet) equatorial methyl of CMe$_2$$^b$
   2.036 3H(doublet, $J = 7.2$ Hz) axial methyl at C-14
   2.136 3H(singlet) axial methyl of CMe$_2$
   2.246 6H(singlet) imine methyls.

2. $[\text{Co(Me}_5[14]\text{diene})\text{Cl}_2][\text{ClO}_4]$ in $d_6$-DMSO$^c$
   
   1.456 3H(doublet, $J = 7.2$ Hz) axial methyl at C-14
   1.58 3H(singlet) axial methyl of CMe$_2$
   2.466 3H(singlet) equatorial methyl of CMe$_2$
   2.516 6H(singlet) imine methyls.

3. $[\text{Ni(Me}_6[14]\text{diene})][\text{ClO}_4]$ (TFA solvent)
   
   1.46 6H(singlet) equatorial methyl of CMe$_2$
   2.156 6H(singlet) axial methyl of CMe$_2$
   2.226 6H(singlet) imine methyls.

a. In nickel(II) complexes the equatorial methyls occur at high field$^{51}$.

b. CMe$_2$ = Geminal dimethyl.

c. In cobalt(III) complexes the axial methyls occur at high field$^{114,115}$. 
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94. The net absolute configuration A derives from six A and two A skew pairs of lines (octahedron edges) joining donor atoms in the unsymmetrical-[Co(hexacyclen)]\(^{3+}\) topology.

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E. STORE