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SYNTHETIC AND KINETIC STUDIES OF POLYAMINE AND MACROCYCLIC COMPLEXES

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Doctor of Philosophy

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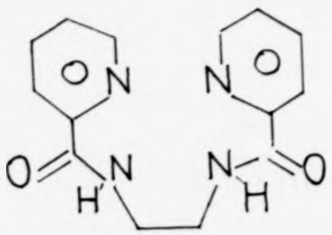
I WISH TO THANK DR. K.W. MUIR FOR UNDERTAKING THE X RAY STRUCTURAL DETERMINATION OF THE COMPLEX $\alpha\alpha\text{-}[\mathrm{Co(TETREN)CL}](\mathrm{CLO_4})\mathrm{CL}$.

ABSTRACT

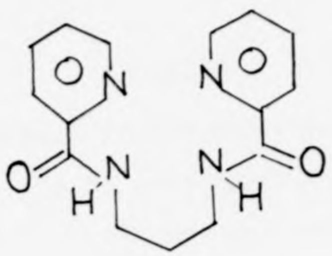
The thesis consists of four sections. Section I deals with complexes of the general type $[Co(tetren)X]^{n+}$ (where tetren is 1,11-diamino-3,6,9-triazaundecane = tetraethylenepentamine and X is a unidentate ligand). Several geometric isomers are possible and synthetic methods have been developed to prepare pure isomers rather than isomeric mixtures. The complexes have been characterised by i.r., ^{13}C n.m.r. and *d*-*d* spectra. The kinetics of base hydrolysis of the various isomers of $[Co(tetren)X]^{n+}$ have been studied ($X = Cl^-$, Br^-, NO_2^-, DMF, DMSO, ^-O_2CH, $^-O_2CCH_3$, $^-O_2CC_2H_5$, $^-O_2CCH_2Cl$, $^-O_2CCHCl_2$, $NCCH_3$, NCC_6H_5 and NCC_6H_4OMe). Activation parameters for base hydrolysis ($X = Cl^-$ and Br^-) have been determined and Hg(II) promoted aquation studied. The acid catalysed decarboxylation of $[Co(tetren)OCO_2]^+$ has been studied and activation parameters obtained. The reaction of N_3^- with $[Co(tetren)NCCH_3]^{3+}$ gives the tetrazolato complex $[Co(tetren)\text{-}N_4CCH_3]^{2+}$ and this reaction has been studied kinetically. The tetrazolato complexes $[Co(tetren)N_4CR]^{2+}$ (R = Me,Ph) have been isolated and characterised.

Section II discusses complexes of the type $[Co(trien)\text{-}(A)Cl]^{2+}$ (trien = 1,8-diamino-3,7-diazaoctane and A is a monodentate amine, imidazole (ImH), pyridine (py), *n*-butylamine (Bu^nNH_2) and 2,2-dimethoxyethylamine ($NH_2CH_2CH(OCH_3)_2$). Reactions of $[Co(trien)Cl_2]^+$ with ImH, $BuNH_2$ and ($NH_2CH_2CH(OCH_3)_2$) gave *cis*-α-$[Co(trien)(A)Cl]^{2+}$ while for A = py the complex



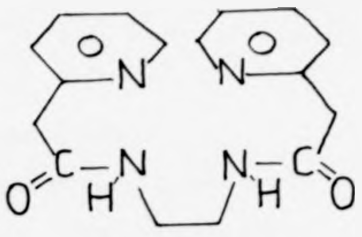
L_AH_2

(1)



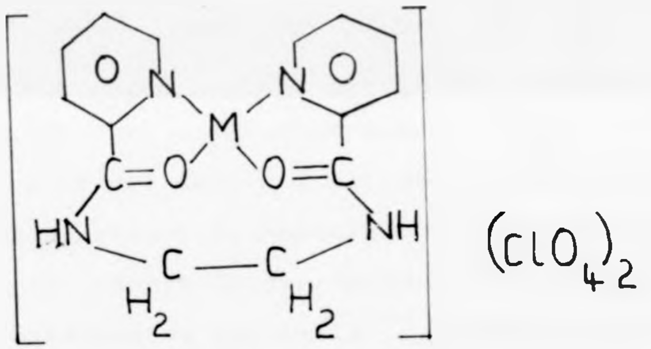
L_BH_2

(2)

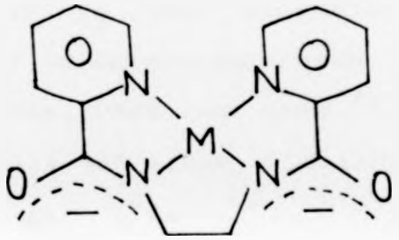


L_CH_2

(3)



(4)



(5)

cis-β_2-[Co(trien)(py)Cl]$^{2+}$ was isolated. Base hydrolysis kinetics were measured for the four complexes and the kinetics of the mercury (11) promoted aquation of *cis*-β_2-[Co(trien)-(py)Cl]$^{2+}$ studied.

Section III concerns the preparation of the open chain diamide ligands shown in structures (1) L_AH_2, (2) L_BH_2, and (3) L_CH_2. Copper (11) and nickel (11) gave cationic complexes, $[M(LH_2)](ClO_4)_2$ structure (4) and under basic conditions neutral complexes of the deprotonated ligands [M(L-2H)] structure (5). Redox studies were carried out on the neutral complexes with the ease and reversibility of the oxidation processes examined as a function of ligand structure.

Section IV describes the preparation of diamide macrocyclic ligands prepared by the condensation of diethyl malonate with (a) 1,4,7,10-tetra-azacyclotridecane-11,13-dione, (b) 1,4,8,11-tetra-azacyclotetradecane-11,13-dione, (c) 1,4,8,12-tetra-azacyclopentadecane-12,14-dione and (d) tetraethylene-pentamine. Complexation of the resultant ligands with Cu(11), Ni(11) and Pd(11) were examined using pH and spectrophotometric titrations. Redox studies were performed on complexes of the deprotonated amides [ML] for M = Cu(11) and Ni(11) and the reversibility of the oxidations examined as a function of the metal ion and the ligand structures.

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THROUGHOUT THIS THESIS EXTINCTION COEFFICIENTS (ε) ARE EXPRESSED IN UNITS OF ($dm^3\ mol^{-1}\ cm^{-1}$)

SECTION I

Synthetic and Kinetic Studies on complexes of the type $[Co(tetren)X]^{n+}$ where X is a unidentate ligand

GENERAL INTRODUCTION

Hydrolysis of Co(lll) pentaamine complexes of the type $[CoN_5X]^{n+}$ where X is a unidentate ligand coordinated to Co(lll) follows the rate law shown in equation (1)

$$-\frac{d[CoN_5X^{n+}]}{dt} = k_a[CoN_5X^{n+}] + k_b[CoN_5X^{n+}][OH^-] \qquad (1)$$

where k_a is the pseudo first order rate constant for spontaneous aquation and k_b is the second order rate constant for base hydrolysis. Aquation of octahedral Co(lll) complexes is believed to proceed by D or I_d mechanisms. A great deal of experimental data support an SN1CB mechanism for the base hydrolysis of acidoammine complexes of cobalt (lll). The mechanism involves formation of a conjugate base of the complex in a rapid pre-equilibrium step followed by loss of the leaving group in a rate-determining step:

$$[(NH_3)_5CoX]^{n+} + OH^- \xrightleftharpoons{K_a} [(NH_3)_4(NH_2)CoX]^{(n-1)+} + H_2O$$

$$[(NH_3)_4(NH_2)CoX]^{(n-1)+} \xrightarrow{k_{CB}} [(NH_3)_4(NH_2)Co]^{n+} + X^-$$

$$[(NH_3)_4(NH_2)Co]^{n+} + H_2O \rightarrow [(NH_3)_5CoOH]^{n+}$$

with the corresponding rate law shown in (2)

$$-\frac{d[(NH_3)_5CoX^{n+}]}{dt} = \frac{k_{CB}K_a[OH^-]}{1 + K_a[OH^-]}[(NH_3)_5CoX^{n+}] \qquad (2)$$

K_a can be replaced by K_{NH}/K_W where K_{NH} is the acid dissociation constant for the NH proton and K_W is the ionic product of water. If $K_a[OH^-] << 1$ then equation (2) reduces to (3).

$$-\frac{d[(NH_3)_5CoX^{n+}]}{dt} = k_{CB}K_a[(NH_3)_5CoX^{n+}][OH^-] \qquad (3)$$

The experimentally determined rate expression is shown in (4)

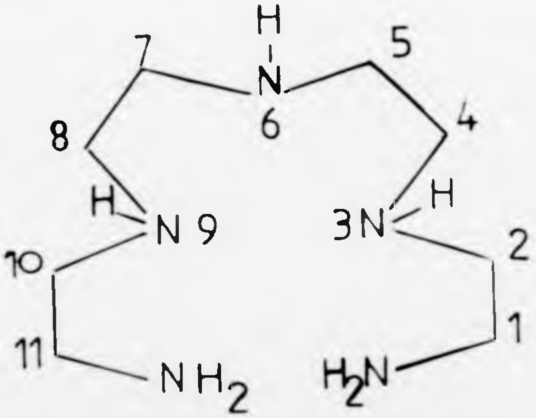
$$-\frac{d[Complex]}{dt} = k_{OH}[Complex][OH^-] \qquad (4)$$

with $k_{OH} = k_{CB}K_a$.

Support for an SN1CB mechanism for base hydrolysis of Co(111) pentaammines comes from many sources and the topic has been reviewed by House[1], Tobe[2] and Edwards et al.[3]. The dissociative nature of the process is supported by the rate acceleration that results from increasing the bulkiness of the non replaced amine ligands.[4,5] Measurement of enthalpic changes in the base hydrolysis reactions of $[(NH_3)_5CoX]^{2+}$ for an extensive series of unidentate X^- ligands supports a transition state in which the leaving group is essentially dissociated.[6] The values of isotopic fractionation factors $d\ln[O^{16}]/d\ln[O^{18}]$ in the hydrolysis of some complexes of the type $[(NH_3)_5CoX]^{2+}$ have been investigated. For X = Cl^-, Br^- and NO_2^- the ratio of O^{16} to O^{18} in the final hydroxy product $[(NH_3)_5CoOH]^{2+}$ is independent of the nature of X^- supporting an SN1CB reaction mechanism.[7] Spontaneous aquation of $[(NH_3)_5CoX]^{2+}$ is believed to take place by a dissociative mechanism[8] and a plot of LOG k_{aq}(X) versus LOG k_{OH}(X) for a series of complexes $[(NH_3)_5CoX]$

gives a line having unit slope.[9] The result implies that base hydrolysis is also a dissociative process. A major piece of evidence to support the SN1CB mechanism has been the demonstration of the formation of a very reactive intermediate species that can be trapped by nucleophiles other than the solvent. The bulk of evidence comes from careful study of the reaction products. The first successful demonstration of base catalysed substitution in aqueous solution[10] showed that reaction of $[(NH_3)_5CoX]^{2+}$ (X = Cl, Br, I, NO_3) with hydroxide in the presence of a large excess of an anionic nucleophile, Y^-, gave significant quantities of $[(NH_3)_5CoY]^{2+}$ as product. It was shown that Y^- could not have entered the complex before the act of base hydrolysis, nor could it have displaced OH^- from the product $[(NH_3)_5CoOH]^{2+}$, consequently it must have been formed in competition with the hydroxo complex after a common act of activation. Thus the dissociative nature of the reaction in basic solution has been demonstrated from the quantitative study of the distribution and stereochemistry of the products. These so-called competition experiments show that the ratios of reaction products $[(NH_3)_5CoOH]^{2+}/[(NH_3)_5CoY]^{2+}$ are not completely independent of the nature of the leaving group as would be required by a limiting D mechanism suggesting that there is not enough time for the five-coordinate intermediate to fully equilibrate its environment before it is captured by a suitable nucleophile. Further evidence for the SN1CB reaction mechanism comes from the observation that hydroxide is a unique nucleophile, other strong nucleophiles CN^-, N_3^-, HO_2^- display a much slower ligand exchange rate with $[(NH_3)_5CoX]^{n+}$,[11,12] and this suggests that hydroxide functions as a base, rather than as a nucleophile, and removes a proton from a suitably located amine ligand to form the conjugate base. Finally Henderson and Tobe[1] have rationalised base hydrolysis rate data for a wide range of Co(111) pentaamines in terms of an SN1CB reaction mechanism where the reaction proceeds through a trigonal bipyramidal intermediate. By studying the effects of steric constraints on reaction rate five requirements for lability to base hydrolysis were proposed and it was found that complexes which have the stereochemistry that allows the trigonal bipyramidal intermediate to have optimum π overlap between the lone pair of the amido nitrogen atom and an empty p orbital on Co(111) undergo the most rapid base hydrolysis.

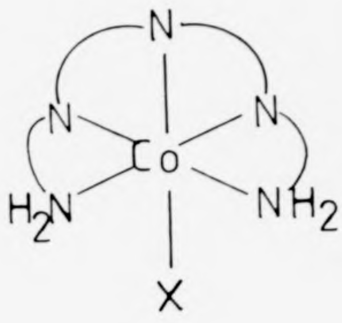
The present study is concerned with base hydrolysis reactions of Co(111) complexes of a particular pentaamine ligand, that is tetraethylenepentamine (1,11-diamino-3,6,9-triazaundecane) abbreviated to tetren and shown in structure (1).



(1)

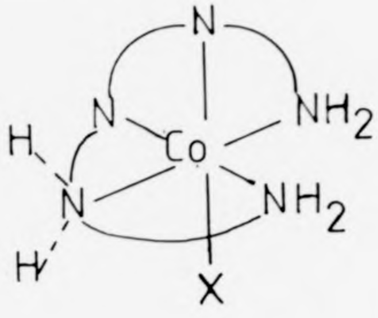
This pentadentate ligand forms complexes of the type $[Co(tetren)X]^{n+}$ which can exist in four topological forms[14] shown in structures (2), A, B, C and D.

The αα-isomer (2)A has a plane of symmetry and can exist in one diastereoisomeric form (fac fac). The αβ-isomer (2)B is asymmetric and could exist in two diastereoisomeric forms resulting from alternative configurations of the single chiral nitrogen centre present in the mer ring of the tetren ligand. The ββ-isomer (2)C is asymmetric and has only one possible diastereoisomer. The β-trans isomer (2)D is asymmetric and has four possible diastereoisomers arising from arrangements of the two secondary nitrogen atoms which fuse the coplanar chelate rings. The length of the chelate segment N-C-C-N in tetren precludes inversion at secondary nitrogen atoms which are linked by orthogonal chelates and inversion only takes place when the secondary nitrogen atom is formed by coplanar chelates. Two diastereoisomers of the αβ geometrical isomer have been characterised. The nomenclature αβR- and αβs- has been adopted to describe the two forms which are shown in structures (3)A and B.



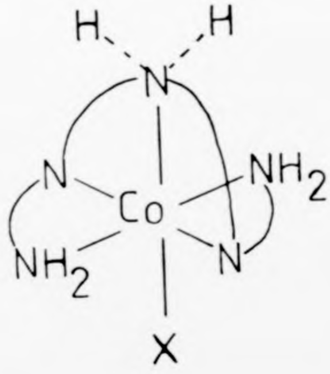
αα-

A



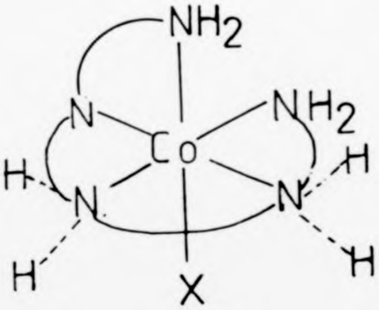
αβ-

B



ββ-

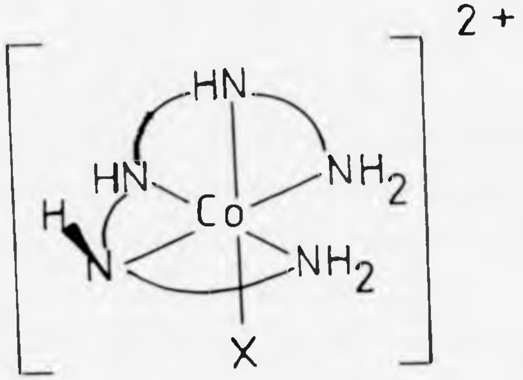
C



β-*trans*

D

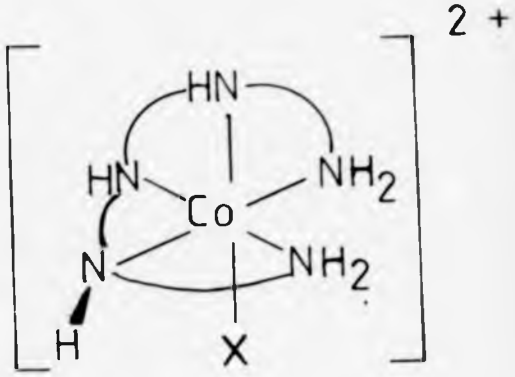
(2)



A

αβS

(3)



B

αβR

Complexes of [Co(tetren)X]$^{n+}$ were first characterised by House and Garner.[15,16] These workers prepared αβR- and αβS-diastereoisomers where X = (Cl, Br, OH, OH_2, -ONO, NO_2, N_3, NCS). Prior to the work of House and Garner [Co(tetren)X]$^{2+}$ X = Cl^-, NO_2^- and Br^- had been reported only as poorly characterised materials containing unknown geometric isomers.[17,18,19,20]

The X-ray crystal structures of αβR- and αβS-[Co-(tetren)Cl]$^{2+}$ have been reported[21] as has the crystal structure of αα-[Co(tetren)Cl]$^{2+}$ by Snow[22] although no synthetic details or physical properties can be found for the αα-isomer in the literature.

Ni and Garner studied the aquation kinetics of the αβR- and αβS- diastereoisomers of [Co(tetren)Cl]$^{2+}$ over a range of temperatures and also determined approximate rate constants for base hydrolysis.[23] Further kinetic studies on $\alpha\beta$R-[Co(tetren)Cl]$^{2+}$ have been reported by Lin and Chen.[24] The isomerisation rate of $\alpha\beta$R-[Co(tetren)NCS]$^{2+}$ to the $\alpha\beta$S-diastereoisomer has been monitored[25] as has the kinetics of base hydrolysis for these two diastereoisomers.[26]

$\alpha\beta$S-[Co(tetren)OSO$_2$]$^{2+}$ has been prepared and the kinetics of intramolecular isomerisation of this oxygen bonded sulphito complex to the sulphur bonded analogue have been measured. A second order rate constant for base hydrolysis of sulphur bonded $\alpha\beta$S-[Co(tetren)SO$_3$]$^{2+}$ has also been evaluated.[27]

The kinetics of acid and base hydrolysis of the azido complex [Co(tetren)N$_3$]$^{2+}$ have been reported by El-Awady.[28] Kinetic studies have been undertaken by Dasgupta and Harris on the decarboxylation of $\alpha\beta$S-[Co(tetren)CO$_3$]$^{+}$ and carbon dioxide uptake by $\alpha\beta$S-[Co(tetren)H$_2$O]$^{3+}$.[29] The kinetics of base hydrolysis of the salicylato complex [Co(tetren)OCOC$_6$H$_4$OH]$^{2+}$ was studied by Dash and Harris.[30,31] Interest has also been shown in the redox properties of [Co(tetren)X]$^{2+}$ with studies on the Fe(II) reduction of [Co(tetren)Cl]$^{2+}$ demonstrating an extremely slow reaction rate.[32]

The literature on [Co(tetren)X]$^{n+}$ is limited and the system deserves further investigation. Approximate rate constants for base hydrolysis of $\alpha\beta$R-[Co(tetren)Cl]$^{2+}$ evaluated by extrapolation of acid hydrolysis rate data show that the complex undergoes extremely rapid base hydrolysis in comparison with other complexes of cobalt (III) pentaamines. The hydroxy complex itself generates interest as a potential model for the metalloenzyme carbonic anhydrase. It has been found that Co-OH^{n+} species are relatively good nucleophiles, as demonstrated in the hydrolysis of 4-nitrophenyl acetate by [Co[15]aneN$_5$OH]$^{2+}$,[33] and in the intramolecular hydrolysis of N-coordinated amino acid esters and amides by Co(III)-OH species. To continue in this vein substitution of X in [Co(tetren)X]$^{n+}$ by a wide range of ligands, for example, X = DMF, RCN, O$_2$CR$^-$ may labilise the group X to reactions which are not possible for the uncoordinated ligand.

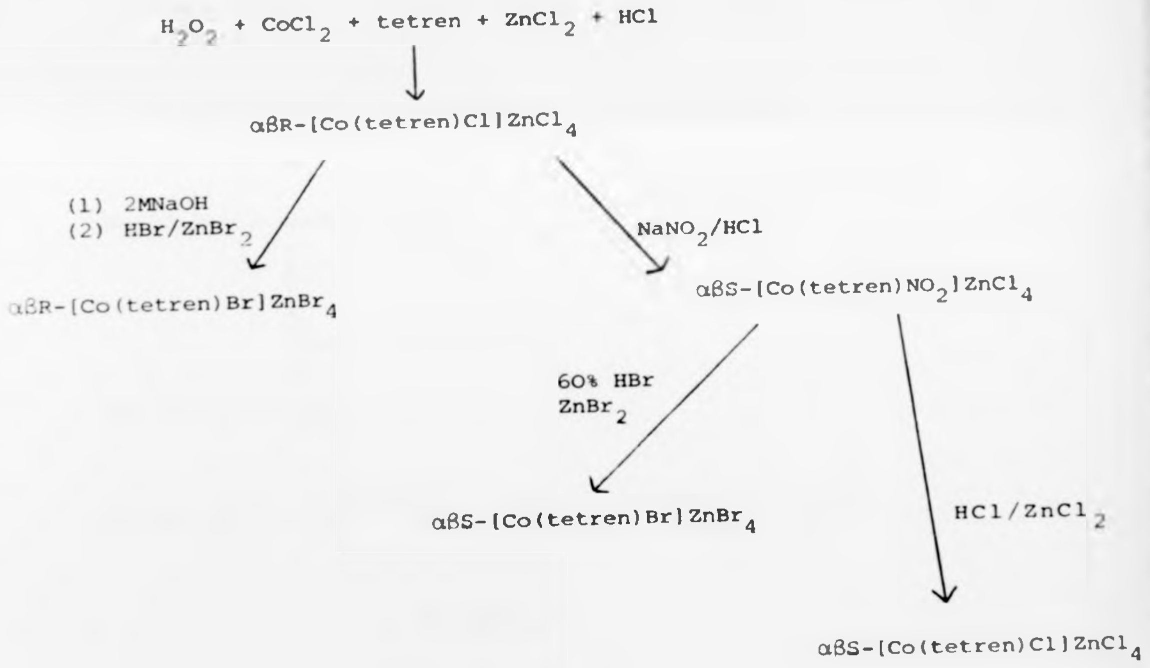
Another aspect of Co(III) tetren chemistry requiring clarification is an understanding of the preparative conditions that lead to particular isomers. Conditions are required to prepare the αα-isomer which requires to be fully characterised. An interesting analogue of the tetren ligand is the linear sulphur containing pentadentate ligand, 1,11-diamino-3,6,9-trithiaundecane (L) which coordinates to Co(III) via two terminal NH$_2$ groups and three thiaether donor centres and has the formula $H_2N\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}NH_2$. Preparations of complexes of the type [Co(L)X]$^{2+}$ (X = Cl$^-$, Br$^-$, N$_3^-$, NO$_2^-$, SCN$^-$) have shown that the bond angle requirements around the coordinated sulphur atoms limit the geometric isomer distribution to the αα-topology.[34,35,36]

CHAPTER 1

Synthesis and REACTION Kinetics of Complexes of the type $[Co(tetren)X]^{n+}$ $(X = Cl^-, Br^-, NO_2^-, CO_3^{2-}, H_2O)$

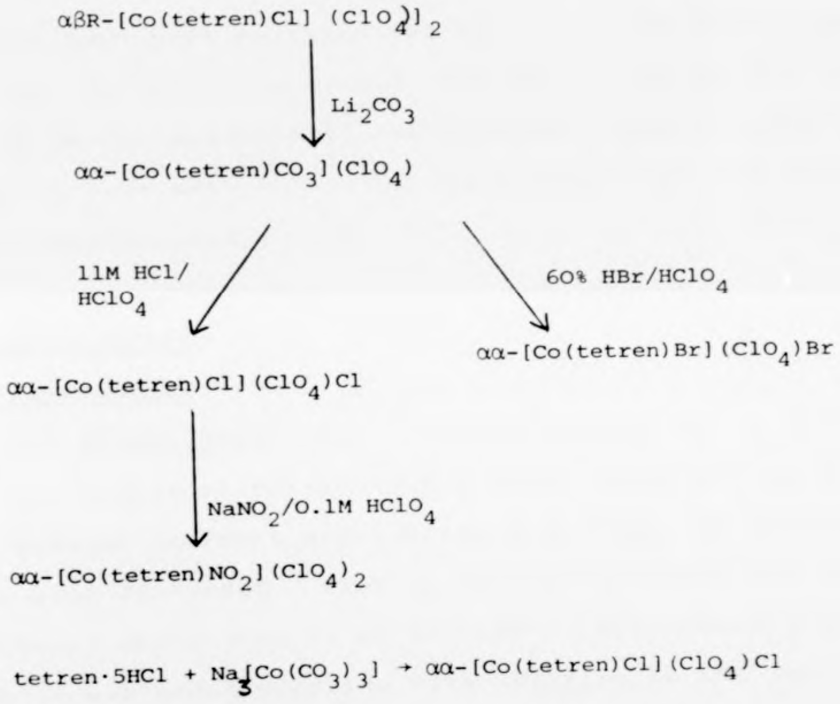
1.1 Introduction

The literature on $\alpha\beta R$- and $\alpha\beta S$-$[Co(tetren)X]^{2+}$ $(X = Cl, Br, NO_2)$ describes the preparation of complexes according to Scheme 1.



Scheme 1

In this work the above Scheme has been used to prepare $\alpha\beta R$- and $\alpha\beta S$-isomers with i.r. spectra confirming isomer purity. Experimental conditions have been found for the isolation of isomerically pure $\alpha\alpha$-$[Co(tetren)X]^{2+}$ ($X = Cl, Br, NO_2$) by the routes shown in Scheme 2.



Scheme 2

The Experimental Section gives synthetic details for all the preparations shown above, together with microanalyses, i.r., visible spectra and ^{13}C NMR spectra. The purity of the starting ligand tetren was checked by preparing the pentahydrochloride salt tetren.5HCl and titrating it against sodium hydroxide to establish the experimental molecular weight. The five pK_a's have been determined.

With regard to kinetics, a literature survey reveals that only the base hydrolysis of αβR- and αβS-$[Co(tetren)Cl]^{2+}$ have been studied. In the present work the base hydrolysis reactions have been analysed for all halo- and nitro-complexes prepared. In the cases of αβR- and αα-$[Co(tetren)Cl]^{2+}$ and αβR- and αα-$[Co(tetren)Br]^{2+}$ activation parameters for base hydrolysis have been evaluated and kinetic data for mercury (II) induced aquation collected.

1.2 Experimental

Preparations

Tetren.5HCl

Technical tetren (B.D.H.) was fractionally distilled under reduced pressure and initial fractions containing lower amines were discarded. Freshly distilled tetren was dissolved in methanol and cooled in an ice bath. Hydrochloric acid (11.5 mol dm^{-3}) was added dropwise with stirring to the solution to precipitate the colourless tetren.5HCl. Addition of concentrated hydrochloric acid was continued until no more solid precipitated. The product was filtered off, washed with methanol and air dried. Tetren.5HCl was recrystallised twice by suspending the solid in hot methanol containing a few drops of conc.HCl and adding water dropwise to dissolve the solid. Upon cooling, tetren.5HCl crystallised out and was filtered, washed with methanol and dried in vacuo. Calc. for $C_8H_{23}N_5.5HCl$: C,25.81; H,7.60; N,18.85; Found: C,25.61; H,7.63; N,18.85%.

A ^{13}C NMR spectrum of tetren.5HCl was recorded in D_2O with NaTMS as the internal reference. The values were found: δ(integral): 37.96(157.7), 45.97(397.3), 47.25(183.4). (δ in ppm)

The purity of tetren.5HCl prepared in the present work was assessed by titrating a known weight of tetren.5HCl dissolved in 1.0 mol dm^{-3} ($NaClO_4$) against 0.1 mol dm^{-3} (NaOH) at 25°C, under nitrogen. The resulting titration curve shows a series of overlapping end points. The second end point is sharply defined and the volume of titrant required to reach this end point is noted. The theoretical volume of titrant required to reach the second end point is readily calculated and a comparison between experimental and calculated titrant volume allows the experimental molecular weight of tetren.5HCl to be evaluated at 375 amu. The theoretical molecular weight of tetren.5HCl with the formulation $C_8H_{23}N_5.5HCl$ is 370 amu.

$\alpha\beta R$-[Co(tetren)Cl]$ZnCl_4$

By the method of House,[15] a solution containing $CoCl_2.6H_2O$ (24g., 0.101 moles) and 20 cm^3 of 30% H_2O_2 in 75 cm^3 water was added dropwise at room temperature to tetren (19g., 0.10 moles) dissolved in 50 cm^3 water. After addition was complete the solution was left to stand for 30 minutes. Zinc chloride (30g., 0.22 moles) and 75 cm^3 of 11.5 mol dm^{-3} HCl were then added and the solution heated on a water bath for 2 hours at 80°C. Upon cooling dark red crystals deposited which were filtered, washed with ethanol, ether and

air dried. Calc. for $[Co(C_8H_{23}N_5)Cl]ZnCl_4$: C,19.57; H,4.72; N,14.26;
Found: C,19.95; H,4.64; N,13.89%.
The i.r. spectrum (KBr) of this complex has four ν NH bands of approximately equal intensity at 3130, 3160, 3215 and 3260 cm^{-1}. A single band at 1575 cm^{-1} is assigned to the NH_2 asymmetric deformation. These data agree with those reported.[15] The visible spectrum of the complex measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 525 nm (ε = 110) and 363 nm (ε = 103) with a shoulder at 480 nm (ε = 105). The literature reports the following values λ_{max} 522 nm (ε = 109) λ_{max} 362 nm (ε = 103) with a shoulder at 480 nm (ε = 105). A F.T. ^{13}C NMR spectrum was recorded in Me_2SO-D_6 using NaTMS as an internal reference. 8,800 transients were recorded to give the values: (δ in ppm)
δ(integral): 42.95(11.2), 48.57(8.9), 50.76(10.1), 51.63(9.6), 53.27(8.0), 55.83(7.6), 57.85(11.2).

αβR-$[Co(tetren)Cl]CoCl_4$

Tetren.5HCl (70g, 0.19 moles) (for preparation see above) was dissolved in 250 cm^3 water and $Na_3[Co(CO_3)_3]$[37] (60g., 0.20 moles) added. After stirring the mixture at 50°C for three hours the solution was filtered and the filtrate evaporated to dryness to give an orange solid. The solid was taken up in 300 cm^3 of 11.5 mol dm^{-3} HCl and heated at 60°C for two hours. Upon cooling 5 cm^3 72% $HClO_4$ was added providing a source of ClO_4^- ions. Many fractions crystallised from this mixture over several days. The first fraction was exclusively αβR-$[Co(tetren)Cl]CoCl_4$ (14.8g, 0.03 moles). The second crop

was αα-[Co(tetren)Cl](ClO$_4$)Cl (4.8g., 0.011 moles) and later crops were isomer mixtures of αβR- and αβS-[Co(tetren)Cl](ClO$_4$)$_2$. (2.7g., 0.005 moles). Calc. for [CoC$_8$H$_{23}$N$_5$)Cl]CoCl$_4$: C,19.83; H,4.78; H,14.45;
Found: C,19.48; H,4.89; N,14.39%.
The i.r. spectrum (KBr) has four ν NH bands of approximately equal intensities at 3130, 3160, 3215 and 3260 cm^{-1}. A single band at 1569 cm^{-1} is assigned to the NH$_2$ asymmetric deformation. The complex can be converted to the diperchlorate salt αβR[Co(tetren)Cl](ClO$_4$)$_2$ by recrystallisation from 0.1 mol dm^{-3} HClO$_4$.

αβS-[Co(tetren)NO$_2$]ZnCl$_4$

By the House method[16] an isomer mixture of αβR- and αβS-[Co(tetren)Cl]ZnCl$_4$ (3.0g., 6.11 mmoles) was dissolved in 0.2 mol dm^{-3} HCl (75 cm^3) and NaNO$_2$ (12g., 0.17 moles) added. Upon heating the mixture at 70°C for 30 minutes effervescence accompanied a colour change from red to yellow. Zinc chloride (3.0g., 0.022 moles) was added and the solution left to cool. Precipitation of the complex as a fine yellow powder was achieved by adding isopropanol-methanol: (300 cm^3, 1:1 v/v) to the solution. The product was filtered, washed with ethanol and air dried. Recrystallisation from 0.1 mol dm^{-3} HClO$_4$ gave αβS-[Co(tetren)NO$_2$](ClO$_4$)$_2$. Calc. for [Co(C$_8$H$_{23}$N$_5$)NO$_2$](ClO$_4$)$_2$: C,19.48; H,4.70; N,17.04;
Found: C,19.45; H,4.27; N,16.67%. An i.r. spectrum (KBr) of the complex shows a broad absorption in the range 2850-3300 cm^{-1} due to ν NH. Two bands at 1570 and 1585 cm^{-1} are assigned to

the NH_2 asymmetric deformations. The visible spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 460 nm (ε = 212) and 328 nm (ε = 1,844). The literature reports the following values. λ_{max} 460 nm (ε = 224) and λ_{max} 328 (ε = 1,820). A F.T. ^{13}C NMR spectrum was recorded in $Me_2SO\text{-}D_6$ using NaTMS as an internal reference. 9,002 transients were recorded giving the values: (δ in ppm)
δ(integral) 48.19(25.9), 48.57(68.9), 51.19(46.4), 51.68(78.2), 52.77(132.2), 53.81(67.0), 55.01(71.0), 55.94(117.7), 57.36(231.5), 59.43(59.3).

αβS-[Co(tetren)Cl]$ZnCl_4$

By the method of House[15] αβS-[Co(tetren)NO_2]$ZnCl_4$ (1g., 1.99 mmoles) in 15 cm^3 of 10% $ZnCl_2$ in 11.5 mol dm^{-3} HCl was warmed at 70°C for two hours. During this time the colour changed from yellow to red. Upon cooling, dark red crystals deposited which were filtered, washed with ethanol and air dried. Calc. for $[Co(C_8H_{23}N_5)Cl]ZnCl_4$: C,19.57; H,4.72; N,14.26;
Found: C,20.14; H,4.67; N,14.02%. An i.r. spectrum (KBr) of the complex has a sharp ν NH at 3270 cm^{-1} and a broad ν NH band around 3200 cm^{-1}. Two bands at 1570 and 1585 cm^{-1} are assigned to NH_2 asymmetric deformations. The visible spectrum of the complex measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 525 nm (ε = 102), 480 nm (ε = 103) and 360 nm (ε = 107). The literature reports the following values λ_{max} 525 nm (ε = 98.6), 480 nm (ε = 101) and 360 nm (ε = 107). A F.T. ^{13}C

NMR spectrum was recorded in Me_2SO-D_6 using NaTMS as an internal reference. 9080 transients were recorded to give the values: (δ in ppm)
δ(integral) 48.03(20.48), 52.23(29.81), 55.83(17.23), 57.96(31.90), 58.40(11.90), 59.81(10.12).

αα-[Co(tetren)CO_3](ClO_4).$3H_2O$

By the method of Dasgupta and Harris[29] isomerically impure [Co(tetren)Cl]$(ClO_4)_2$ (19.0g., 0.039 moles) was dissolved in the minimum volume of water, and silver oxide, (4.63g., 0.02 moles) added to the solution. The mixture was heated at 60°C for 30 minutes during which time a colour change from red to orange took place. The solution was cooled and filtered to remove silver chloride. To the filtrate was added excess lithium carbonate until a pH of *ca*. 9 was attained. The mixture was stirred at room temperature for 30 minutes then filtered to remove lithium carbonate. The orange solution was treated with lithium perchlorate (4.25g., 0.04 moles) then cooled and ethanol was added to precipitate a fine orange crystalline solid. The product, αα-[Co(tetren)CO_3](ClO_4) was filtered off, washed with ethanol, ether and dried *in vacuo*. Yield 15g. Calc. for [Co($C_8H_{23}N_5$)CO_3](ClO_4) $3H_2O$: C,23.40; H,6.29; N,15.18;
Found: C,23.68; H,6.19; N,15.29%. The i.r. spectrum (KBr) has ν NH at 2900, 3140, 3260 and 3400 cm^{-1}. The electronic spectrum measured in dilute aqueous sodium bicarbonate has a band maximum at 492 nm (ε = 148) with a steep charge transfer absorbance increasing near 350 nm characteristic of monodentate

carbonato ligand. A ^{13}C NMR was recorded in D_2O (pH8) using NaTMS as an internal reference. 11,894 transients were recorded giving the values δ(integral) 45.1(39.8), 55.9(36.0), 57.7(38.9), 59.8(38.7). (δ in ppm)

αα-[Co(tetren)Cl](ClO_4)Cl

Method A

The complex αα-[Co(tetren)CO_3](ClO_4) (15g., 0.036 moles) was dissolved in 200 cm^3 11.5 mol dm^{-3} HCl and heated at 60°C until CO_2 evolution ceased and the colour change from orange to dark red was complete. A few drops of 72% perchloric acid were added and the solution volume was concentrated on the water bath until crystallisation commenced. Upon cooling the crystals were filtered off, washed with ethanol, ether and air dried. The first crop from the reaction mixture was identified as αα-[Co(tetren)Cl](ClO_4)Cl. Subsequent crops were found to be mixtures of αβR- and αβS-[Co(tetren)Cl]$(ClO_4)_2$.

αα-[Co(tetren)Cl](ClO_4)Cl

Method B

Tetren.5HCl (10g., 27 mmoles) was taken up in the minimum of cold water and a two-fold excess of $Na_3[Co(CO_3)_3]$ (16.62g., 54 mmoles) added. The mixture was heated at 60°C until effervescence ceased. After cooling, the solution was filtered to remove unreacted $Na_3[Co(CO_3)_3]$ and the orange filtrate was evaporated to dryness to give αα-$[Co(tetren)CO_3]^+$ and sodium chloride. The solid mixture was taken up in 11.5 mol dm^{-3} HCl and sodium chloride filtered off. The orange

filtrate was heated at 60°C with CO_2 evolution accompanying a colour change to dark red. Heating was continued until crystallisation commenced. Upon cooling, the crystals of αα-[Co(tetren)-Cl](ClO$_4$)Cl were filtered off, washed with ethanol ether and air dried. Subsequent crops of crystals from this reaction were found to be mixtures of αβR- and αβS-[Co(tetren)Cl](ClO$_4$)$_2$. Crude αα-[Co(tetren)](ClO$_4$)Cl was recrystallised from 0.1 mol dm^{-3} HClO$_4$. Calc. for αα[Co($C_8H_{23}N_5$)Cl](ClO$_4$)Cl: C,22.96; H,5.54; N,16.73;
Found: C,22.82; H,5.40; N,17.07%.
The i.r. spectrum (KBr) has sharp ν NH at 2280 and 3290 cm^{-1}, with a broad ν NH band centred around 3100 cm^{-1}. A single band at 1600 cm^{-1} is assigned to the NH_2 asymmetric deformations. A visible spectrum measured in 0.1 mol dm^{-3} HClO$_4$ has band maxima at 533 nm (ε = 96) and 362 nm (ε = 92) with a shoulder at 470 nm (ε = 52). A ^{13}C NMR spectrum was recorded in Me$_2$SO-D$_6$ using Na TMS as an internal reference. 19,040 transients were recorded giving the values (δ in ppm)
δ(integral) 43.83(102.8), 56.27(137.5), 57.36(108.9), 57.96(86.5). The ^{13}C NMR spectrum was also recorded in D_2O containing a drop of DCl to suppress base hydrolysis. Na TMS was the internal reference. 12,102 transients were recorded to give: (δ in ppm)
δ(integral) 45.74(1.89), 57.91(1.98), 59.27(1.94), 60.42(1.43).
αα-[Co(tetren)Cl](ClO$_4$)Cl can be converted to the di-perchlorate salt by four successive ion exchanges on Amberlite IRA-400 (in the ClO$_4^-$ form). The sample was eluted with water. Concentration of the eluted fraction under reduced pressure

gives αα-[Co(tetren)Cl](ClO$_4$)$_2$. Calc. for [Co(C$_8$H$_{23}$N$_5$)Cl](ClO$_4$)$_2$: C,19.91; H,4.80; N,14.51;
Found: C,19.68; H,4.88; N,14.16%.

αβR-[Co(tetren)Br]ZnBr$_4$

By the House method,[16] αβR-[Co(tetren)Cl]ZnCl$_4$ (1 g., 2.03 mmoles) was dissolved in 2 mol dm^{-3} NaOH (20 cm^3). Hydrolysis was indicated by a rapid colour change from dark red to orange, 15 cm^3 of 10% ZnBr$_2$ in 60% HBr was added to the solution which upon heating on a water bath at 60°C became violet and deposited crystals which were filtered, washed with ethanol and air dried. Calc. for [Co(C$_8$H$_{23}$N$_5$)Br]ZnBr$_4$: C,13.47; H,3.25; N,9.82;
Found: C,13.21; H,3.28; N,9.91%. An i.r. spectrum (KBr) of this complex has four ν NH bands of approximately equal intensities at 3120, 3150, 3210 and 3245 cm^{-1}. A single band at 1568 cm^{-1} is assigned to the NH$_2$ asymmetric deformations. The visible spectrum of the complex measured in 0.1 mol dm^{-3} HClO$_4$ has a band maximum at 548 nm (ε = 122) with a shoulder at 480 nm (ε = 93). The literature reports the following values λ_{max} 548 nm (ε = 132) with a shoulder at 480 nm (ε = 100).

αβS-[Co(tetren)Br]ZnBr$_4$

The complex αβS-[Co(tetren)NO$_2$]ZnCl$_4$ (1g., 1.99 mmoles) was dissolved in 15 cm^3 of 10% ZnBr$_2$ in 60% HBr and warmed at 70°C for two hours. The violet crystals which deposited upon cooling were filtered, washed with ethanol, ether and air dried. Calc. for [Co(C$_8$H$_{23}$N$_5$)Br]ZnBr$_4$: C,13.47; H,3.25; N,9.82;

Found: C,13.93; H,3.15; N,9.49%.

An i.r. spectrum (KBr) of the complex has a sharp ν NH at 3260 cm^{-1} and a broad ν NH band around 3200 cm^{-1}. Two bands at 1565 cm^{-1} and 1580 cm^{-1} are assigned to NH_2 asymmetric deformations. The visible spectrum of the complex measured in 0.1 mol dm^{-3} $HClO_4$ has a band maximum at 550 nm (ε = 113) with a shoulder at 480 nm (ε = 92). The literature reports the following values λ_{max} 550 nm (ε = 121) and 480 nm (ε = 98).

A ^{13}C NMR spectrum was recorded in Me_2SO-D_6 using Na TMS as an internal reference. 11,600 transients were recorded to give the values: (δ in ppm)

δ(integral) 43.93(161), 48.25(132), 52.34(288), 55.67(148), 57.90(170), 58.67(126), 60.03(126).

αα-[Co(tetren)Br](ClO$_4$)Br

The complex αα-[Co(tetren)CO_3](ClO_4) (1g., 2.1 mmoles) was dissolved in 25 cm^3 of 60% HBr and a few drops of 72% $HClO_4$ were added. Vigorous effervescence was accompanied by a colour change from orange to violet. The solution was heated on a water bath until crystallisation commenced. Upon cooling, the crystals were filtered off, washed with ethanol and air dried. The crystals are isomerically pure αα-[Co(tetren)Br]-(ClO_4)Br. Subsequent crops from this preparation gave mixtures of αβR- and αβS-[Co(tetren)Br]$(ClO_4)_2$. Crude αα-[Co(tetren)Br]-(ClO_4)Br was recrystallised from 0.1 mol dm^{-3} $HClO_4$. Calc. for αα-[Co($C_8H_{23}N_5$)Br] ClO_4Br: C,18.93; H,4.56; N,13.79;

Found: C,19.05; H,4.43; N,13.60%.

The i.r. spectrum (KBr) measured in 0.1 mol dm^{-3} $HClO_4$ has

sharp ν NH bands at 2880 and 3260 cm^{-1} and a broad ν NH absorption band centred around 3120 cm^{-1}. A single band at 1600 cm^{-1} is assigned to NH_2 asymmetric deformations. A visible spectrum of the complex in 0.1 mol dm^{-3} $HClO_4$ has a band maximum at 552 nm (ε = 98) and a shoulder at 480 nm (ε = 43). A ^{13}C NMR spectrum was recorded in Me_2SO-D_6 using Na TMS as an internal reference. 12,924 transients were recorded giving the values: δ(integral) 43.93(123), 56.76(103), 57.58(96), 58.23(96).
The ^{13}C NMR was also recorded in D_2O containing a drop of DCl to suppress base hydrolysis. Na TMS was the internal reference. 24,024 transients were recorded to give: (δ in ppm)
δ(integral) 45.74(34.2), 58.50(32.1), 59.97(23.5), 60.19(31.5).
αα-[Co(tetrenBr](ClO$_4$)Br was converted to the diperchlorate salt by four successive ion exchanges on Amberlite IRA400 (in the ClO_4^- form) eluting with water. Calc. for [Co($C_8H_{23}N_5$)Br]-(ClO_4)$_2$: C,18.23; H,4.40; H,13.29;
Found: C,17.80; H,4.41; N,13.29%.

αα-[Co(tetren)NO$_2$](ClO$_4$)$_2$

The complex αα-[Co(tetren)Cl](ClO$_4$)Cl (1g., 2.38 mmoles) was taken up in the minimum of 0.1 mol dm^{-3} $HClO_4$ and $NaNO_2$ (0.27g., 3.9 mmoles) added. The solution was heated on a water bath at 60°C until the colour change from violet to yellow was complete. Upon cooling yellow crystals deposited which were filtered, washed with ethanol and air dried. Calc. for [Co($C_8H_{23}N_5$)NO_2](ClO_4)$_2$: C,19.48; H,4.70; N,17.04;
Found: C,19.50; H,4.73; N,18.37%.
The i.r. spectrum (KBr) displays ν NH as a broad band in the

range 3000-3300 cm^{-1}. A single band at 1590 cm^{-1} is assigned to NH_2 asymmetric deformations. A visible spectrum measured in 0.1 mol dm^{-3} $HClO_4$ shows a band maximum at 450 nm (ε = 154). A ^{13}C NMR spectrum was recorded in Me_2SO-D_6 using Na TMS as an internal reference. 12,000 transients were recorded giving the values: (δ in ppm)

δ(integral) 43.99(103.5), 55.18(87.0). 56.81(111.4), 57.47(111.6).

<u>αα-[Co(tetren)H_2O]$(ClO_4)_3$</u>

To a solution of αα-[Co(tetren)Cl](ClO_4)Cl (3.0g., 7.16 mmoles) dissolved in the minimum volume of perchloric acid (0.1 mol dm^{-3}) was added silver perchlorate (3.1g., 15 mmoles). The mixture was stirred at 60°C until the colour change from deep red to orange was complete *ca*. 1 hour. The solution was cooled to 0°C and filtered to remove precipitated silver chloride and unreacted silver perchlorate. The filtrate was left to stand at room temperature during which time orange crystals began to appear. The product was filtered off, washed with ethanol, ether and dried *in vacuo*. Calc. for [$Co(C_8H_{23}N_5)H_2O$]$(ClO_4)_3$: C,17.02; H,4.46; N,12.40; Found: C,16.88; H,4.02; N,12.48%.

The i.r. spectrum (KBr) of this complex has a sharp ν NH at 2270 cm^{-1} with a broad ν NH in the range 3030-3210 cm^{-1}. A single band at 1600 cm^{-1} is assigned to the NH_2 asymmetric deformations. The visible spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 494 nm (ε = 70) and 346 nm (ε = 73). A ^{13}C NMR spectrum was recorded in D_2O containing one drop of DCl using Na TMS as an internal reference. 4,208 transients were recorded giving values: (δ in ppm) δ(integral) 45.68(38.0), 56.70(36.4), 58.40(32.1), 60.70(36.9). A potentiometric titration of αα-$[Co(tetren)H_2O](ClO_4)_3$ against sodium hydroxide was performed in 0.5 mol dm^{-3} (KNO_3) at 25°C using an automatic titrator. Data were refined by the Miniquad computer programme to give pK_a = 5.75 for the equilibrium αα-$[Co(tetren)H_2O]^{3+} \rightleftharpoons [Co(tetren)OH]^{2+} + H^+$. The pK_a of αβs-$[Co(tetren)H_2O](ClO_4)_3$ determined by Dasgupta and Harris[29] by titrating the complex against sodium hydroxide in 0.5 mol dm^{-3} NaCl was found to be 6.3 ± 0.1 at 25°C.

Kinetic Measurements

In the present work both pH stat and spectrophotometric techniques have been used to measure the rates of base hydrolysis. The spectrophotometric method was used when substantial changes in the electronic spectrum accompany the reaction under study. Data were collected by monitoring the change in absorbance with time at a fixed preset wavelength. The instrument used was a Unicam SP500 spectrophotometer interfaced with an Apple II computing system and associated printer. The reaction is initiated by adding a small amount of solid complex to the quartz cell containing buffer solution which has been thermostatted to the appropriate temperature. All buffer solutions were prepared by known formulations.[38]

Kinetics obtained by the pH stat method were studied using a Radiometer TTTL automatic titrator. A high alkalinity glass electrode type G202B was used as the indicator electrode. The electrode system was standardised before each run with NBS borate buffer (pH 9.18 at 25°C) and phthalate buffer (pH = 4.01 at 25°C). The pH stat apparatus consists of a thermostatted cell containing 50 cm^3 of 0.1 mol dm^{-3} (KNO_3) through which nitrogen gas is constantly bubbled. Dipping into the cell is a burette containing sodium hydroxide of known concentration. Sodium hydroxide from this burette enters the cell through a valve which is controlled by an automatic titrator unit. The experiment is initiated by dropping a weighed sample of the complex under study into the cell with magnetic stirring ensuring rapid dissolution. The automatic titrator is set at the desired pH and this pH is maintained throughout the experiment by making incremental additions of sodium hydroxide from the burette into the reaction cell. The burette volume is monitored against time. The choice between using pH stat or spectrophotometry for measuring reaction rate is made by considering reaction characteristics: Potentiometric titration of the aqua complex αα-$[Co(tetren)H_2O]^{3+}$ gives a pK_a of 5.7 for the aqua $\rightleftharpoons$ hydroxo equilibrium at 25°C and $I = 0.1$ mol dm^{-3} therefore when base hydrolysis of $[Co(tetren)X]^{2+}$ takes place below pH6 the product $[Co(tetren)OH]^{2+}$ rapidly equilibrates towards $[Co(tetren)H_2O]^{3+}$ releasing hydroxyl ions into solution; under these circumstances if the pH stat method is used the experimental base consumption will be much lower than that predicted, thus the spectrophotometric technique is used. Conversely, when base hydrolysis takes place above pH 6 the pH stat METHOD is much preferred, this is because the product $[Co(tetren)OH]^{2+}$ undergoes rapid reaction with carbon dioxide giving the monodentate carbonato complex $[Co(tetren)CO_3]^{+}$. The large spectral changes accompanying this reaction interfere with the spectral changes due to base hydrolysis. The pH stat method allows base hydrolysis to take place in a solution which has been made free of carbon dioxide by the constant bubbling of nitrogen gas through the reaction mixture.

For all the base hydrolysis reactions studied in the present work the rate expression is of the form shown in equation (5):

$$-\frac{d[complex]}{dt} = k_{OH}[complex][OH^-] \qquad (5)$$

where k_{OH} is the overall second order rate constant having the units (dm^3 mol^{-1} s^{-1}). Under reaction conditions of constant pH the reaction will be pseudo first order in the complex and equation (5) reduces to equation (6) where k_{obs} is the pseudo first order rate constant having the units (s^{-1}).

$$k_{OH} = \frac{k_{obs}}{[OH^-]} \qquad (6)$$

By the spectrophotometric technique k_{obs} is evaluated by plotting ln $(A_\infty - A_t)$ versus time, when A is the absorbance measured at a time equal to ten half-lives and A_t is the absorbance measured at time (t). This linear plot has a gradient equal to k_{obs}. By the pH stat method a plot is made of ln $(V_\infty - V_t)$ versus time where V_∞ is the volume of base consumed at a time equal to ten half lives and V_t is the volume of base consumed at time (t). The gradient of this linear plot equals k_{obs}. Two types of calculation have been used to evaluate k_{obs} directly from the experimental data without drawing graphs. These are (a) the sixteen point first order kinetics programme which requires an infinity absorbance value at ten half-lives and (b) the Swinbourne calculation where k_{obs} can be evaluated from rate data collected over ca. three half lives, that is an infinity value is not required. In some cases graphs of log$(V_\infty - V_t)$ versus time have been found to give curved plots. This indicates that two reactions are taking place.

This plot can be resolved to give a k_{obs} value for each of the two reactions designated "fast" and "slow" in Figure 1.1.

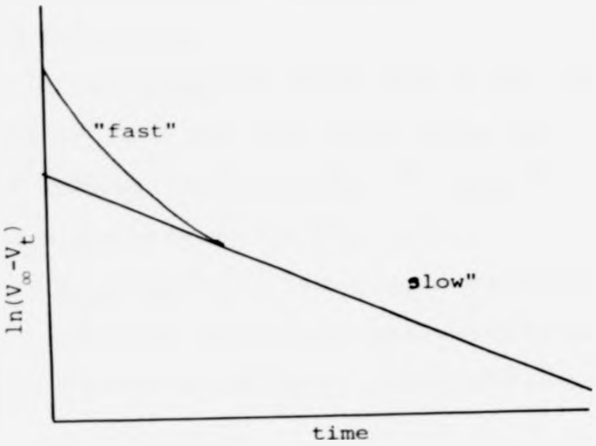


Figure 1.1

The line for the "slow" reaction is extrapolated back to the ordinate (t = o) and the value of $(V_\infty - V_t)$ at this point gives the infinity value for the first reaction. If this infinity value is subtracted from the $(V_\infty - V_t)$ data for the original curve then a corrected plot of the fast reaction can be obtained.

After evaluating k_{obs} for the base hydrolysis reactions, equations (5) and (6) above are combined to give equation (7):

$$k_{obs} = k_{OH}[OH^-] \qquad (7)$$

Plots of k_{obs} versus $[OH^-]$ were made and the gradient evaluated to give k_{OH} the overall second order rate constant for base hydrolysis.

After studying base hydrolysis at 25°C the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for base hydrolysis of αβ**R**-,αα-$[Co(tetren)Cl]^{2+}$ and αβ**R**-,αα-$[Co(tetren)Br]^{2+}$ were evaluated from the temperature dependence of the overall second order rate constants k_{OH} using least squares analysis of Eyring plots.

The acid catalysed decarboxylation of αα-$[Co(tetren)CO_3]ClO_4$ was studied by stopped-flow techniques. The kinetics were followed on a Durrum D110 stopped-flow spectrophotometer. The signal was stored by a Datalab 901 transient recorder on line to a CBM 3016 computer.

The Hg^{2+} assisted aquation reactions of αβ**R**-,αα-$[Co(tetren)Cl]^{2+}$ and αβ**R**-,αα-$[Co(tetren)Br]^{2+}$ were studied at 25°C, under pseudo first order conditions, that is with $[Hg^{2+}] > 10\ [[Co(tetren)X]^{2+}]$. Mercury (II) solutions of varying concentrations were prepared by dissolving the appropriate amounts of $Hg(NO_3)_2.H_2O$ in aqueous nitric acid and adding KNO_3 to bring the solutions to the desired ionic strength. After preliminary spectral scans to establish isosbestic points kinetic data were obtained by adding a small amount of solid $[Co(tetren)X]^{2+}$ (X = Br,Cl) to the Hg^{2+} solution and monitoring the absorbance change with time, at a pre-set wavelength.

1.3 Results and Discussion

STEREOCHEMICAL ASPECTS

The ligand, tetren was fractionally distilled and its purity confirmed by titration of the pentahydrochloride salt tetren.5HCl against sodium hydroxide, this established an experimental molecular weight of 375 amu while the calculated molecular weight is 370 amu.

The protonation constants for tetren were obtained from the titration of Tetren.5HCl against sodium hydroxide in 0.1 mol dm^{-3} (KNO_3) at 25°C. The following equilibria apply to tetren (abbreviated to L):

$$L + H^+ \rightleftharpoons LH^+; \qquad K_1 = [LH^+]/[H^+][L]$$

$$LH^+ + H^+ \rightleftharpoons LH_2^{2+}; \qquad K_2 = [LH_2^{2+}]/[H^+][LH^+]$$

$$LH_2^{2+} + H^+ \rightleftharpoons LH_3^{3+}; \qquad K_3 = [LH_3^{3+}]/[H^+][LH_2^{2+}]$$

$$LH_3^{3+} + H^+ \rightleftharpoons LH_4^{4+}; \qquad K_4 = [LH_4^{4+}]/[H^+][LH_3^{3+}]$$

$$LH_4^{4+} + H^+ \rightleftharpoons LH_5^{5+}; \qquad K_5 = [LH_5^{5+}]/[H^+][LH_4^{4+}]$$

The experiment was performed using an automatic titrator unit. The data were calculated and refined using a Miniquad computer programme to give stepwise formation constants log K_1 = 10.02, log K_2 = 9.40, log K_3 = 8.53, log K_4 = 5.12 and log K_5 = 3.35. Prior to, and subsequent to, the titration of tetren.5HCl against sodium hydroxide "Gran runs" were performed, these are titrations of standard hydrochloric acid against sodium hydroxide and are used to check the stability of the cell-potential in the apparatus.

The stepwise formation constants of tetren have been determined by Jonassen and Westerman[73] by titrating tetren.5HCl against potassium hydroxide in 0.075 mol dm^{-3} ($KClO_4$) at 25°C.

The following values were obtained: log K_1 = 9.78, log K_2 = 9.38, log K_3 = 8.14, log K_4 = 4.83 and log K_5 = 3.15.

The complexes αβR- and αβs-$[Co(tetren)X]^{2+}$ (X = Cl,Br) and αβs-$[Co(tetren)NO_2]^{2+}$ were prepared by the methods of House and Garner[15,16] given in Scheme 1 with i.r. and electronic spectra in good agreement with the literature data. The carbonato complex $[Co(tetren)CO_3]^+$ was isolated by the method of Dasgupta and Harris[29] by the action of lithium carbonate on $[Co(tetren)OH]^{2+}$. The hydroxo complex was prepared *in situ* by reaction of silver oxide with isomerically impure $[Co(tetren)Cl](ClO_4)_2$. Dasgupta and Harris isolated αβS-$[Co(tetren)CO_3]^+$. However, in the present work αα-$[Co(tetren)CO_3](ClO_4)$ was obtained. Decarboxylation of this monodentate carbonato complex occurs in acidic solution and the acid-catalysed decarboxylation of this new isomer was studied kinetically by stopped-flow techniques over a range of temperatures.

The complex αα-$[Co(tetren)CO_3]^+$ was used to prepare αα-$[Co(tetren)X]^{2+}$ (X = Cl,Br) by dissolving the carbonato complex in a concentrated solution of the appropriate mineral acid *e.g.* 11.5 mol dm^{-3} HCl or 60% HBr). Detailed characterisation of these new halo complexes was undertaken including an X-ray crystallographic analysis of αα-$[Co(tetren)Cl](ClO_4)Cl$. Reaction of αα-$[Co(tetren)Cl](ClO_4)Cl$ with sodium nitrite was found to proceed with full retention of configuration giving αα-$[Co(tetren)NO_2](ClO_4)_2$. In view of the extensive kinetic studies of the hydrolysis reactions undertaken on all of the above COMPLEXES it was important to characterise the potential products

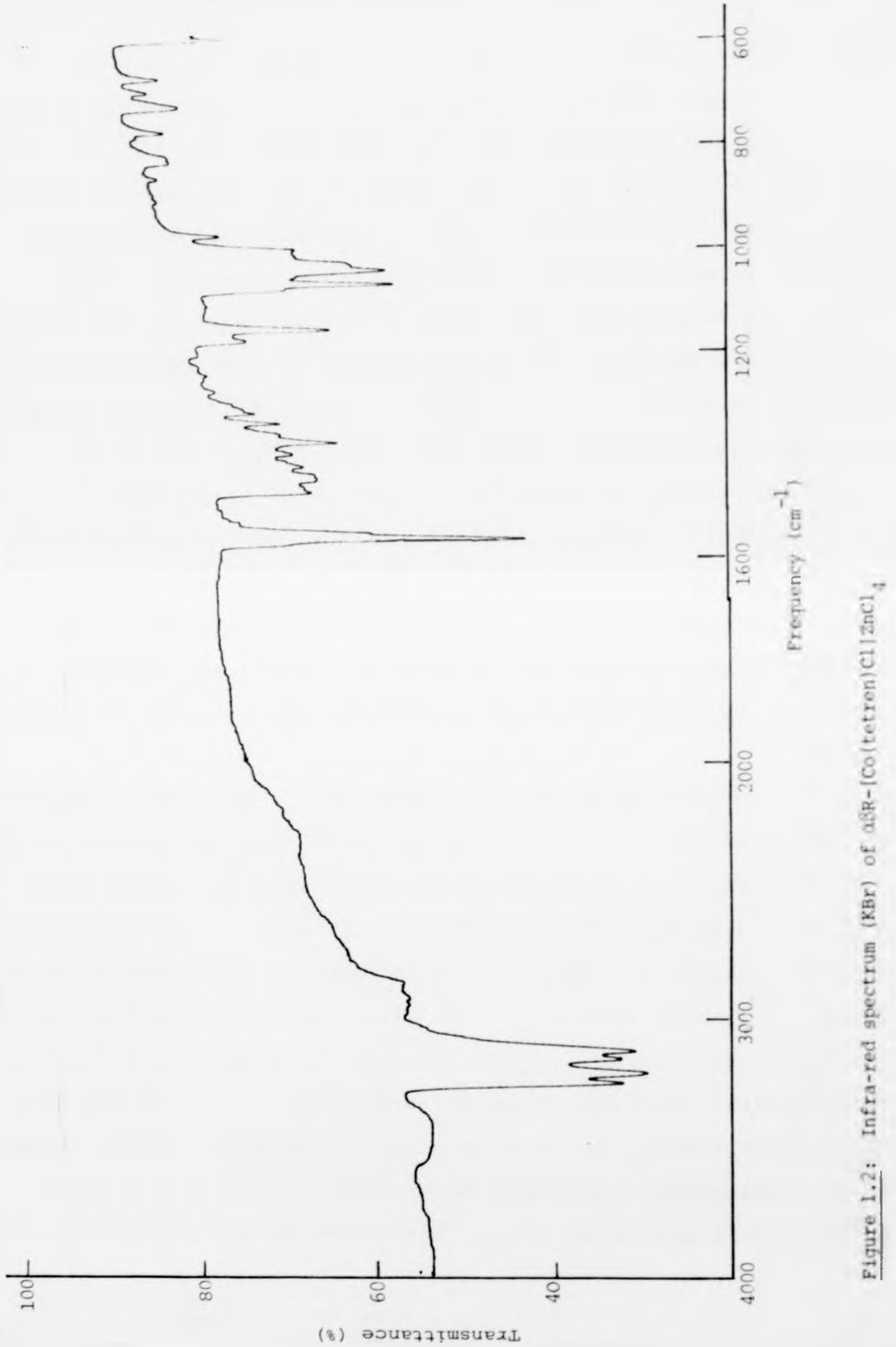


Figure 1.2: Infra-red spectrum (KBr) of αβR-$[Co(tetren)Cl]ZnCl_4$

of hydrolysis that is the hydroxo, aqua and carbonato complexes. Thus αα-$[Co(tetren)H_2O](ClO_4)_3$ was prepared by silver catalysed aquation of αα-$[Co(tetren)Cl](ClO_4)Cl$, the reaction proceeded with full retention of configuration. Potentiometric titration of the αα-aquo complex gave $pK_a = 5.7$ for the aqua $\rightleftharpoons$ hydroxo equilibrium.

An assessment of isomer purity of samples of αβR- and αβS-$[Co(tetren)X]^{2+}$ based purely on analysis of spectrophotometric data is sometimes difficult as the two isomers have very similar i.r., electronic and ^{13}C NMR spectral characteristics. The most effective technique for detecting the presence of isomer mixtures is to perform a kinetic study of the base hydrolysis reaction of the sample. As αβR- and αβS-isomers have different reaction rates a graphical analysis of the experimental kinetic data can reveal not only the presence of an isomer mixture but also the percentage of each isomer present in the sample. Having established the isomer purity of samples of αβR-, αβS- and αα-$[Co(tetren)X]^{2+}$ by kinetic studies, spectral characterisations were made by analysing i.r., electronic and ^{13}C NMR data.

I.r. data

The αβR-, αβs- and αα-isomers of $[Co(tetren)X]^{2+}$ show distinct differences in their i.r. spectra which are illustrated in Figures 1.2, 1.3 and 1.4 for $[Co(tetren)Cl]^{2+}$. Previous work[39] has shown that metal amine complexes have four main absorption regions: (a) NH stretching ca. 3300 cm^{-1}; (b) NH_2 asymmetric deformations ca. 1600 cm^{-1}; (c) NH_2 symmetric deformations ca. 1300 cm^{-1}; (d) NH_3 rocking ca. 800 cm^{-1}.

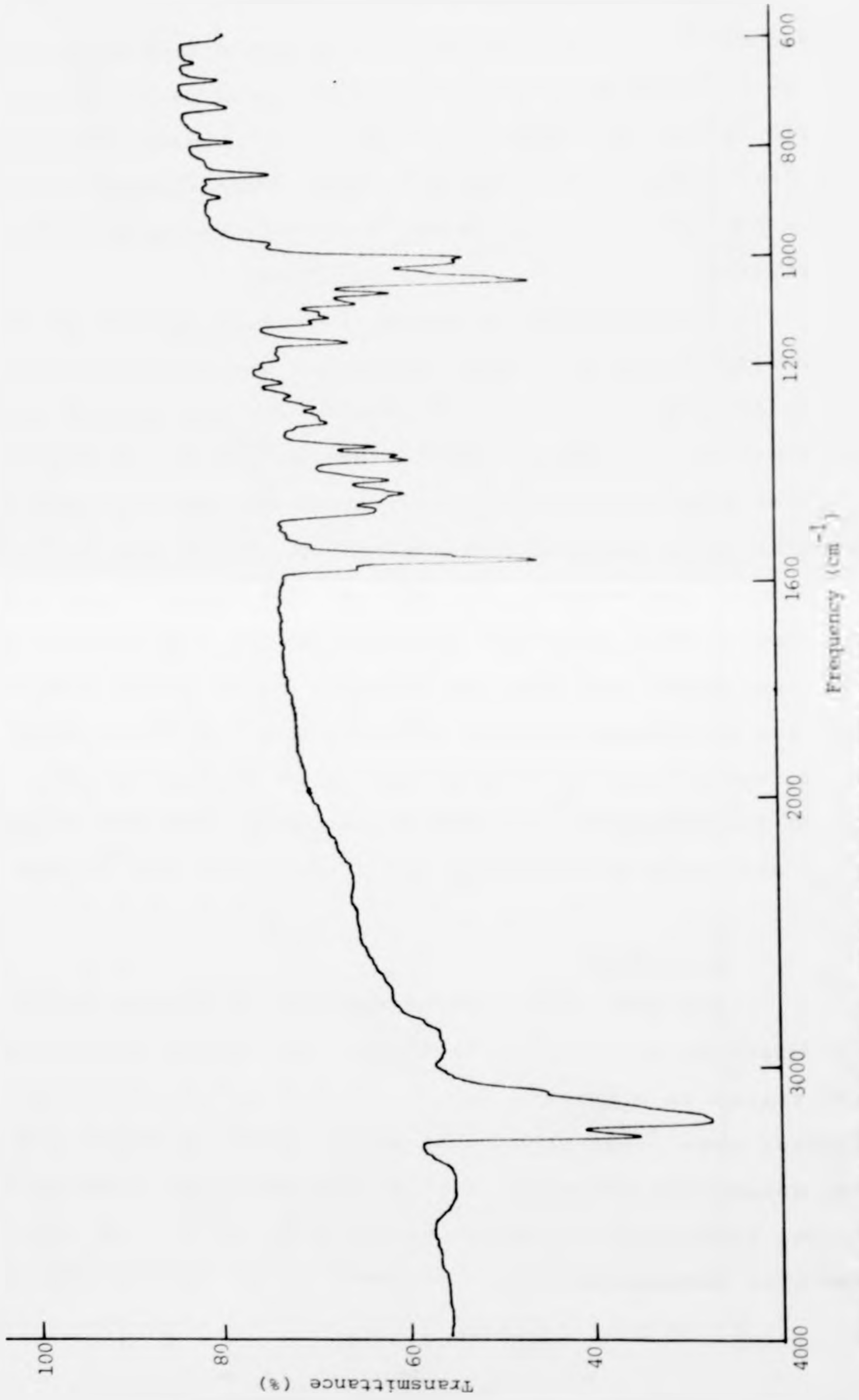


Figure 1.3: Infra-red spectrum (KBr) of αβs-[Co(tetren)Cl]ZnCl$_4$

For the NH$_2$ asymmetric deformation ca. 1600 cm^{-1} three points emerge: (1) If all NH$_2$ groups in the molecule have identical environments there will be only one absorption peak; (2) If there are two non-equivalent NH$_2$ groups there will be two absorption bands; (3) If the nitrogen atom of the NH$_2$ group under examination is able to adopt a strain free tetrahedral geometry then the absorption peak will occur at a lower frequency than if the nitrogen atom is forced into a distorted tetrahedral geometry. Considering the i.r. data for [Co(tetren)-Cl]$^{2+}$ in Table 1.1 it is seen that the αβR- isomer has a single NH$_2$ absorption peak at 1565 cm^{-1} consistent with a structure having two equivalent NH$_2$ groups in strain-free tetrahedral environments. The αβs-isomer has two NH$_2$ bands at 1570 cm^{-1} and 1585 cm^{-1} consistent with the molecule having one NH$_2$ group in a pure tetrahedral geometry and the other in a distorted, strained environment. The αα-isomer has one NH$_2$ absorption band at 1600 cm^{-1} in keeping with the molecule having both NH$_2$ groups in equivalently strained environments. The same arguments hold for αβR-, αβs- and αα-isomers of [Co(tetren)X]$^{2+}$, (X = Br$^-$, NO$_2^-$).

Electronic spectra

The i.r. data were determined for solid samples (KBr discs), visible electronic spectra were determined using aqueous solutions. Before interpreting the electronic spectra it was necessary to establish whether the isomer geometry of the solid samples is maintained in the aqueous medium used to measure the extinction coefficients. To this end αβR-[Co(tetren)Cl]CoCl$_4$ was dissolved in 0.1 mol dm^{-3} HCl and allowed to evaporate to

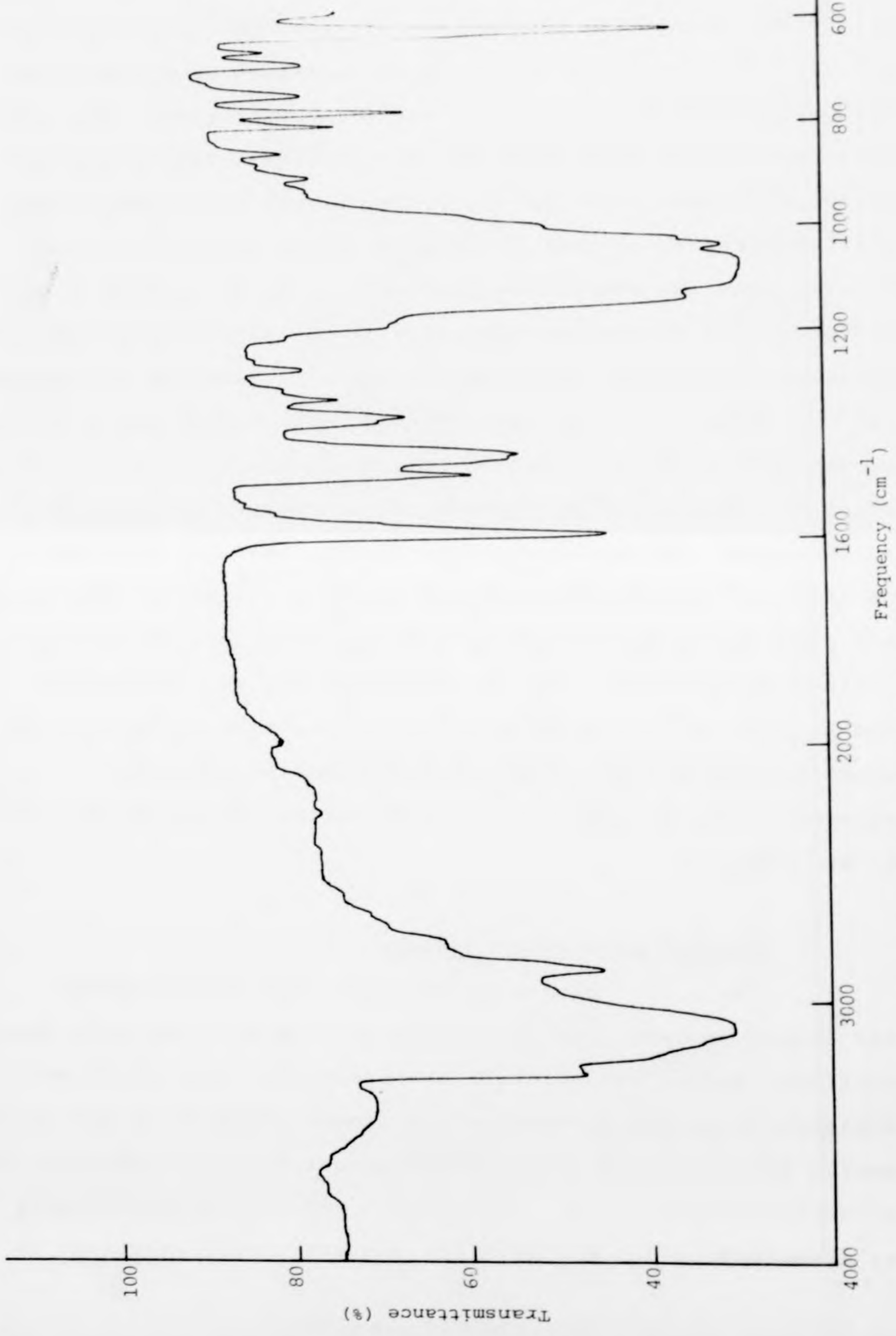


Figure 1.4: Infra-red spectrum (KBr) of αα-[Co(tetren)Cl](ClO$_4$)Cl.

TABLE 1.1

I.r. absorption bands* (cm^{-1}) for complexes of the type [Co(tetren)X]$^{2+}$ (X = Cl,Br,NO$_2$)

Complex	ν NH	
αβR-[Co(tetren)Cl]ZnCl$_4$	1575 (s)	
αβR-[Co(tetren)Cl]CoCl$_4$	1569 (s)	
αβS-[Co(tetren)Cl]ZnCl$_4$	1585 (m)	1570 (s)
αα-[Co(tetren)Cl](ClO$_4$)(Cl)	1600 (s)	
αβR-[Co(tetren)Br]ZnBr$_4$	1565 (s)	
αβS-(Co(tetren)Br]ZnBr$_4$	1580 (m)	1563 (s)
αα-[Co(tetren)Br](ClO$_4$)Br	1600 (s)	
αβS-[Co(tetren)NO$_2$]ZnCl$_4$	1590 (m)	1570 (s)
αα-[Co(tetren)NO$_2$](ClO$_4$)$_2$	1590 (s)	

* Spectra recorded as KBr discs

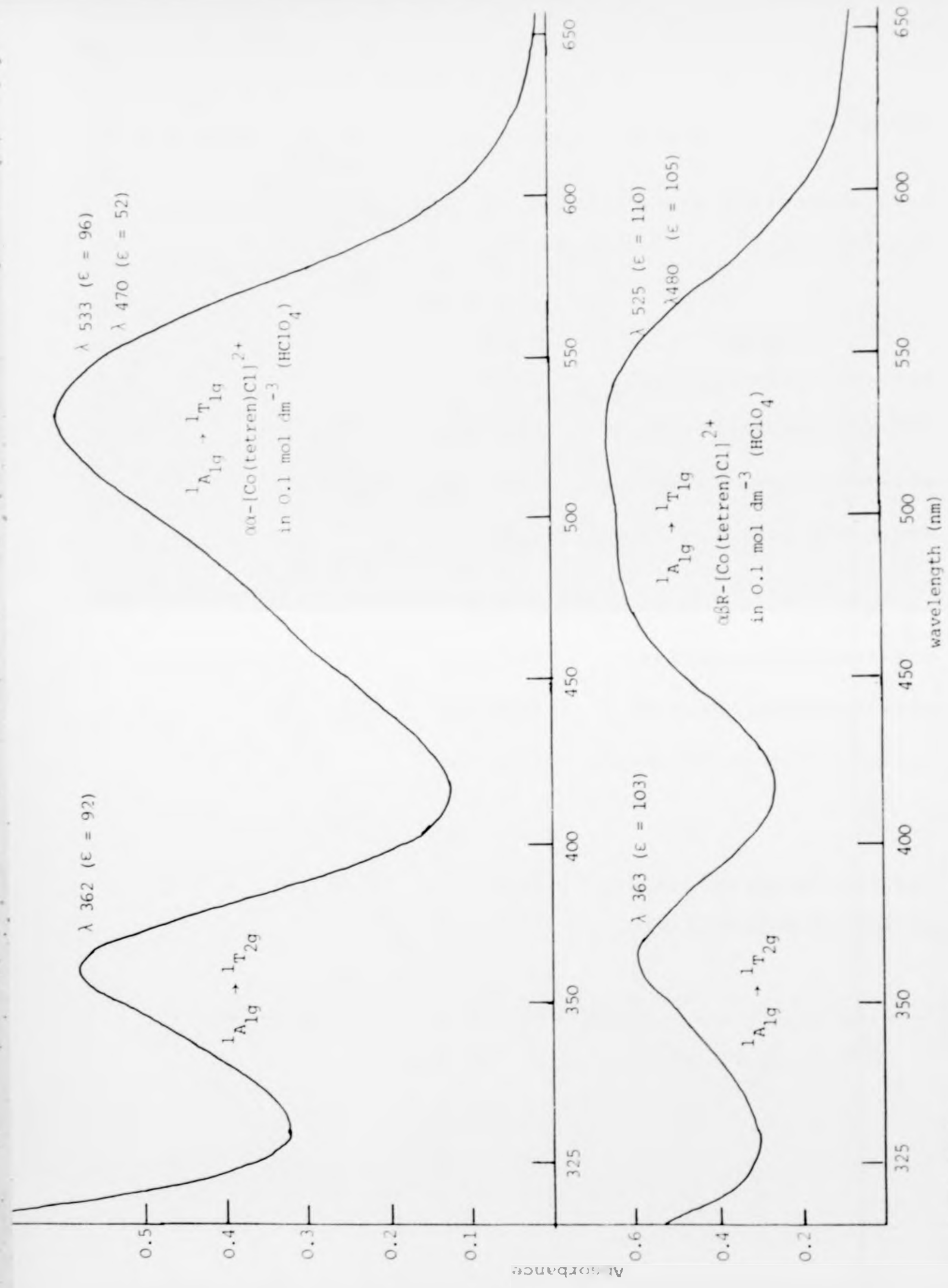
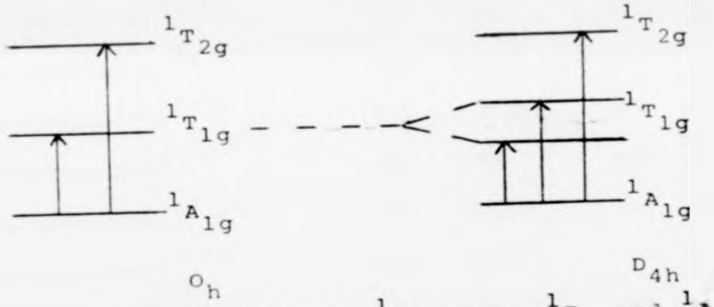


Figure 1.5

dryness at room temperature. An i.r. spectrum of the residue showed full retention of αβR-isomer geometry. Furthermore, an electronic spectrum of αβR-[Co(tetren)Cl]$^{2+}$ in 0.1 mol dm^{-3} HClO$_4$ remains unchanged after 24 hours. The same was true of the αβS- and αα-isomers of [Co(tetren)Cl]$^{2+}$. It therefore seems justifiable to conclude that solution electronic spectra reflect the isomer geometries of the solid samples.

The electronic spectra of αβR-, αβS- and αα-[Co(tetren)Cl]$^{2+}$ show two d-d bands due to transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^2T_{1g}$ as expected for octahedral low spin d^6 cobalt (III) complexes



The splitting of $^1T_{1g}$ into ^1E_g and $^1A_{2g}$ components due to the distorted octahedral field is manifested in the unsymmetrical appearance of the d-d band, Figure 1.5. The splitting is present to a lesser extent for the αα-isomer than for αβR- and αβS-isomers due to the greater symmetry of the αα ligand field. The greater symmetry of the αα-isomer is further illustrated by comparing extinction coefficients, with $\varepsilon_{\alpha\alpha} < \varepsilon_{\alpha\beta R} \approx \varepsilon_{\alpha\beta S}$ see Table 1.2. The same arguments hold for the bromo complexes [Co(tetren)Br]$^{2+}$ although in this case the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is obscured by a large charge transfer band. The LOWER ligand field symmetry of tetren versus (NH$_3$)$_5$ is illustrated by comparing extinction coefficients for a series of complexes $[Co(tetren)X]^{2+}$ and $[Co(NH_3)_5X]^{2+}$ $\varepsilon_{(NH_3)_5} \rightarrow \varepsilon_{Tetren}$ Table 1.2.

TABLE 1.2

Visible absorption spectra of $[CoN_5X]^{2+}$ (X = Cl, Br, NO_2)

Numbers in parentheses are the extinction coefficients in M^{-1} cm^{-1}

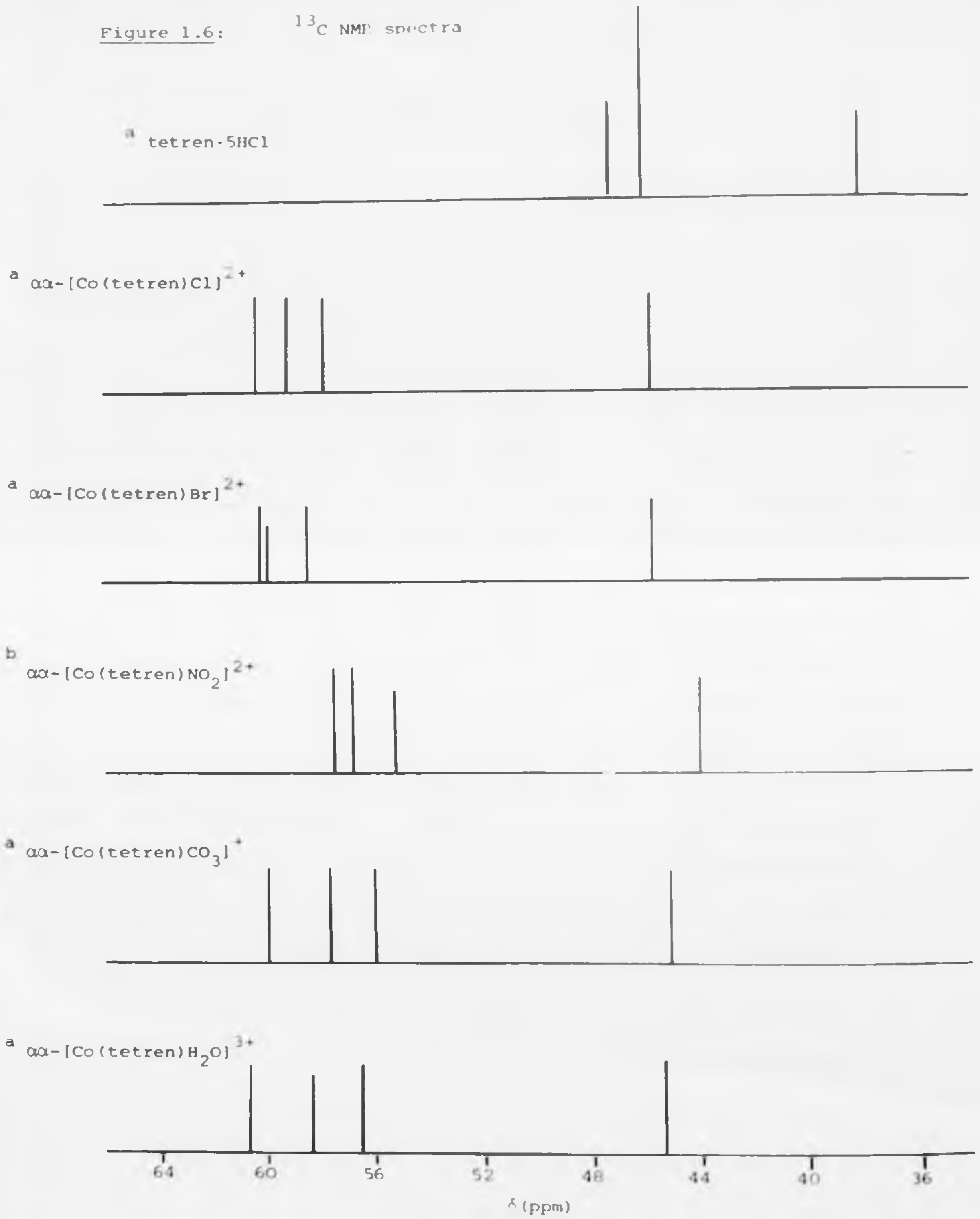
Complex	λ_{max} /nm	ε	λ_{max} /nm	ε	λ_{max} /nm	ε
αβR-$[Co(tetren)Cl]^{2+}$ ^{a}	525	(110)^{c}	480	(105)^{c}	363	(103)^{c}
αβs-$[Co(tetren)Cl]^{2+}$ ^{a}	525	(102)	480	(103)	360	(107)
αα-$[Co(tetren)Cl]^{2+}$ ^{a}	533	(96)	470	(52)	362	(92)
αβR-$[Co(tetren)Br]^{2+}$ ^{a}	548	(122)	480	(93)		
αβs-$[Co(tetren)Br]^{2+}$ ^{a}	550	(113)	480	(92)		
αα-$[Co(tetren)Br]^{2+}$ ^{a}	552	(98)	480	(43)		
αβs-$[Co(tetren)NO_2]^{2+}$ ^{a}	456	(212)	328	(1844)		
αα-$[Co(tetren)NO_2]^{2+}$ ^{a}	450	(154)				
$[Co(NH_3)_5Cl]^{2+}$ ^{b}	532	(50.1)	467	(11)	364	(46.8)
$[Co(NH_3)_5Br]^{2+}$ ^{b}	552	(57.6)	470	(11.5)	310	(83.1)
$[Co(NH_3)_5NO_2]^{2+}$	458	(100)	325	(1660)		

a. determined in present work in 0.1 mol dm^{-3} $HClO_4$

b. taken from reference 16 (recorded in water).

c. values in parentheses are extinction coefficients (dm^3 mol^{-1} cm^{-1})

Figure 1.6: ^{13}C NMR spectra

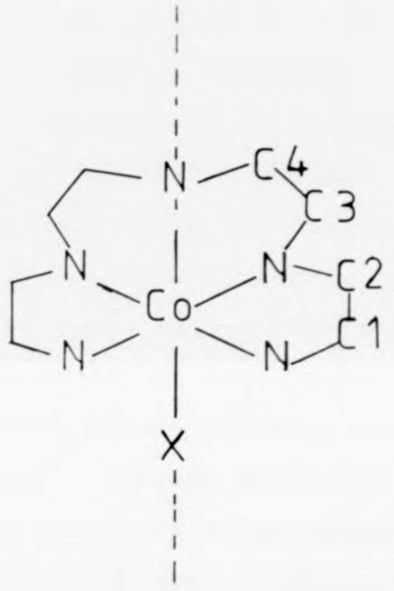


a spectrum measured in D_2O; b spectrum measured in Me_2SO-D_6

^{13}C NMR data

In the past ^{13}C n.m.r has facilitated the assignment of isomer stereochemistry in cobalt (111) tetraamine complexes[40,72] and in the present work it has been used to distinguish between αβ and αα-isomers in the Co(111)-tetren system. Spectra were collected by Fourier Transform (FT) ^{13}Cn.m.r. using a broad band technique which eliminates all C-H couplings, thus the number of resonances depends on the number of carbon atoms and the symmetry of the complex. The peak intensity in FT n.m.r. depends on the Nuclear Overhauser Effect and relaxation time in addition to the number of carbon atoms which the peak represents, however, in these complexes the carbon atoms are sufficiently similar that intensity comparisons can be made. The assignment of a resonance signal to a specific carbon atom is made by considering the electronic shielding around the carbon nucleus. Carbon atoms are deshielded by proximity to nitrogen atoms in the chelate with deshielding increasing in the order primary NH_2, secondary NH. Steric compression (that is compressed bond distances and unusually large bond angles) increase shielding around the carbon atoms.

Considering αα-[Co(tetren)X]$^{2+}$ (4) with its plane of symmetry, four non-equivalent carbon atoms are present and indeed the spectra display four signals of approximately equal intensity, Figure 1.6 and Table 1.3. The carbon atom labelled C_1 in (4) attached directly to the NH_2 group of the chelate is expected to have the greatest shielding and will occur at the highest field. The carbon atoms labelled C_2, C_3 and C_4 will resonate further downfield of C_1.



(4)

It is known that complexation of a ligand to a Co(111) ion deshields the carbon atom of the chelate by electron donation to the central metal ion. In the case of αα-[Co(tetren)X]$^{2+}$ this is illustrated by comparing the ^{13}C n.m.r. of free tetren with that of αα-[Co(tetren)X]$^{2+}$, Figure 1.6 and Table 1.3. The carbon atom signals of the chelate appear at higher chemical shift (smaller shielding) than the carbon atoms of the free ligand.

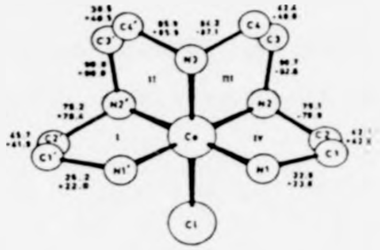
TABLE 1.3

^{13}C NMR data for tetren.5HCl and αα-[Co(tetren)X]$^{2+}$ (X = Cl, Br, NO_2) in D_2O and Me_2SO-D_6 δ values; ppm with respect to Na TMS as 0.00. Relative intensities in parentheses.

Compound	δ	δ	δ	δ
tetren.5HCl[a]	37.96(157.7)	45.97(397.3)	47.25(183.4)	
αα-[Co(tetren)Cl]-(ClO_4)Cl [a]	45.74(1.89)	57.91(1.98)	59.27(1.94)	60.42(1.43)
αα-[Co(tetren)Br]-(ClO_4)Br [a]	45.74(34.2)	58.50(32.1)	59.97(23.5)	60.19(31.5)
αα-[Co(tetren)NO_2]-$(ClO_4)_2$ [b]	43.99(103.5)	55.18(87.0)	56.81(111.4)	57.47(111.6)
αα-[Co(tetren)Br]-(ClO_4)Br [b]	43.93(123)	56.76(103)	57.58(96)	58.23(96)
αα-[Co(tetren)Cl]-(ClO_4)Cl [b]	43.83(102.8)	56.27(137.5)	57.36(108.9)	57.96(86.5)
αα-[Co(tetren)CO_3]-(ClO_4) [a]	45.13(39.8)	55.89(36.0)	57.74(38.9)	59.87(38.7)
αα-[Co(tetren)H_2O]-$(ClO_4)_3$ [a]	45.68(38.0)	56.70(36.4)	58.40(32.1)	60.70(36.9)

a. spectra measured in D_2O

b. spectra measured in Me_2SO-D_6



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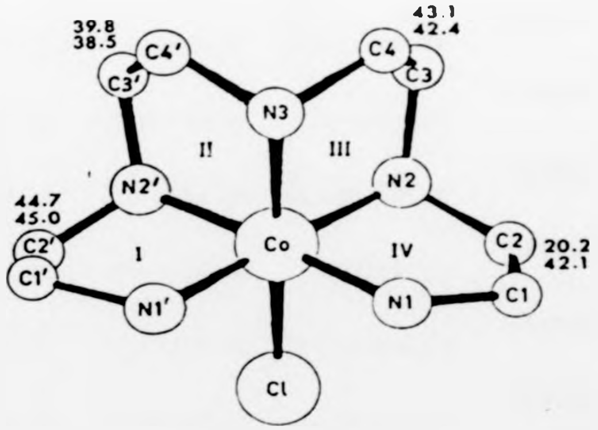
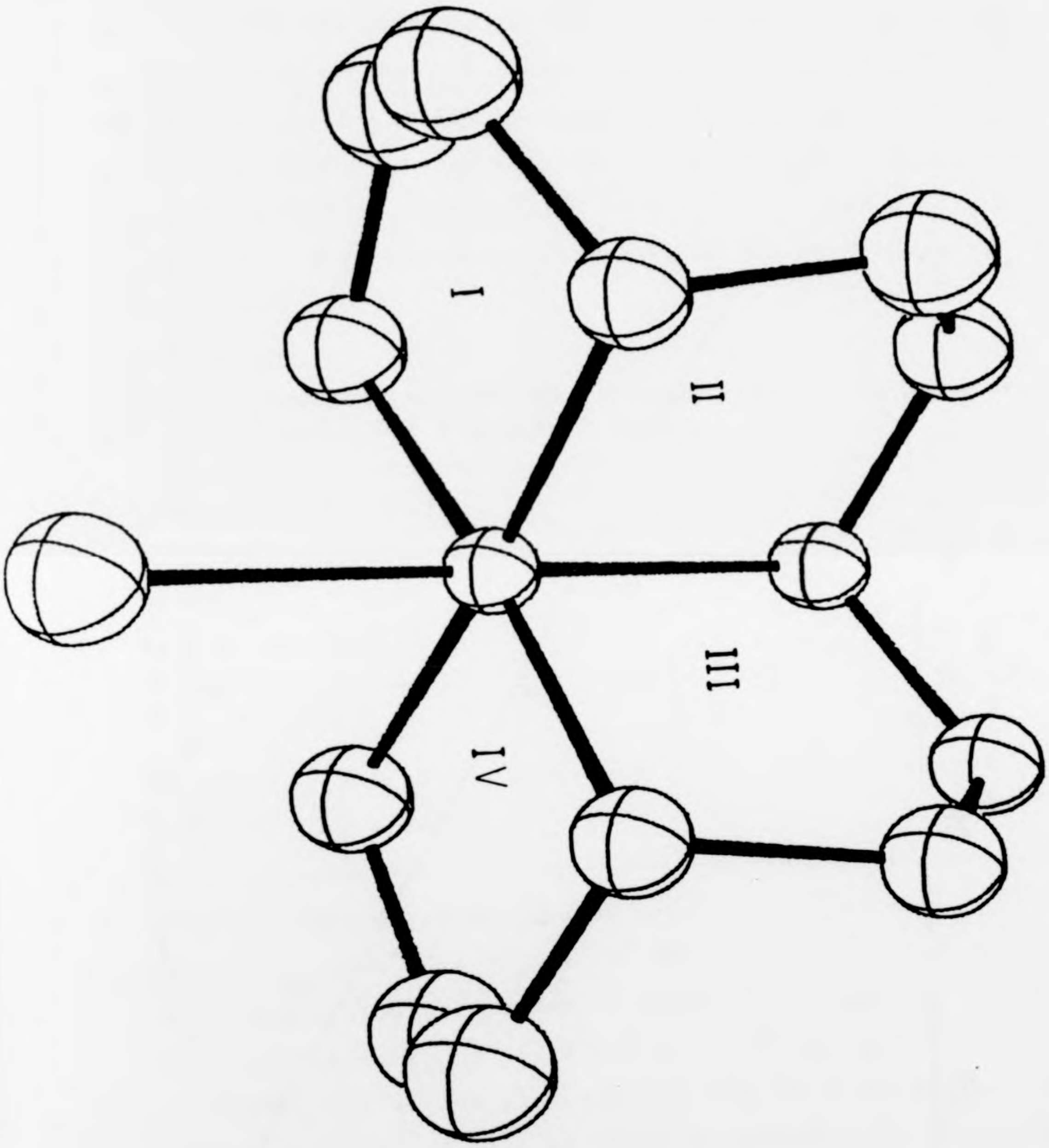


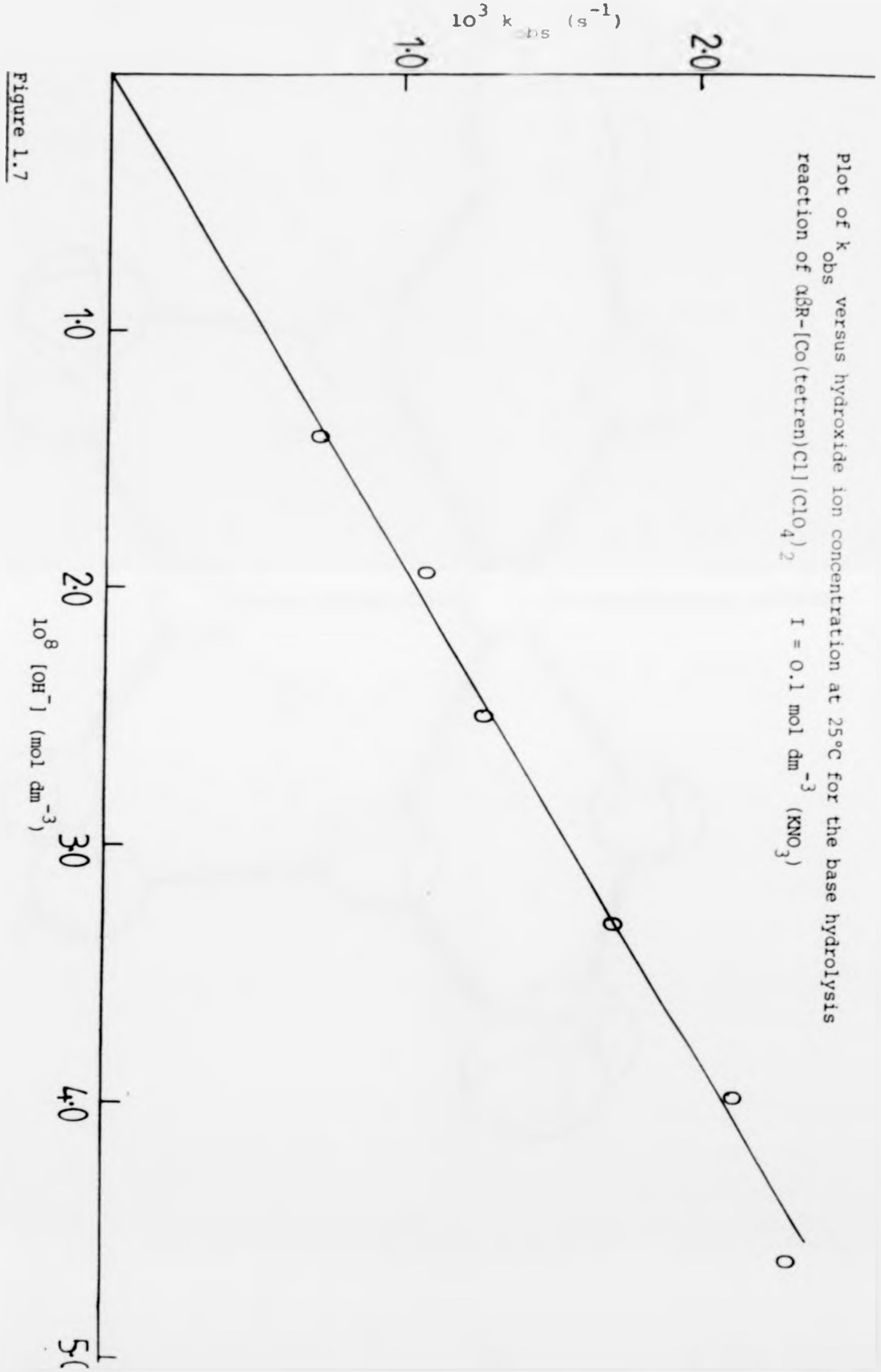
(6)

X-ray crystallographic data

When αα-[Co(tetren)Cl](ClO$_4$)Cl was first prepared in this laboratory its configuration was unknown. Infra-red and visible spectra indicated a more symmetrical configuration than αβR- or αβs- as confirmed by ^{13}C NMR which showed the presence of only four non-equivalent carbon atoms. However, these data could not distinguish between αα- and ββ-configurations (2)A and (2)C and an X-ray crystallographic structural determination was required to confirm the isomer stereochemistry as αα-.

It is interesting to compare the structure of αα-[Co(tetren)Cl](ClO$_4$)Cl determined by Snow[22] and the structure found for αα-[Co(tetren)Cl](ClO$_4$)Cl in the present work as differences do exist. Both crystals are monoclinic but Snow's αα- sample has cell constants a = 12.31Å, b = 11.20Å, c = 12.67Å and β = 119.3°; ν = 1637.8Å^3. The crystal examined in the present work has cell constants a = 9.85Å, b = 13.80Å, c = 13.91Å and β = 111.9°; ν = 1620Å^3. A theoretical gas phase structure calculated for the αα-isomer structure (5) shows the complex to have mirror symmetry, however, the crystal examined by Snow was found to have the mirror symmetry destroyed by an envelope conformation of the chelate ring (IV), see (6). This distortion is assigned to packing forces. An X-ray analysis of a crystal of αα-[Co(tetren)Cl](ClO$_4$)Cl prepared in the present work has the structure shown in (7), closer to the calculated gas phase structure with the chelate ring (IV), having a gauche conformation.


I
II
III
IV



Plot of k_{obs} versus hydroxide ion concentration at 25°C for the base hydrolysis reaction of $\alpha\beta R$-$[Co(tetren)Cl](ClO_4)_2$ $I = 0.1\ mol\ dm^{-3}\ (KNO_3)$

Figure 1.7

Kinetic data

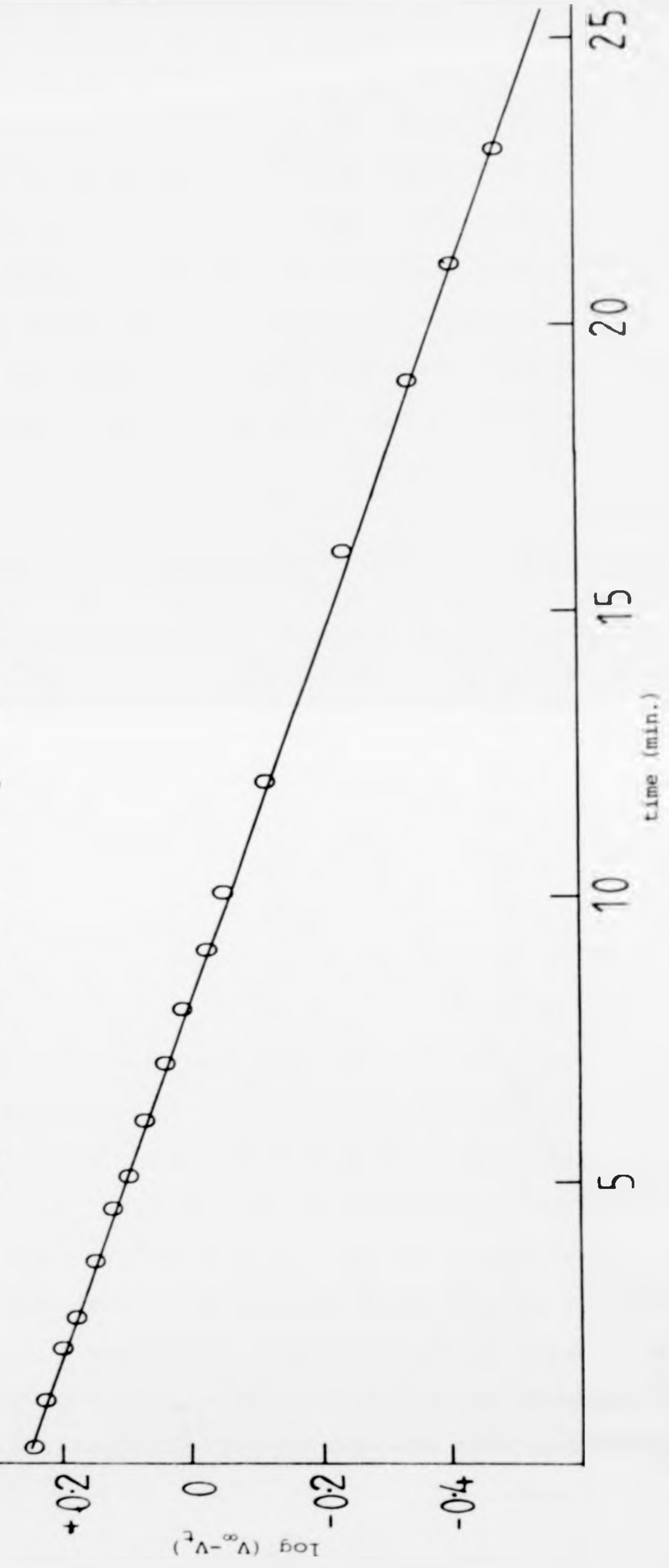
The base hydrolysis kinetic results are presented and discussed for αβR-, αβS- and αα-$[Co(tetren)X]^{2+}$ ($X = Cl^-, Br^-$) and for αβS- and αα-$[Co(tetren)NO_2]^{2+}$. The mercury (II) assisted aquation kinetics were studied for αβR- and αα-$[Co(tetren)X]^{2+}$ ($X = Cl^-, Br^-$) and the acid catalysed decarboxylation kinetics of αα-$[Co(tetren)CO_3](ClO_4)$ analysed.

TABLE 1.4

Base hydrolysis of αβR-$[Co(tetren)Cl](ClO_4)_2$ by pH stat at 25°C and $I = 0.1\ mol\ dm^{-3}\ (KNO_3)$

pH	$10^8[OH^-]$ ($mol\ dm^{-3}$)	$10^3\ k_{obs}$ (s^{-1})	$10^{-4}\ k_{obs}/[OH^-]$ ($dm^3\ mol^{-1}\ s^{-1}$)
6.03	1.40	0.72	5.14
6.17	1.93	1.10	5.70
6.28	2.48	1.30	5.24
6.40	3.28	1.74	5.30
6.48	3.94	2.16	5.48
6.54_5	4.58	2.34	5.10

The mean value for the second order rate constant $k_{OH} = k_{obs}/[OH^-]$ is $5.33 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$. The plot of k_{obs} versus $[OH^-]$ is shown in Figure 1.7. Linear regression analysis gives $k_{OH} = (5.15 \pm 0.2) \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$. Plots of $\log(V_\infty - V_t)$ versus time plotted over four half lives are linear and a typical plot is shown in Figure 1.8. Close agreement is found between experimental and theoretical base consumption data indicating that the sample of αβR-$[Co(tetren)Cl](ClO_4)_2$ is isomerically pure.



Kinetic plot for the base hydrolysis reaction of αβR-[Co(tetren)Cl]$(ClO_4)_2$
at 25°C   I = 0.1 mol dm^{-3} (KNO_3)   pH = 6.22

Figure 1.8

TABLE 1.5

Base hydrolysis of αβS-[Co(tetren)Cl]$ZnCl_4$ at 25°C and I = 0.1 mol dm^{-3} ($NaClO_4$)[a]

pH	10^{10}[OH^-] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^{-5} k_{obs}/[OH^-] (dm^3 mol^{-1} s^{-1})
4.51	4.22	0.30	7.10
4.69	6.39	0.48	7.51
4.98	12.47	0.91	7.29
5.15	18.44	1.31	7.10
5.50	41.29	2.91	7.04

[a] Fresh succinate buffers were used and the reaction was monitored at 280 nm.

The mean value for the second order rate constant for base hydrolysis k_{OH} = 7.20 x 10^5 dm^3 mol^{-1} s^{-1}. Linear regression analysis gives k_{OH} = (6.99 ± 0.05) x 10^5 dm^3 mol^{-1} s^{-1}.

A sample of [Co(tetren)Cl]$(ClO_4)_2$ containing both αβR- and αβS-isomers was base hydrolysed by the pH stat method at pH 5.8. A plot of log($V_\infty - V_t$) versus time is curved as shown in Figure 1.9. The initial part of the curve corresponds to base hydrolysis of αβS-[Co(tetren)Cl]$(ClO_4)_2$ while the latter part represents base hydrolysis of αβR-[Co(tetren)Cl]$(ClO_4)_2$. The plot was resolved by extrapolation to give separate second order rate constants for base hydrolysis of the two isomers. These constants are in good agreement with the values determined independently for the pure isomers which are summarised in Tables 1.4 and 1.5.

Kinetic plot for the base hydrolysis reaction of a mixture of αβR-[Co(tetren)Cl]$(ClO_4)_2$ and αβs-[Co(tetren)Cl]$(ClO_4)_2$ at 25°C I = 0.1 mol dm^{-3} (KNO_3) pH = 5.90

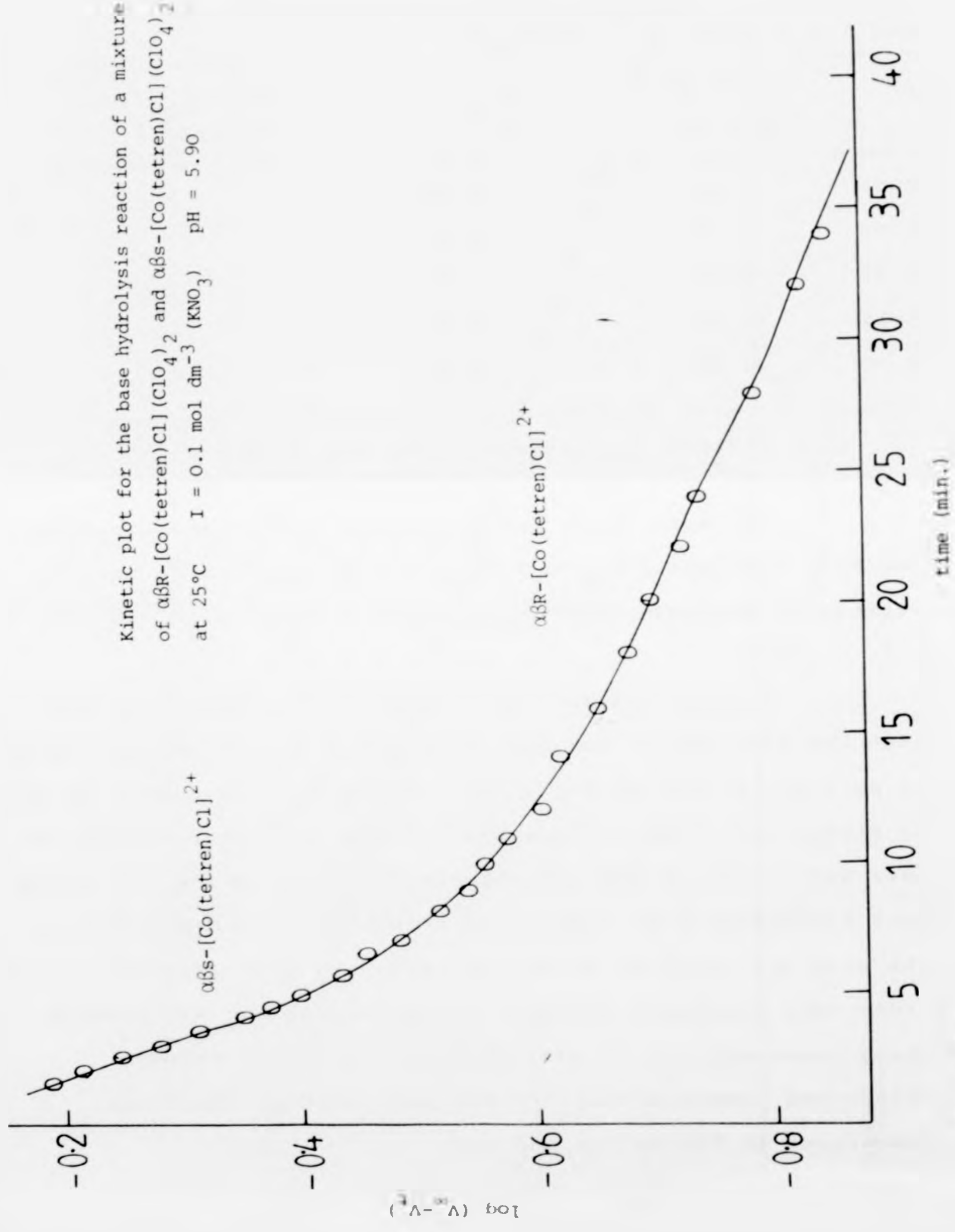


Figure 1.9

TABLE 1.6

Base hydrolysis of αα-[Co(tetren)Cl](ClO_4)Cl monitored by pH stat at 25°C and I = 0.1 mol dm^{-3} (KNO_3)

pH	10^6 [OH$^-$] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^{-2} k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
8.63	5.57	6.60	1.18
8.74	7.17	8.22	1.14
8.95	11.63	13.83	1.19
9.17	19.31	22.41	1.16

The mean values for the overall second order rate constant k_{OH} is 1.16 x 10^2 dm^3 mol^{-1} s^{-1}. A linear regression gives k_{OH} = (1.5 ± 0.02) x 10^2 dm^3 mol^{-1} s^{-1}. The results were calculated using the 16 point first order programme after measuring an infinity volume at ten half-lives. Graphs of log$(V_\infty - V_t)$ versus time gave linear plots over four half-lives. Close agreement was found between the experimental and theoretical base consumption indicating an isomerically pure sample of αα-[Co(tetren)Cl](ClO_4)Cl. Base hydrolysis of αα-[Co(tetren)Cl]-(ClO_4)Cl was also studied spectrophotometrically. The rapid reaction of [Co(tetren)OH]$^{2+}$ with CO_2 precludes the use of the 16 point first order kinetics programme as an "infinity" absorbance value is required. In this case k_{obs} was calculated from measurements over three half-lives using the Swinbourne method. The absorbance changes which take place during base hydrolysis of αα-[Co(tetren)Cl](ClO_4)Cl are shown by an interval scan spectrum (Figure 1.10). An isosbestic point is seen at 529 nm.

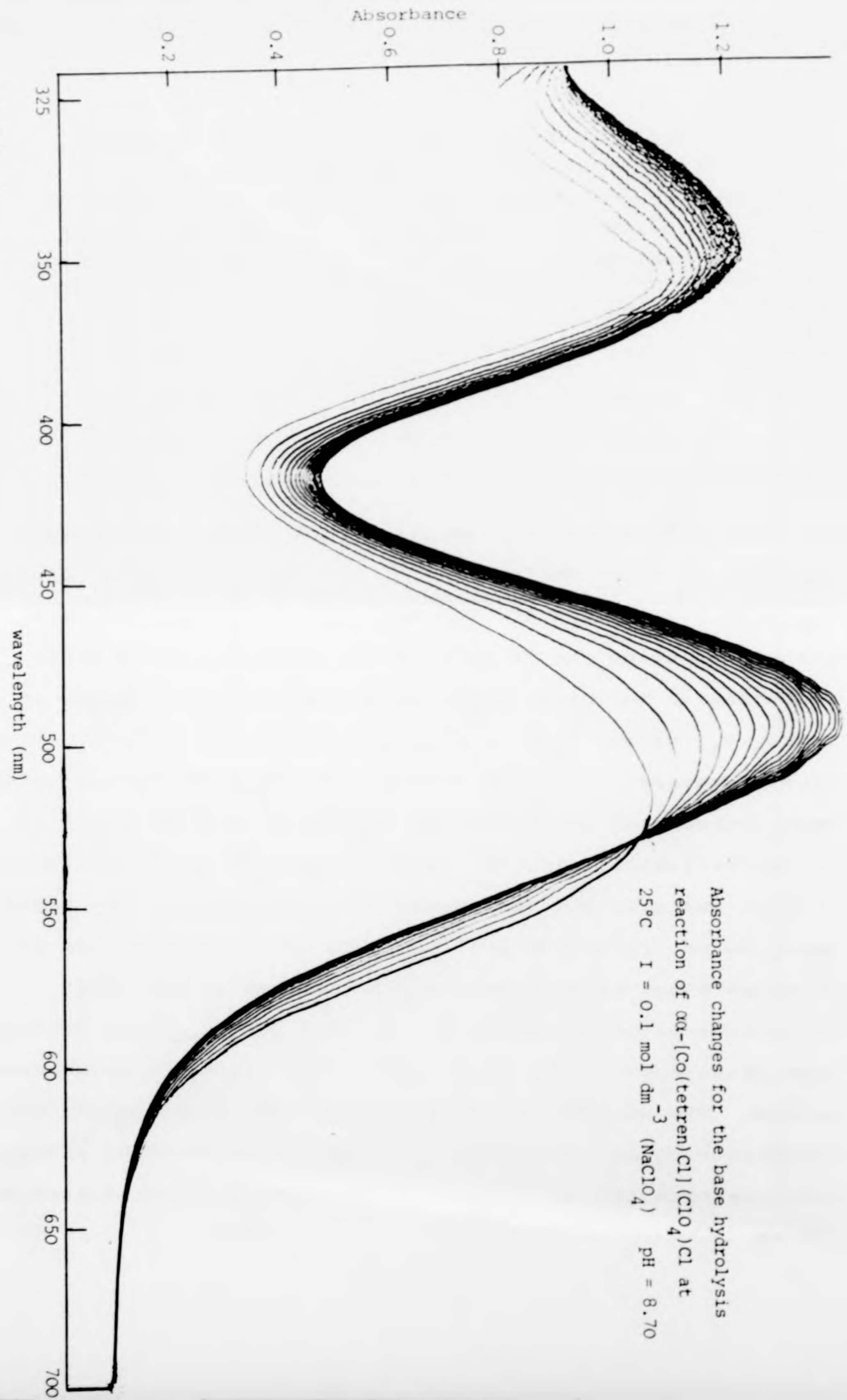


Figure 1.10

Absorbance changes for the base hydrolysis reaction of αα-[Co(tetren)Cl](ClO$_4$)Cl at 25°C I = 0.1 mol dm^{-3} (NaClO$_4$) pH = 8.70

TABLE 1.7

Base hydrolysis of αα-[Co(tetren)Cl](ClO$_4$)Cl at 25°C and I = 0.1 mol dm^{-3} (NaClO$_4$)^a

pH	10^6[OH$^-$] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^{-2} k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
8.30	2.60	0.32	1.23
8.46	3.76	0.51	1.35
8.73	7.01	0.85	1.21
8.92	10.86	1.38	1.27
9.02	13.67	1.63	1.19

a. Freshly prepared trishydroxymethylaminomethane buffers were used and the reaction was monitored at 280 nm.

The mean value of the second order rate constant is $k_{OH} = 1.25 \times 10^2$ dm^3 mol^{-1} s^{-1}. Linear regression analysis gives $k_{OH} = (1.19 \pm 0.04) \times 10^2$ dm^3 mol^{-1} s^{-1}. This value is in reasonable agreement with that found by the pH stat method, see Table 1.6.

TABLE 1.8

Base hydrolysis of αβR-[Co(tetren)Br]ZnBr$_4$ at 25°C and I = 0.1 mol dm^{-3} (NaClO$_4$)^a

pH	10^{10}[OH$^-$] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^{-5} k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
4.70	6.54	0.45	6.88
4.89	10.13	0.69	6.81
5.16	18.87	1.38	7.31
5.31	26.66	1.84	6.91

a. Freshly prepared succinate buffers were used and the reaction was monitored at 330 nm.

The mean value for $k_{OH} = 6.97 \times 10^5$ dm^3 mol^{-1} s^{-1}. Linear regression analysis gives $k_{OH} = (7.03 \pm 0.3) \times 10^5$ dm^3 mol^{-1} s^{-1}. Plots of log(A_∞-A_t) versus time showed some initial curvature due to contamination of the sample with a small amount of αβs-[Co(tetren)Br]$^{2+}$. The rate constants shown in Table 1.8 were thus calculated by the Swinbourne method discarding the first few data points.

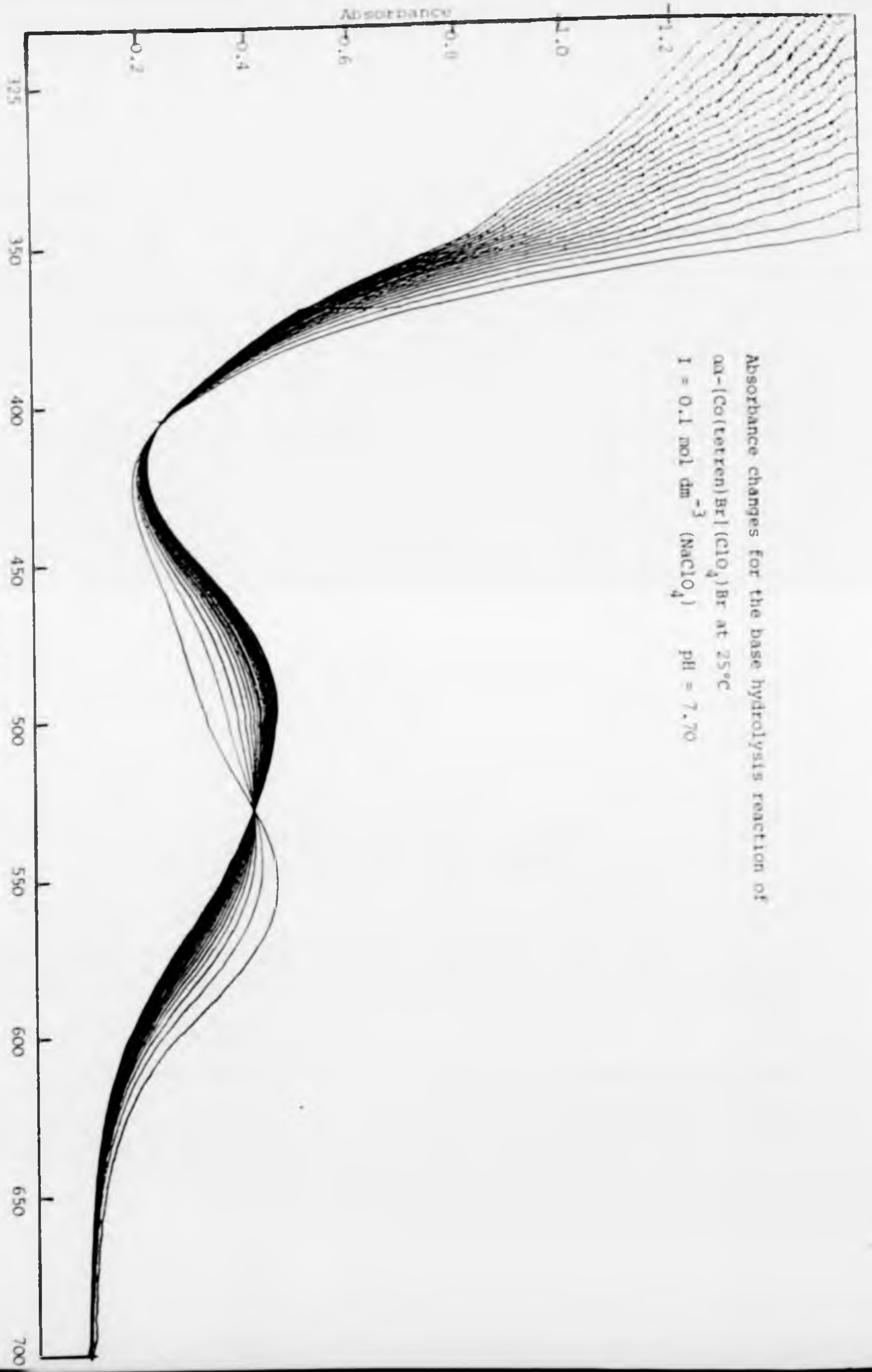
TABLE 1.9

Base hydrolysis of αβs-[Co(tetren)Br]ZnBr$_4$ at 25°C and I = 0.1 mol dm^{-3} (NaClO$_4$)^a

pH	10^{10}[OH$^-$] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^{-6} k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
4.50	4.13	1.27	3.07
4.69	6.39	1.75	2.74
4.89$_5$	10.25	3.04	2.96
5.11	16.82	5.14	3.05
5.30	26.02	7.26	2.78

a. Freshly prepared succinate buffers were used and the reaction was monitored at 330 nm.

The mean value for $k_{OH} = 2.92 \times 10^6$ dm^3 mol^{-1} s^{-1}. Linear regression analysis gives $k_{OH} = (2.80 \pm 0.1) \times 10^6$ dm^3 mol^{-1} s^{-1}. Plots of log(A_∞-A_t) versus time over four half-lives were linear with no indication of any contamination by αβR-[Co(tetren)Br]$^{2+}$.



Absorbance changes for the base hydrolysis reaction of αα-[Co(tetren)Br](ClO$_4$)Br at 25°C
I = 0.1 mol dm^{-3} (NaClO$_4$)   pH = 7.70

Figure 1.11

TABLE 1.10

Base hydrolysis of αα-[Co(tetren)Br](ClO$_4$)Br monitored by pH stat at 25°C and I = 0.1 mol dm^{-3} (KNO$_3$)

pH	10^7[OH$^-$] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^{-3} k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
7.40	3.28	0.47	1.43
7.50	4.13	0.57	1.38
7.69	6.39	0.96	1.50
7.88	9.90	1.54	1.54
8.03	13.99	1.89	1.35

The mean value for the second order rate constant k_{OH} = 1.44 x 10^3 dm^3 mol^{-1} s^{-1}. By linear regression analysis k_{OH} = (1.37 ± 0.1) x 10^3 dm^3 mol^{-1} s^{-1}. Plots of log($V_\infty - V_t$) versus time give straight lives over four half-lives. Close agreement between experimental and theoretical base consumption is further evidence that the sample is isomerically pure αα-[Co(tetren)Br]$^{2+}$. Base hydrolysis of αα-[Co(tetren)Br](ClO$_4$)Br was also studied spectrophotometrically using freshly prepared buffers. An interval scan spectrum showing the absorbance changes accompanying base hydrolysis of αα-[Co-(tetren)Br](ClO$_4$)Br is given in Figure 1.11. Two isosbestic points are observed in 404 nm and 527 nm. Due to the rapid reaction of [Co(tetren)OH]$^{2+}$ with carbon dioxide the Swinbourne method was used to calculate the pseudo first order rate constant (k_{obs}).

TABLE 1.11

Base hydrolysis of αα-[Co(tetren)Br](ClO$_4$)Br [a] at 25°C and I = 0.1 mol dm^{-3} (NaClO$_4$)

pH	10^7[OH$^-$] (mol dm^{-3})	10^3 k$_{obs}$ (s^{-1})	10^{-3} k$_{obs}$/[OH$^-$] (dm^3 mol^{-1} s^{-1})
7.70	6.54	1.12	1.71
7.90	10.37	1.97	1.89
8.14	18.02	3.12	1.73
8.22	21.67	3.58	1.65
8.33	27.91	4.59	1.64

a. Freshly prepared trishydroxymethylaminomethane buffers were used and the reaction was monitored at 280 nm.

The mean value for k$_{OH}$ = 1.69 x 10^3 dm^3 mol^{-1} s^{-1}. Linear regression analysis gives k$_{OH}$ = (1.57 ± 0.06) x 10^3 dm^3 mol^{-1} s^{-1}. This value is in reasonable agreement with that found by the pH stat method, see Table 1.10.

TABLE 1.12

Base hydrolysis of αβs-[Co(tetren)NO$_2$](ClO$_4$)$_2$ [a] at 25°C and I = 0.1 mol dm^{-3} (NaClO$_4$)

pH	10^4[OH$^-$] (mol dm^{-3})	10^3 k$_{obs}$ (s^{-1})	k$_{obs}$/[OH$^-$] (dm^3 mol^{-1} s^{-1})
10.49	4.03	0.85	2.10
10.61	5.32	1.13	2.12
10.71	6.69	1.55	2.31
10.82	8.62	1.72	1.99
10.91	10.61	2.21	2.08
11.02	13.67	2.89	2.11

a. Freshly prepared butylamine buffers were used and the reaction was monitored at 345 nm.

Plot of k_{obs} versus hydroxide ion concentration at 25°C for the base hydrolysis reaction of αβs-$[Co(tetren)NO_2](ClO_4)_2$ I = 0.1 mol dm^{-3} ($NaClO_4$)

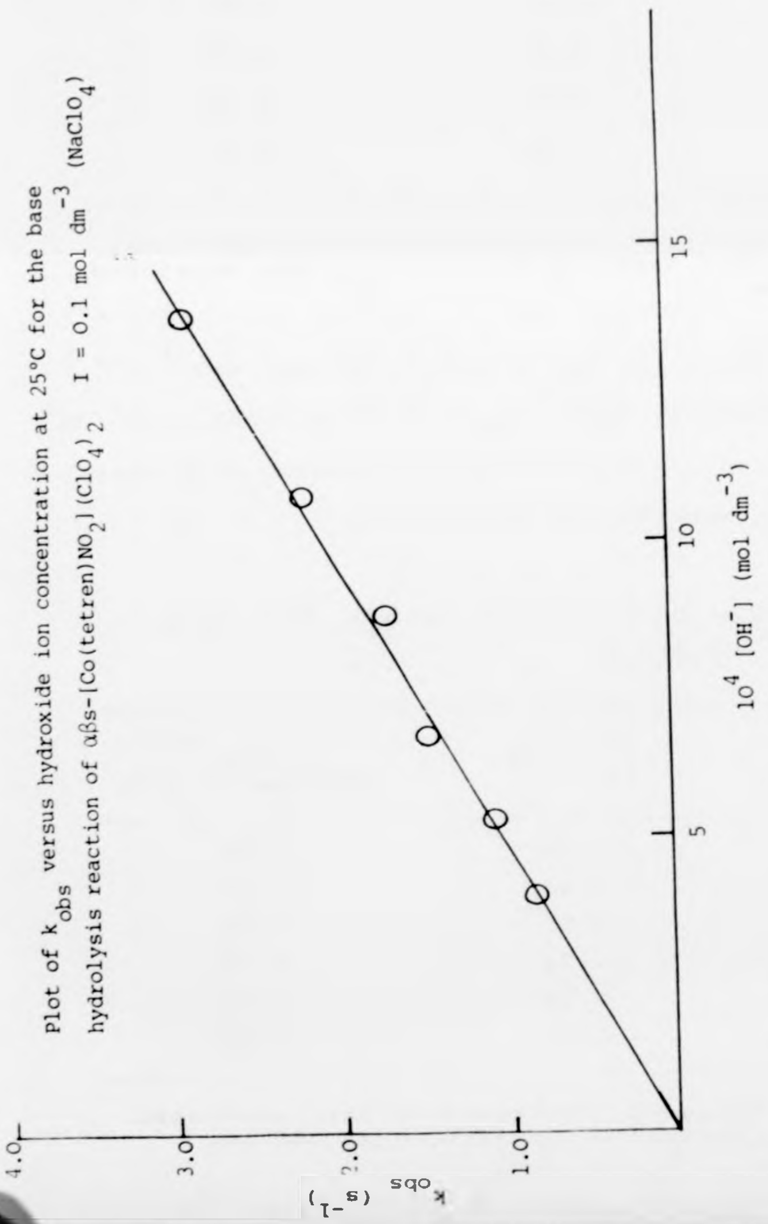


Figure 1.12A

The mean value for k_{OH} = 2.11 dm^3 mol^{-1} s^{-1}. A linear regression analysis gives k_{OH} = (2.09 ± 0.2) dm^3 mol^{-1} s^{-1}. A plot of k_{obs} versus $[OH^-]$ is shown in Figure 1.12A. Plots of $\log(A_\infty - A_t)$ versus time are linear confirming the isomeric purity of the sample.

TABLE 1.13

Base hydrolysis of αα-$[Co(tetren)NO_2](ClO_4)_2$ [a] at 25°C and I = 0.5 mol dm^{-3}

$[NaOH]$ (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^4 $k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
0.3	1.93	6.43
0.4	2.50	6.25
0.5	3.17	6.34

a. Sodium hydroxide solutions were used and the reaction was monitored at 330 nm.

The mean value for k_{OH} = 6.34 x 10^{-4} dm^3 mol^{-1} s^{-1}. Linear regression analysis gives k_{OH} = (6.20 ± 0.2) x 10^{-4} dm^3 mol^{-1} s^{-1}. Plots of $\log(A_\infty - A_t)$ versus time are linear, confirming the isomeric purity of the sample.

The activation parameters for the base hydrolysis reactions of αβR-, αα-$[Co(tetren)Cl]^{2+}$ and αβR-, αα-$[Co(tetren)Br]^{2+}$ were evaluated and are summarised in Table 1.14.

All samples of $[Co(tetren)X]^{2+}$ (X = Br,Cl,NO_2) display an overall second order rate equation for base hydrolysis, with a first order dependence of rate on the hydroxide ion concentration, giving a rate equation of the form:

$$-\frac{d[[Co(tetren)X]^{2+}]}{dt} = k_{OH}[[Co(tetren)X]^{2+}][OH^-]$$

The kinetic data are summarised in Table 1.15.

TABLE 1.14

Temperature dependence of rate constants for base hydrolysis of various [Co(tetren)X]$^{2+}$ (X = Cl, Br) in 0.1 mol dm^{-3} (KNO$_3$)

Complex	Θ°C	$k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}_{298}$ (JK^{-1} mol^{-1})
αβ**R**-[Co(tetren)Cl]$^{2+}$	25	5.33 x 10^4		
	35	1.69 x 10^5	+89.9±3.8	+147±12
	40	3.23 x 10^5	correlation coefficient = 0.999	
αα-[Co(tetren)Cl]$^{2+}$	25	1.25 x 10^2		
	35	3.60 x 10^2	+82.8±4.0	+73±13
	40	6.60 x 10^2	correlation coefficient = 0.998	
αβ**R**-[Co(tetren)Br]$^{2+}$	25	0.69 x 10^6		
	34	2.34 x 10^6	+94.8±3.9	+185±13
	42	5.71 x 10^6	correlation coefficient = 0.999	
αα-[Co(tetren)Br]$^{2+}$	25	1.36 x 10^3		
	35	3.61 x 10^3	+79.9±7.0	+83±23
	40	6.88 x 10^3	correlation coefficient = 0.996	

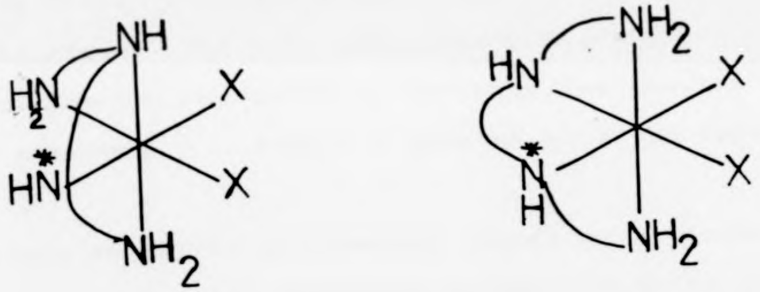
TABLE 1.15

Base hydrolysis data at 25°C and I = 0.1 mol dm^{-3}

Complex	k_{OH} (dm^3 mol^{-1} s^{-1})	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}_{298}$ JK^{-1} mol^{-1}
αβR-[Co(tetren)Cl]$^{2+}$	5.33×10^4	89.9 ± 3.8	+ 147 ± 12
αβS-[Co(tetren)Cl]$^{2+}$	7.20×10^5		
αα-[Co(tetren)Cl]$^{2+}$	1.16×10^2	82.8 ± 4.0	+ 73 ± 13
αβR-[Co(tetren)Br]$^{2+}$	6.97×10^5	94.8 ± 3.9	+ 185 ± 13
αβS-[Co(tetren)Br]$^{2+}$	2.92×10^6		
αα-[Co(tetren)Br]$^{2+}$	1.44×10^3	79.9 ± 7.0	+ 83 ± 23
αβS-[Co(tetren)NO$_2$]$^{2+}$	2.11		
αα-[Co(tetren)NO$_2$]$^{2+}$	6.34×10^{-4}		

The activation parameters determined for base hydrolysis of [Co(tetren)Cl]$^{2+}$ and [Co(tetren)Br]$^{2+}$ indicate large, positive entropies of activation consistent with base hydrolysis proceeding by a dissociative SN1CB mechanism. A number of factors can influence the course of the reaction. These include (a) the site of deprotonation to give the conjugate base, (b) the geometry of the five coordinate intermediate that is trigonal bipyramidal or square pyramidal, (c) the rate determining step, that is formation of the conjugate base or dissociation of the conjugate base to give the five coordinate intermediate.

Henderson and Tobe[13] proposed five requirements for rapid base hydrolysis of octahedral acidoaminecobalt(lll) complexes (where the reactions occur by an SN1CB mechanism and proceed via a trigonal bipyramidal intermediate). The kinetic data collected in the present work for base hydrolysis of $[Co(tetren)X]^{2+}$ ($X = Br, Cl, NO_2$) can be rationalised in terms of Henderson and Tobe's five criteria for rapid base hydrolysis which are as follows: (a) the secondary nitrogen atom which deprotonates to form the amido group should be the middle member of a meridional set of nitrogen donor atoms, that is it should be "flat" rather than orthogonal as shown in (8),

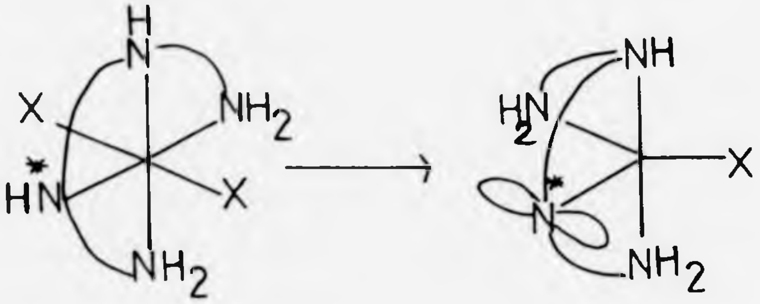


flat *NH orthogonal *NH

(8)

(b) the amido group must be <u>cis</u> to the leaving group,

(c) the plane of the amido group in the trigonal bipyramidal intermediate should be able to lie perpendicular to the trigonal plane of the cobalt, structure (9). This arrangement allows a favourable overlap between a π donor orbital of the amido nitrogen atom N* and an acceptor orbital on Co(lll).



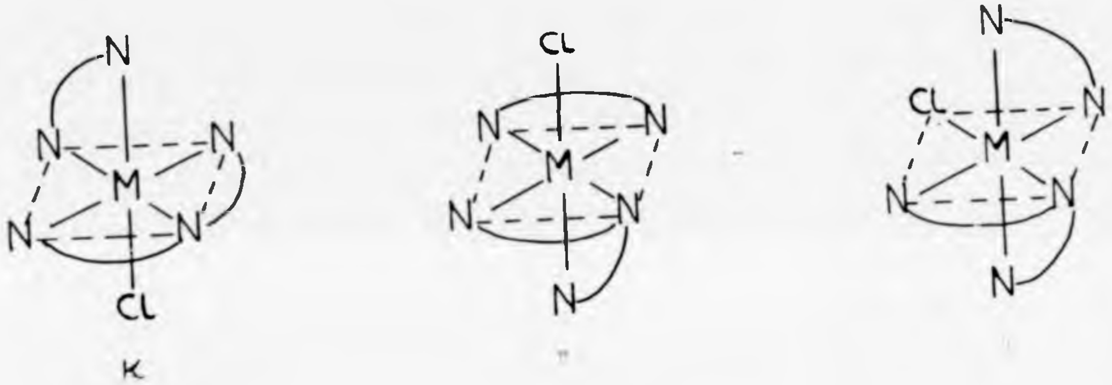
(9)

(d) the "flat" nitrogen atom should link two five-membered rings. For this arrangement the minimum strain conformation has the correct orientation for maximum overlap of the "flat" nitrogen filled π orbital with the empty Co(111) orbital,

(e) there should be monodentate amines or a six-membered chelate occupying the remaining equatorial sites in the intermediate, so that there is minimal strain.

Considering αβR-, and αβS-[Co(tetren)X]$^{2+}$, these complexes fulfil requirements a, b, c and d above for rapid base hydrolysis, only condition e is not met.

On the basis of Henderson and Tobe's ideas the αα-isomer would be expected to undergo base hydrolysis much more slowly than either the αβR- or αβS-isomers. The αα-isomer, shown in structure (2A), has no "flat" nitrogen atom available to form the amido group and the amido group will be trans to the leaving group. This expectation of slower base hydrolysis is borne out as αα-$[Co(tetren)Cl]^{2+}$ hydrolyses some 460 times slower than αβR-$[Co(tetren)Cl]^{2+}$ (Table 1.15). A close analogy can be drawn between $[Co(tetren)Cl]^{2+}$ and another Co(111) pentaamine, $[Co(en)(dien)Cl]^{2+}$ which contains the bidentate 1,2-diaminoethane (en) and tridentate 1,5-diamino-3-azapentane (dien) ligands. This complex can exist as three geometric isomers denoted K-, π- and ω- which are shown in (10).



(10)

The second order rate constants for base hydrolysis of these complexes have been determined at 25°C by Hay and Nolan.[41] For K-$[Co(en)(dien)Cl]^{2+}$, $k_{OH} = 3 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$; π-$[Co(en)(dien)Cl]^{2+}$, $k_{OH} = 26.6\ dm^3\ mol^{-1}\ s^{-1}$; and for ω-$[Co(en)(dien)Cl]^{2+}$, $k_{OH} = 7.3\ dm^3\ mol^{-1}\ s^{-1}$. These kinetic data can be interpreted by considering the requirements for lability listed above. The isomer K-$[Co(en)(dien)Cl]^{2+}$ which UNDERGOES base hydrolysis some 3×10^4 times faster than the ω- and π-isomers has a "flat" secondary nitrogen atom cis to the leaving group which is available for deprotonation to give the amido group. The π- and ω-isomers do not have "flat" nitrogen atoms available to form the amido group, and the nitrogen atoms that can deprotonate are trans to the leaving group.

The rate constants for base hydrolysis of αβR- and αα-$[Co(tetren)X]^{2+}$ ($X = Br^-, Cl^-$) are related to the free energy changes of the activation processes and may be divided into enthalpic ($\Delta H^{\neq}$) and entropic ($\Delta S^{\neq}$) contributions. These parameters were evaluated from the temperature dependence of the k_{OH} values, using Eyring plots. Inspection of Table 1.15 shows that the $\Delta S^{\neq}_{298}$ values are large and positive, as expected for reactions proceeding by a dissociative SN1CB mechanism. Comparisons of the $\Delta S^{\neq}$ values for the αβR- and αα-isomers of $[Co(tetren)X]^{2+}$ show that the difference in base hydrolysis rates is predominantly an entropy effect with $\Delta S^{\neq}\alpha\beta R/\Delta s^{\neq}\alpha\alpha$ ca. 2.0.

A comparison between the base hydrolysis reaction rates of αβR- and αβS-$[Co(tetren)X]^{2+}$ ($X = Cl^-, Br^-$) shows that the αβS-isomer reacts faster than the corresponding αβR-isomer. The differences in strain energy between the two forms may explain this result. Calculations[1] have shown that the strain energy relative to αβR-$[Co(tetren)Cl]^{2+}$ as zero, is 10.9 kJ $mole^{-1}$ for αβS-$[Co(tetren)Cl]^{2+}$. In energy terms, the αβS-isomer is closer to the transition state and is therefore expected to react faster than the αβR-isomer. The free energy effect is shown in Figure 1.12B.

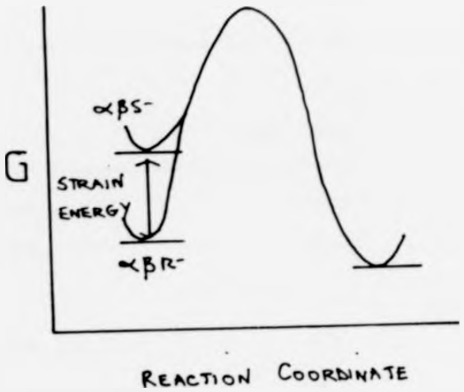


Figure 1.12B

A comparison can be made between the base hydrolysis rates of chloro and bromo complexes of the same isomers with αβR-[Co(tetren)Br]$^{2+}$ reacting 12 times faster than αβR-[Co(tetren)Cl]$^{2+}$ and αα-[Co(tetren)Br]$^{2+}$ reacting 12 times faster than αα-[Co(tetren)Cl]$^{2+}$. It is commonly found that bromo complexes of Co(III) pentaamines are more labile to base hydrolysis than the chloro analogues. Some data is supplied for comparison in Table 1.16.

There is an entropy contribution to this rate difference between bromo and chloro complexes which can possibly be assigned to solvation effects. If the solvation entropies of the complexes [Co(tetren)X]$^{2+}$ (X = Br,Cl) are less dependent on the nature of the leaving group (X) than are the solvation entropies of X then this difference should be reflected in the

TABLE 1.16

Kinetic data for base hydrolysis of halopentaamine Co(111) complexes

Complex	k_{OH} ($dm^3\ mol^{-1}\ s^{-1}$)	T (°K)	Ionic strength ($mol\ dm^{-3}$)
cis-$[Co(en)_2(NH_3)Br]^{2+}$ [a]	3.3	273	0.1
cis-$[Co(en)_2(NH_3)Cl]^{2+}$	0.23	273	0.1
cis-$[Co(en)_2(NH_2CH_3)Br]^{2+}$ [a]	50	298	0.1
cis-$[Co(en)_2(NH_2CH_3)Cl]^{2+}$	7.3	298	0.1
cis-$[Co(en)_2(NH_2OH)Br]^{2+}$ [a]	48	298	0.1
cis-$[Co(en)_2(NH_2OH)Cl]^{2+}$	7.0	298	0.1
$\alpha\beta R$-$[Co(tetren)Br]^{2+}$ [b]	0.69×10^6	298	0.1
$\alpha\beta R$-$[Co(tetren)Cl]^{2+}$	5.33×10^4	298	0.1
$\alpha\alpha$-$[Co(tetren)Br]^{2+}$ [b]	1.36×10^3	298	0.1
$\alpha\alpha$-$[Co(tetren)Cl]^{2+}$	1.25×10^2	298	0.1

a. taken from reference 1

b. present work

$\Delta S^{\neq}$ values, where the reaction mechanism is dissociative; this is indeed observed with $\Delta S^{\neq}$ greater for X = Br than for X = Cl. Some data which show this trend are presented in Table 1.17.

TABLE 1.17

$\Delta S^{\neq}_{298}$ values for base hydrolysis of some halopentaamine Co(111) complexes[a] $\Delta S^{\neq}_{298}$ UNITS $(JK^{-1}mol^{-1})$

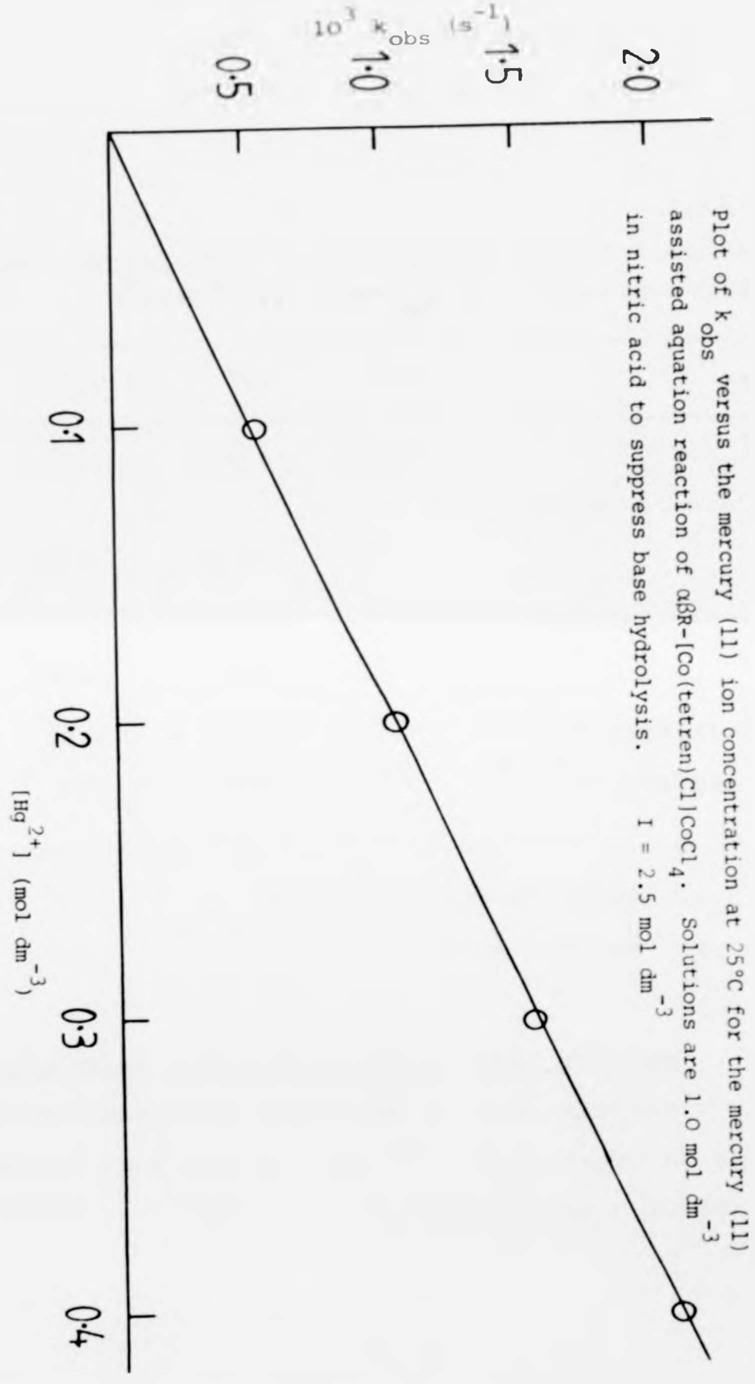
Complex	F^-	Cl^-	Br^-	I^-
$[(NH_3)_5CoX]^{2+}$ [a]	+20.4	+34.8	+37.7	+42.6
cis-$[Co(en)_2(NH_2CH_3)X]^{2+}$ [a]		+100	+120	
cis-$[Co(en)_2(NH_2OH)X]^{2+}$ [a]		+99	+120	
αβR-$[Co(tetren)X]^{2+}$ [b]		+147	+185	
αα-$[Co(tetren)X]^{2+}$ [b]		+73	+83	

a. taken from reference 1

b. present work

Mercury (11) promoted aquation reactions

Kinetic data for mercury (11) promoted aquation of αβR- and αα-$[Co(tetren)X]^{2+}$ (X = Br,Cl) were collected under pseudo first order conditions with $[Hg^{2+}] > 10[Co(tetren)X]^{2+}$.



Plot of k_{obs} versus the mercury (II) ion concentration at 25°C for the mercury (II) assisted aquation reaction of αβR-[Co(tetren)Cl]$CoCl_4$. Solutions are 1.0 mol dm^{-3} in nitric acid to suppress base hydrolysis. I = 2.5 mol dm^{-3}

Figure 1.13

TABLE 1.18

Hg(II) promoted aquation of αβR-[Co(tetren)Cl]$CoCl_4$ at 25°C and I = 2.5 mol dm^{-3} [a]

[Hg^{II}] mol dm^{-3}	10^3 k_{obs} (s^{-1})	10^3 k_{obs}/[Hg^{II}] (dm^3 mol^{-1} s^{-1})
0.1	0.58	5.80
0.2	1.09	5.45
0.3	1.58	5.26
0.4	2.13	5.32

a. Hg(II) solutions are 1.0 mol dm^{-3} in (HNO_3) to suppress base hydrolysis. The absorbance change was monitored at 470 nm.

The mean value of k_{Hg} = k_{obs}/[Hg^{2+}] is 5.45×10^{-3} dm^3 mol^{-1} s^{-1}. A plot of k_{obs} versus [Hg^{2+}] is shown in Figure 1.13. Linear regression analysis gives k_{Hg} = (5.14 ± 0.08) × 10^{-3} dm^3 mol^{-1} s^{-1}. Plots of log(A_∞-A_t) versus time are linear as shown in Figure 1.14. The visible spectrum of the product from this reaction is identical to that found for an authentic sample of αβR-[Co(tetren)H_2O]$^{3+}$ having band maxima at 350 and 472 nm. An interval scan for the reaction shows isosbestic points at 354 and 510 nm.

Kinetic plot for the mercury (11) assisted aquation of αβR-[Co(tetren)Cl][CoCl$_4$] in 0.2 mol dm^{-3} (Hg(NO$_3$)$_2$) I = 2.5 mol dm^{-3}

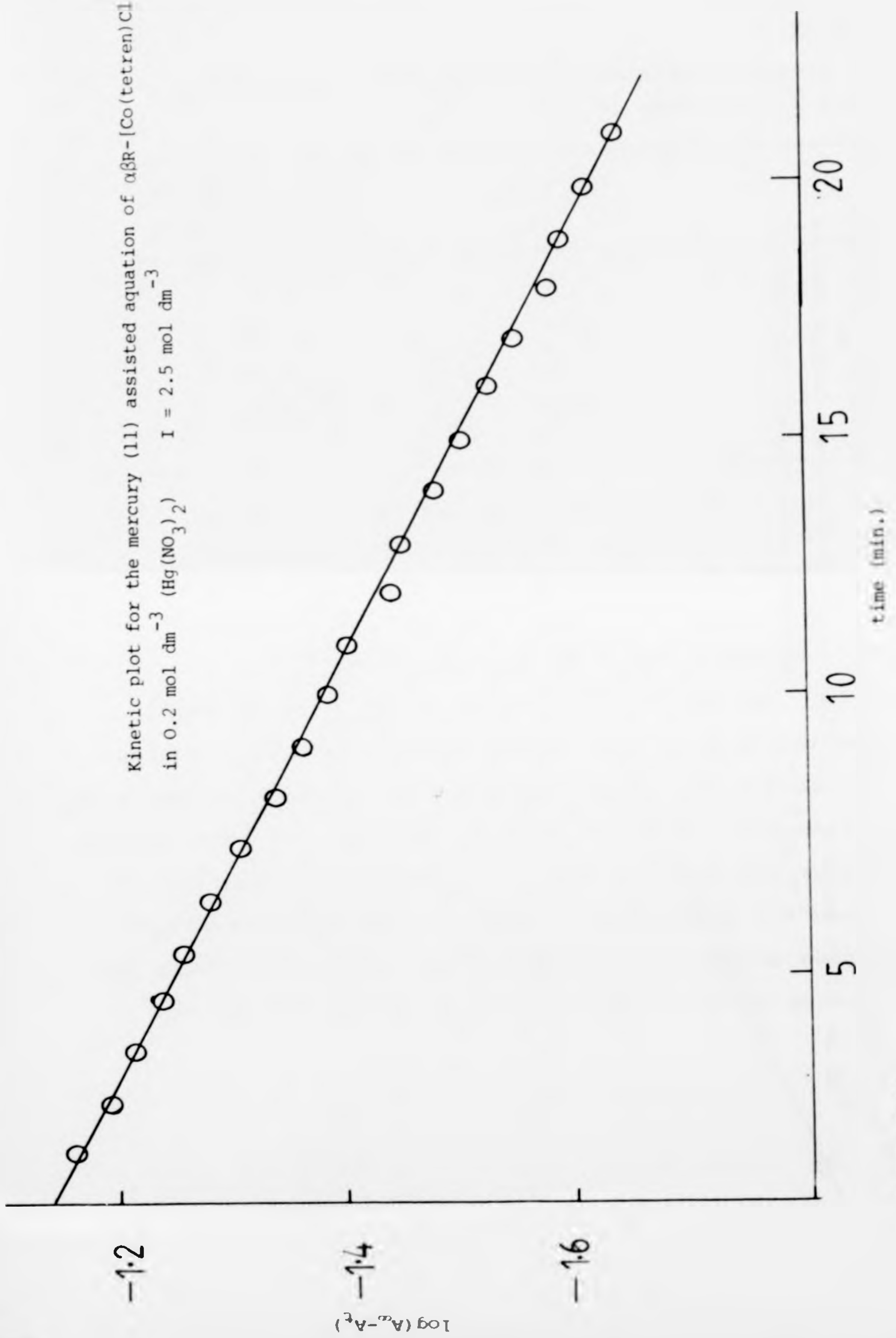


Figure 1.14

TABLE 1.19

Hg(11) promoted aquation of αα-[Co(tetren)Cl](ClO$_4$)Cl at 25°C and I = 0.3 mol dm^{-3} a

[Hg^{II}] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^2 k_{obs}/[Hg^{II}] (dm^3 mol^{-1} s^{-1})
0.02	2.73	1.36
0.03	4.41	1.47
0.04	5.76	1.44
0.05	7.29	1.45
0.06	8.48	1.41

a. Hg(11) solutions are 0.1 mol dm^{-3} in (HNO$_3$) to suppress base hydrolysis. The absorbance change was monitored at 310 nm.

The mean value of k_{Hg} = 1.42 x 10^{-2} dm^3 mol^{-1} s^{-1}. Linear regression analysis gives k_{Hg} = (1.43 ± 0.04) x 10^{-2} dm^3 mol^{-1} s^{-1}. The visible spectrum of the product from the reaction is identical to that of an authentic sample of αα-[Co(tetren)H$_2$O]$^{3+}$, having band maxima at 341 nm and 494 nm. A typical interval scan spectrum is shown in Figure 1.15. Isosbestic points are observed at 348 nm, 407 nm and 512 nm.

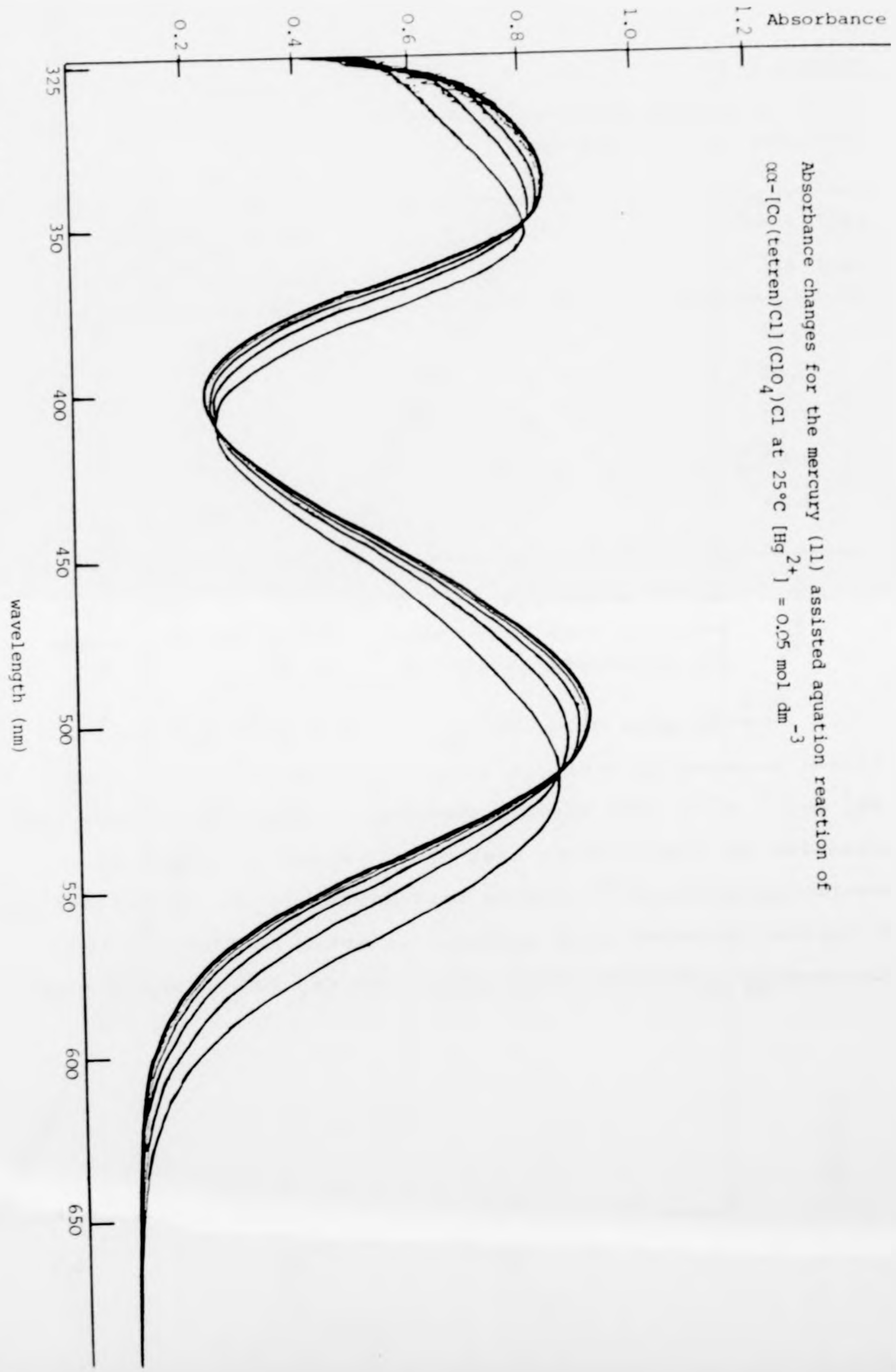


Figure 1.15

Absorbance changes for the mercury (11) assisted aquation reaction of αα-[Co(tetren)Cl](ClO$_4$)Cl at 25°C [Hg^{2+}] = 0.05 mol dm^{-3}

TABLE 1.20

Hg(11) promoted aquation of αβR-[Co(tetren)Br]ZnBr$_4$ at 25°C and I = 1.2 mol dm^{-3} ^{a}

10^3 [Hg^{II}] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	k_{obs}/[Hg^{II}] (dm^3 mol^{-1} s^{-1})
1.0	1.46	1.46
3.0	4.84	1.61
6.0	10.07	1.67
7.0	11.56	1.64
8.0	12.85	1.60

a. Hg(11) solutions are 1.0 mol dm^{-3} in (HNO$_3$) to suppress base hydrolysis. The wavelength change was monitored at 325 nm. The mean value of k_{Hg} = 1.60 dm^3 mol^{-1} s^{-1}. Linear regression analysis gives k_{Hg} = (1.65 ± 0.04) dm^3 mol^{-1} s^{-1}.

TABLE 1.21

Hg(11) promoted aquation of αα-[Co(tetren)Br](ClO$_4$)Br at 25°C and I = 0.3 mol dm^{-3} ^{a}

10^3 [Hg^{II}] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	k_{obs}/[Hg^{II}] (dm^3 mol^{-1} s^{-1})
0.75	5.09	6.78
1.00	7.14	7.14
1.50	10.26	6.80
2.00	12.90	6.45

a. Hg(11) solutions are 0.1 mol dm^{-3} in (HNO$_3$) to suppress base hydrolysis. The wavelength change was monitored at 280 nm. The mean value of $k_{Hg} = 6.79\ dm^3\ mol^{-1}\ s^{-1}$. Linear regression analysis gives $k_{Hg} = (6.18 \pm 0.35)\ dm^3\ mol^{-1}\ s^{-1}$.

From the kinetic data collected for Hg(II) promoted aquation of αβR-, αα[Co(tetren)X]$^{2+}$ (X = Br,Cl), plots of $\log(A_\infty - A_t)$ versus time were linear over several half-lives, indicating that the reactants were isomerically pure. Interval scan spectra showed that the reactions proceed with retention of configuration with αβR-[Co(tetren)X]$^{2+}$ giving αβR-[Co(tetren)H_2O]$^{3+}$ and αα-[Co(tetren)X]$^{2+}$ giving αα-[Co(tetren)H_2O]$^{3+}$ (X = Br,Cl).

For the four complexes studied, plots of k_{obs} versus [Hg^{II}] are linear passing through the origin. The absence of an intercept indicates that no measurable aquation reaction is occurring. A second order rate law is found of the type (8)

$$-\frac{d[[Co(tetren)X]^{2+}]}{dt} = k_{Hg}[[Co(tetren)X]^{2+}][Hg^{II}] \qquad (8)$$

The theoretical rate law for Hg(II) assisted aquation of [Co(tetren)Cl]$^{2+}$ should probably be written[42] as in (9)

$$-\frac{d[complex]}{dt} = k_{aq}[complex] + \sum_{x=0}^{x=4} k_{HgCl_x^{\,2-x}}[HgCl_x^{\,2-x}][complex] \qquad (9)$$

The appearance of HgCl$^+$ in the rate equation arises because of the possibility of combined Hg^{2+} and HgCl$^+$ assisted aquation in the reaction. The relative contributions of Hg^{2+}

and $HgCl^+$ to hydrolysis are unknown and the kinetic parameters are composites referring only to the stated ionic strength, complex ion, halide ion and Hg^{2+} concentrations.

It is commonly observed that Hg(ll) assisted aquation of Co(lll) halopentaamines proceeds with retention of configuration and the present work provides yet another example. It is believed that during Hg(ll) assisted aquation of $[CoN_5X]$ a binuclear species is formed in which X^- is bound simultaneously to Co(lll) and Hg(ll). A rate determining dissociation then takes place to give a five coordinate intermediate. The stereochemistry of the products, suggests that the water molecule rapidly enters the intermediate on the same side of the molecule from which the leaving group departs, thus preserving the original isomer geometry. Research into Hg(ll) and Ag(l) assisted aquation is continuing in an effort to clarify the reaction mechanism. The kinetic data for Hg(ll) assisted aquation of $[Co(tetren)X]^{2+}$ are collected in Table 1.22.

TABLE 1.22

Kinetic data for Hg(ll) assisted aquation of $[Co(tetren)X]^{2+}$ (X = Br,Cl) at 25°C

Complex	k_{Hg} ($dm^3\ mol^{-1}\ s^{-1}$)	Total ionic strength ($mol\ dm^{-3}$)
$\alpha\beta R$-$[Co(tetren)Cl]CoCl_4$	5.45×10^{-3}	2.5
$\alpha\beta R$-$[Co(tetren)Br]ZnBr_4$	1.6	1.2
$\alpha\alpha$-$[Co(tetren)Cl](ClO_4)Cl$	1.42×10^{-2}	0.3
$\alpha\alpha$-$[Co(tetren)Br](ClO_4)Br$	6.79	0.3

The interpretation of rate data for Hg(ll) assisted aquation is complicated by several factors. The rate of reaction is known to be highly dependent on ionic strength and k_{Hg} values should be compared at the same ionic strength.[43] Problems arise from uncertainty about the nature of the mercury catalyst. When a mercury salt is dissolved in acidic solution $HgOH^+$ is found to be present in considerable amounts in the range pH 2-5.[44] Hg^{2+} is also available for reaction as is $HgCl^+$ when chloride ion is present. It has been postulated that $HgCl^+$ may be a better reactant than Hg^{2+} as it is more able to overcome cation-cation repulsions, in fact, in the Hg^{2+} assisted aquation of $[(NH_3)_5CoCl]^{2+}$ [45] it was found that addition of Cl^- caused a rate increase of 8% and this was attributed to $HgCl^+$ catalysis. In the present work, the complexes studied for Hg^{2+} assisted aquation have counter ions containing Cl^- and Br^- thus the contribution of $HgCl^+$ and $HgBr^+$ may be very significant. Despite these difficulties some tentative conclusions can be reached from the data collected in the present work on the Hg(ll) assisted aquation of $[Co(tetren)X]^{2+}$ (X = Br,Cl). First , the rate of reaction is not much affected by the isomer geometry of $[Co(tetren)X]^{2+}$ and second the change in leaving group from Cl^- to Br^- causes an enormous increase in reaction rate. For the αα-isomers of $[Co(tetren)X]^{2+}$ where the Hg(ll) assisted aquation reactions were studied at the same ionic strength $k_{Hg}(Br^-)/k_{Hg}(Cl^-) = 478$. The insensitivity of reaction rate to changes in isomer geometry has been observed in other systems, for example in the Hg(ll) assisted aquation of the π-, Κ-, and ω-$[Co(en)(dien)Cl]^{2+}$

isomers at 25°C and $I = 1.0$ mol dm^{-3} $k_{Hg}(\pi) = 14.7 \times 10^{-3}$ dm^{3} mol^{-1} s^{-1}, $k_{Hg}(\kappa) = 5.1 \times 10^{-3}$ dm^{3} mol^{-1} s^{-1} and $k_{Hg}(\omega) = 4.8 \times 10^{-3}$ dm^{3} mol^{-1} s^{-1}.[42] The effect of leaving group on reaction rate is much greater for Hg^{2+}- assisted aquation than it is for base hydrolysis, although both show the same trend with bromo complexes reacting faster than chloro complexes.

Acid catalysed decarboxylation kinetics of αα-[Co(tetren)CO$_3$](ClO$_4$)

Dasgupta and Harris[29] have studied the kinetics of acid catalysed decarboxylation of αβS-[Co(tetren)CO$_3$](ClO$_4$) and proposed the following reaction scheme

$$[Co(tetren)(CO_3)]^{+} + H^{+} \rightleftharpoons [Co(tetren)(CO_3H)]^{2+} \quad 1/K_c$$

$$[Co(tetren)(CO_3H)]^{2+} \xrightarrow{RDS} [Co(tetren)OH]^{2+} + CO_2 \quad k_1$$

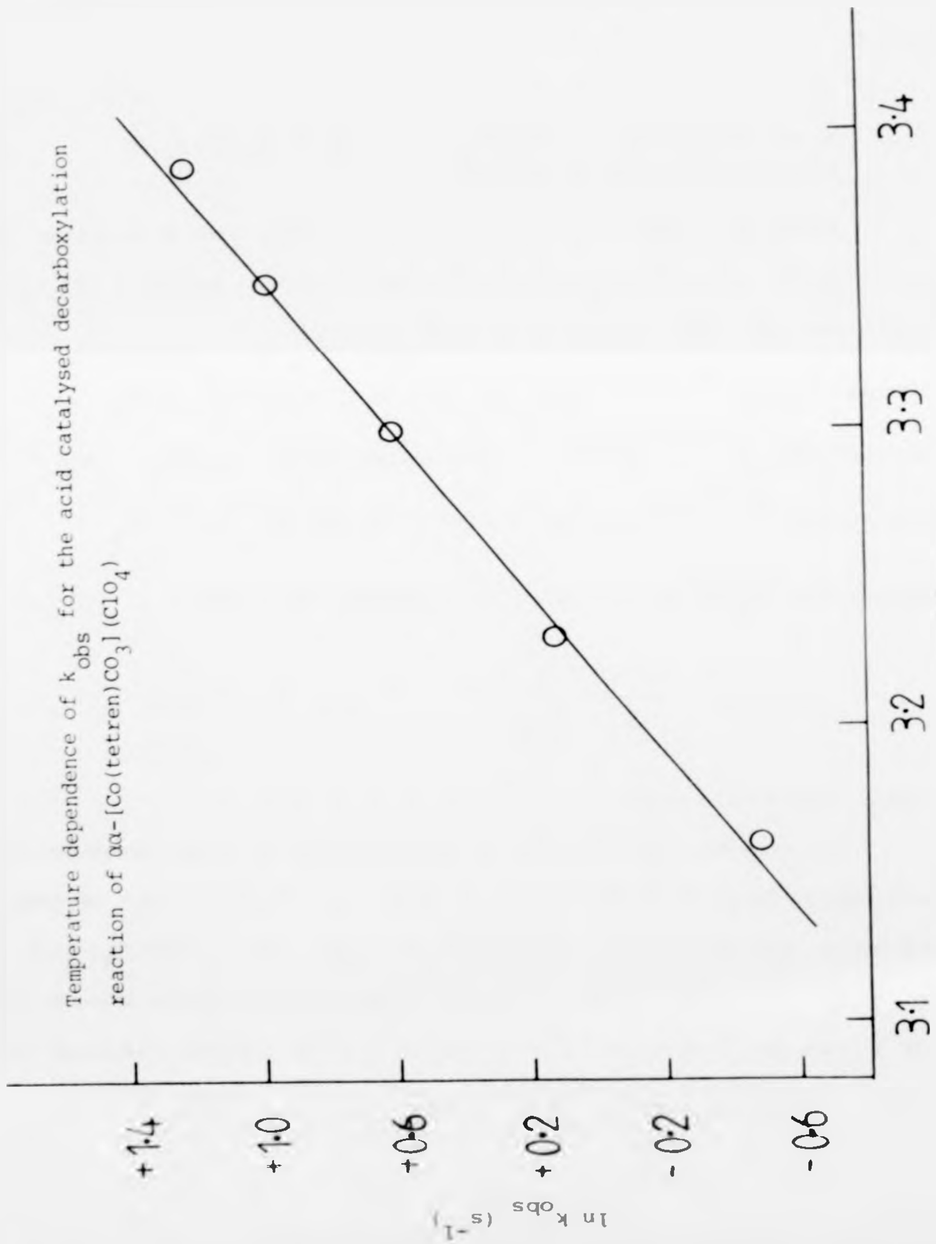
$$[Co(tetren)OH]^{2+} + H^{+} \rightleftharpoons [Co(tetren)H_2O]^{3+} \quad 1/K_A$$

with the rate equation of the form shown in (10)

$$k_{obs} = \frac{k_1[H^+]}{([H^+] + K_c)} \qquad (10)$$

where pK_c has the value 6.4.

In the present work an isomerically pure sample of αα-[Co(tetren)CO$_3$](ClO$_4$) was used for decarboxylation studies. The reaction was carried out using 0.1 mol dm^{-3} (HClO$_4$) as solvent that is under pseudo first order conditions where the term $[H^+]$ can be removed from equation (10) which reduces to $k_{obs} = k_1$. From the measurement of k_{obs} at a series of



Temperature dependence of k_{obs} for the acid catalysed decarboxylation reaction of αα-$[Co(tetren)CO_3](ClO_4)$

Figure 1.16

temperatures the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}_{298}$ were calculated. The stopped-flow spectrophotometric technique was used, monitoring the absorbance decrease at 500 nm as a function of time.

TABLE 1.23

Acid catalysed decarboxylation of αα-$[Co(tetren)CO_3](ClO_4)$ in 0.1 mol dm^{-3} $(HClO_4)$

Temp. (θ°C)	k_{obs} (s^{-1})
21.3	0.30
25.0	0.37
30.0	0.54
36.0	0.90
43.0	1.67

For αα-$[Co(tetren)CO_3](ClO_4)$ $k_1 = 0.37\ s^{-1}$ at 25°C ($\Delta H^{\neq} = 58.0$ kJ mol^{-1}, $\Delta S^{\neq}_{298} = -58.0$ JK^{-1} mol^{-1}). A plot of ln k_{obs}, versus 1/T(K) is shown in Figure 1.16. The decarboxylation reaction of αβS-$[Co(tetren)CO_3](ClO_4)$, studied by Dasgupta and Harris, in the temperature range 15 - 30°C and at an ionic strength of 0.5 mol dm^{-3} (NaCl) was found to have the values $k_1 = 0.28\ s^{-1}$ at 25° ($\Delta H^{\neq} = +65.3$ kJ mol^{-1}, $\Delta S^{\neq}_{298} = -36.0$ JK^{-1} mol^{-1}).

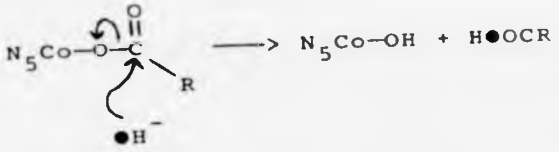
CHAPTER 2

Syntheses and REACTION Kinetics of Complexes of the type $[Co(tetren)O_2CR]^{2+}$ ($R = H, CH_3, C_2H_5, CH_2Cl, CHCl_2$)

2.1 Introduction

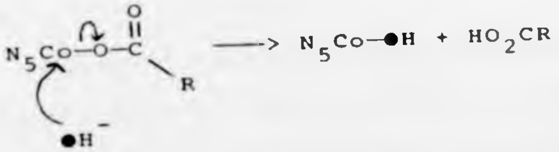
Current interest in carboxylato complexes of Co(111) pentaamines of the type $[CoN_5(O_2CR)]^{2+}$ arises from the possibility that coordination to Co(111) may activate the O_2CR^- group to nucleophilic attack. Where the nucleophile is the hydroxide ion base hydrolysis can proceed by three possible routes, a, b and c, below. Reaction mechanisms can be distinguished by oxygen isotope tracer experiments. In reaction (a) direct attack of hydroxide ion on the carbonyl carbon atom of the carboxylato group takes place leading to cleavage of a carbon-oxygen bond:

(a)



In reaction (b) attack of hydroxide ion on Co(111), leads to cleavage of the Co(111)-oxygen bond; (an SN2 process)

(b)



In reaction (c) an SN1CB type process leads to cleavage of the Co(111)-oxygen bond. Labelled solvent $H_2\bullet$ is used and the equilibrium $OH^- + \bullet H_2 \rightleftharpoons \bullet H^- + H_2O$ takes place to give labelled $\bullet H^-$ ions.

$$[(NH_3)_5CoO_2CR]^{2+} + \bullet H^- \rightleftharpoons [(NH_3)_4(NH_2)CoO_2CR]^{+} + H_2O$$

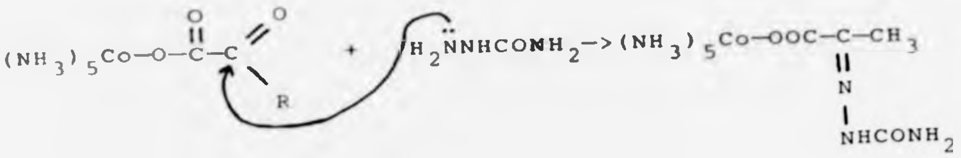
$$\text{(c)} \qquad [(NH_3)_4(NH_2)CoO_2CR]^{+} \longrightarrow [(NH_3)_4(NH_2)Co]^{2+} + O_2CR^-$$

$$[(NH_3)_4(NH_2)Co]^{2+} + H_2\bullet \longrightarrow [(NH_3)_5Co\bullet H]^{2+}$$

The bimolecular reaction (a) with labelled hydroxide ion would yield labelled carboxylate and unlabelled $[N_5CoOH]^{2+}$ while the alternative mechanisms (b) direct replacement on Cobalt (111) and (c) the SN1CB process would give unlabelled carboxylate and labelled $[N_5Co\bullet H]^{2+}$. Electronic effects revealed by linear free energy relationships and values of $\Delta S^{\neq}$ are also helpful in making mechanistic assignments.

Kinetic studies on the base hydrolysis reactions of $[(NH_3)_5Rh(O_2CR)]^{2+}$ [46] have revealed that where R is a powerful electron withdrawing group like CCl_3 or CF_3, base hydrolysis proceeds by a bimolecular mechanism with hydroxide ion attack at the carbonyl carbon atom, However, when (R = H, CH_3, CH_2F) the experimental results are best rationalised in terms of an SN1CB mechanism. The same behaviour is observed for the Co(111) pentaammines $[(NH_3)_5CoO_2CR]^{2+}$.

Enhanced reactivity of coordinated carboxylate is further illustrated by the reactions of $[(NH_3)_5CoO_2CCOR]^{2+}$ with semicarbazides to give coordinated semicarbazones.[48] The products are formed without breaking the bond between Co(III) and the carboxylate oxygen and are thought to follow the pathway:



A number of studies on the reactivity of coordinated carboxylato groups have been carried out in non-aqueous solvents. For example, the reaction of $[(NH_3)_5CoO_2CCH_3]^{2+}$ with acetyl perchlorate in N,N-dimethylformamide (DMF) where rapid solvolytic replacement of the acetato ligand takes place.[49] The proposed mechanism for this reaction involves attack by the electrophile on the acetato group thus converting it to a much less nucleophilic ligand. This ligand then departs yielding a five coordinate species which rapidly reacts with a solvent DMF molecule.

Other aspects of pentaamine (carboxylato) Co(III) chemistry have been investigated including reduction of the complexes with Cr(II) and Ti(III). Cr(II) is believed to bond with coordinated O_2CR^- giving inner sphere electron transfer,[50]

$$N_5Co^{III}O_2CR + Cr(II) \longrightarrow Cr^{III}O_2CR + NH_4^+ + Co(II).$$

The photochemistry of carboxylato complexes has also been investigated as a source of organic free radicals.[51]

It was decided in the present work to prepare complexes of the type $[Co(tetren)O_2CR]^{2+}$ and examine their base hydrolysis reactions. Up to the commencement of the present work the only base hydrolysis study of a carboxylato complex of the Co(111) tetren moiety documented in the literature was for the salicylato complex, αβS-$[Co(tetren)OCOC_6H_4OH](ClO_4)_2$ [30,31] which was found to react by an SN1CB reaction mechanism.

With regard to possible preparative methods a survey of the literature on $[(NH_3)_5CoO_2CR]^{2+}$ complexes has revealed three synthetic procedures:

(1) anation of the aquo complex[52]

$$[(NH_3)_5CoH_2O]^{3+} + RCO_2Na \longrightarrow [(NH_3)_5CoO_2CR]^{2+}$$

(2) silver induced anation[53]

$$[(NH_3)_5CoCl]^{2+} + C_6H_5CO_2^{-}Ag^{+} \longrightarrow [(NH_3)_5CoO_2CC_6H_5]^{2+} + AgCl$$

(3) reaction of the hydroxo complex with an acid anhydride[34,55]

$$[(NH_3)_5CoOH]^{2+} + (C_2H_5CO)_2O \xrightarrow{pH8} [(NH_3)_5CoO_2CC_2H_5]^{2+} + C_2H_5CO_2H.$$

The Experimental section describes the preparation and base hydrolysis studies of $[Co(tetren)O_2CR](ClO_4)_2$ where $R = H, CH_3, C_2H_5, CH_2Cl, CHCl_2$.

2.2 Experimental

Preparations

[Co(tetren)OOCH](ClO$_4$)$_2$

Method A

The complex αα-[Co(tetren)Cl](ClO$_4$)Cl (0.26g., 0.62 mmoles) was suspended in 98% formic acid (15 cm^3, 0.32 moles) and treated with silver perchlorate (0.26g., 1.25 mmoles). The mixture was heated at 60°C for one hour, cooled and the precipitated silver chloride filtered off. A few drops of perchloric acid (40%) were added to the orange solution which upon standing precipitated crystals of [Co(tetren)OOCH](ClO$_4$)$_2$. The product was filtered, washed with ethanol, ether and dried *in vacuo*. A second crop is obtained from the mother liquors by addition of ethanol which causes precipitation of [Co(tetren)OOCH](ClO$_4$)$_2$.

Method B

The complex αα-[Co(tetren)H$_2$O](ClO$_4$)$_3$ (0.5g., 0.88 mmoles) was dissolved in the minimum volume of dilute perchloric acid and 98% formic acid (0.5g., 10.8 mmoles) was added to solution. The reaction mixture was brought to pH4 by dropwise addition of sodium hydroxide. The solution was stirred at 60°C for one hour then left to cool. The product [Co(tetren)OOCH](ClO$_4$)$_2$ which crystallised out was filtered, washed with ethanol, ether and dried *in vacuo*. The crude product was recrystallised by dissolution in the minimum volume of 0.1 molar perchloric acid - 98% formic acid (1:2 v/v).

Calc. for [Co($C_8H_{23}N_5$)OOCH](ClO$_4$)$_2$: C,21.95; H,4.91; N,14.23;
Found: C,20.80; H,4.88; N,13.93%.

A ^{13}C NMR spectrum was recorded in D_2O containing one drop of DCl to suppress base hydrolysis of $[Co(tetren)OOCH]^{2+}$, Na TMS was used as an internal reference, 4,674 transients were recorded to give values for the tetren carbon atom resonances: δ in (ppm)

δ(integral) 43.77(1.5), 50.65(1.7), 51.08(1.7), 51.79(1.7), 54.96(1.7), 56.27(1.7), 57.03(2.1), 59.38(1.6). The carbon atom of the coordinated formato group resonates at 177.7(0.97).

$[Co(tetren)O_2CCH_3](ClO_4)_2$

The complex αα-$[Co(tetren)H_2O](ClO_4)_3$ (0.5g., 0.88 mmoles) was dissolved in glacial acetic acid (15g., 0.25 mmoles) containing a few drops of water. The solution was stirred at 60°C for one hour. Upon cooling, ethanol was added to precipitate $[Co(tetren)O_2CCH_3](ClO_4)_2$ as a fine red powder. The product was filtered, washed with ethanol, ether and dried *in vacuo*.

Calc. for $[Co(C_8H_{23}N_5)O_2CCH_3](ClO_4)_2$: C,23.72; H,5.17; N,13.83;

Found: C,23.86; H,5.44; N,13.20%.

A ^{13}C NMR spectrum was recorded in D_2O containing one drop of DCl to suppress base hydrolysis of $[Co(tetren)O_2CCH_3]^{2+}$, Na TMS was used as an internal reference. 7,204 transients were collected to give values for the tetren carbon atom resonances: δ in (ppm)

δ(integral) 43.44(5.6), 43.66(20.6), 45.46(23.9), 50.54(19.9), 50.81(6.7), 51.03(26.6), 51.74(21.6), 52.45(6.8), 54.96(20.9), 55.99(28.9), 56.38(19.4), 57.58(7.5), 57.96(20.2), 58.34(6.4), 59.27(24.0), 59.87(23.1), 60.69(12.5). Three signals are found for the methyl group of the coordinated acetato ligand: 15.82(0.4), 19.43(2.8), 26.63(17.08).

$[Co(tetren)O_2CC_2H_5](ClO_4)_2$

Method A

The complex αα-$[Co(tetren)Cl](ClO_4)Cl$ (0.5g., 1.19 mmoles) was suspended in propionic acid (15g., 0.20 mmoles). Silver perchlorate (0.5g., 2.4 mmoles) was added and the mixture stirred at 60°C for one hour. During this time a colour change from red to orange took place. Upon cooling, silver chloride was filtered off, and the orange filtrate treated with ethanol to precipitate $[Co(tetren)O_2CC_2H_5](ClO_4)_2$ as a red-orange powder. The product was filtered, washed with ethanol, ether and dried *in vacuo*.

Method B

The complex αα-$[Co(tetren)H_2O](ClO_4)_3$ (0.5g., 0.88 mmoles) was dissolved in dilute perchloric acid and propionic acid (0.1g., 1.35 mmoles) added to solution. Aqueous sodium hydroxide was added dropwise to bring the solution to pH5. The mixture was heated at 60°C for one hour. Upon standing at room temperature $[Co(tetren)O_2CC_2H_5](ClO_4)_2$ crystallised out as large red flakes. The product was filtered off, washed with ethanol, ether and dried *in vacuo*. The crude product was recrystallised from an aqueous mixture of perchloric acid: propionic acid.

Calc. for $[Co(C_8H_{23}N_5)O_2CC_2H_5](ClO_4)_2$: C,25.39; H,5.42; N,13.46:

Found: C,25.09; H,5.57; N,13.31%.

A ^{13}C NMR spectrum was recorded in D_2O containing 1 drop of DCl to suppress base hydrolysis of $[Co(tetren)O_2CC_2H_5]^{2+}$ with Na TMS used as an internal reference, 8,648 transients were collected to give values for the tetren carbon atom resonances at δ in (ppm)

δ(integral) 43.82(20.3), 45.52(28.3), 50.70(19.0), 51.14(21.1), 51.90(19.2), 55.07(21.5), 55.61(3.5), 56.16(20.8), 56.49(27.4), 58.07(31.2), 58.40(6.9), 59.43(22.0), 59.98(25.4), 60.80(8.5). Two resonances are seen at 12.17(15.0), 33.73(20.0) due to carbon atoms in the ethyl group of coordinated $O_2CC_2H_5$.

$[Co(tetren)O_2CCH_2Cl](ClO_4)_2$

The complex αα-$[Co(tetren)H_2O](ClO_4)_3$ (0.5g., 0.88 mmoles) was taken up in monochloroacetic acid (15g., 0.16 mmoles) containing a few drops of water. The solution was stirred at 60°C for one hour. Upon cooling red crystals of $[Co(tetren)$-$O_2CCH_2Cl](ClO_4)_2$ crystallised out. The product was filtered off, washed with ethanol, ether and dried *in vacuo*. The complex was recrystallised from an aqueous mixture of perchloric acid: monochloroacetic acid.

Calc. for $[Co(C_8H_{23}N_5)O_2CCH_2Cl](ClO_4)_2$: C,22.21; H,4.66; N,12.95;

Found: C,22.40; H,4.62; N,12.94%.

A ^{13}C NMR spectrum was recorded in D_2O containing one drop of DCl to suppress base hydrolysis of $[Co(tetren)O_2CCH_2Cl](ClO_4)_2$, Na TMS was used as an internal reference, 8,032 transients were collected to give values for the tetren carbon resonances at δ(integral) 43.55(0.7), 43.71(0.6), 44.81(1.3), 45.52(2.3), 45.8(0.6), 50.70(0.5), 50.97(0.7), 51.90(0.6), 53.16(0.4), 53.65(0.1), 53.87(0.1), 54.14(0.3), 55.23(0.8), 55.56(0.3), 56.27(0.7), 56.54(1.7), 58.18(2.0), 59.05(0.2), 59.54(0.6), 60.04(2.0), 61.84(0.1), 62.05(0.2), 63.91(0.3), 66.15(0.2), 66.58(0.1). δ in ppm

$[Co(tetren)O_2CCHCl_2](ClO_4)_2$

The complex αα-$[Co(tetren)Cl](ClO_4)Cl$ (0.5g., 1.19 mmoles) was taken up in freshly distilled dichloroacetic acid (0.51g., 2.5 mmoles) containing a few drops of water. Silver perchlorate (0.51g., 2.5 mmoles) was added to the solution which was heated at 60°C for one hour. Upon cooling, silver chloride was filtered off. Ethanol was added to the orange filtrate, to precipitate crystals of $[Co(tetren)O_2CCHCl_2](ClO_4)_2$ which were filtered off, washed with ethanol, ether and dried in vacuo.

Calc. for $[Co(C_8H_{23}N_5)O_2CCHCl_2](ClO_4)_2$: C,20.88; H,4.20; N,12.17;

Found: C,20.76; H,3.91; N,12.13%.

A ^{13}C NMR spectrum was recorded in D_2O containing one drop of DCl to suppress base hydrolysis of $[Co(tetren)O_2CCHCl_2](ClO_4)_2$, Na TMS was used as an internal reference, 20.954 transients were collected to give values for the tetren cation atom resonances at

δ(integral) 43.73(22.0), 45.47(17.2), 45.80(10.8), 47.22(2.7), 50.76(25.0), 51.03(26.9), 52.01(23.7), 55.39(25.5), 56.37(23.7), 56.59(25.5), 56.37(23.7), 56.59(20.1), 57.30(27.1), 58.18(19.7), 59.76(24.6), 60.14(20.0), 68.54(5.5), 58.70(17.3). δ in ppm.

Infra-red spectra of $[Co(tetren)O_2CR](ClO_4)_2$

All of the complexes show a broad absorption band in the range 1550 cm^{-1}-1650 cm^{-1} due to the $\nu\ CO_2^-$ asymmetric vibration superimposed upon the $\delta\ NH_2$ asymmetric deformation for the tetren ligand. This overlap in vibrational frequencies does not allow the customary assignment of isomer geometry on the basis of the NH_2 asymmetric deformation. The complexes also show absorptions in the range 1340 cm^{-1}-1400 cm^{-1} due to the $\nu\ CO_2^-$ symmetric, however unequivocal band assignments are not possible due to tetren absorptions in this region.

Electronic spectra of $[Co(tetren)O_2CR](ClO_4)_2$

The visible electronic spectra of these complexes were recorded in 0.1 mol dm^{-3} ($HClO_4$). All complexes showed two d-d absorption bands characteristic of a $Co^{III}N_5O$ chromophore, with band maxima at 351 ± 5 nm and 485 ± 3 nm. While these complexes are analytically pure, ^{13}C NMR and kinetic studies indicate that they are all isomeric mixtures of carboxylato complexes thus band maxima and extinction coefficients have not been accurately determined.

Kinetics

Kinetic studies were made on the base hydrolysis reactions of $[Co(tetren)O_2CR](ClO_4)_2$ (R = H, CH_3, C_2H_5, CH_2Cl, $CHCl_2$) under pseudo first order conditions, at 25°C and I = 0.1 mol dm^{-3} (KNO_3). The pH stat technique was used in the pH range 7-9.5. The possibility of carboxylation (by CO_2) of the product of hydrolysis, $[Co(tetren)OH]^{2+}$ precluded the spectrophotometric technique for kinetic measurement. The pseudo first order constants were determined from the experimental data using the 16 point programme and the Swinbourne calculation.

2.3 Results and Discussion

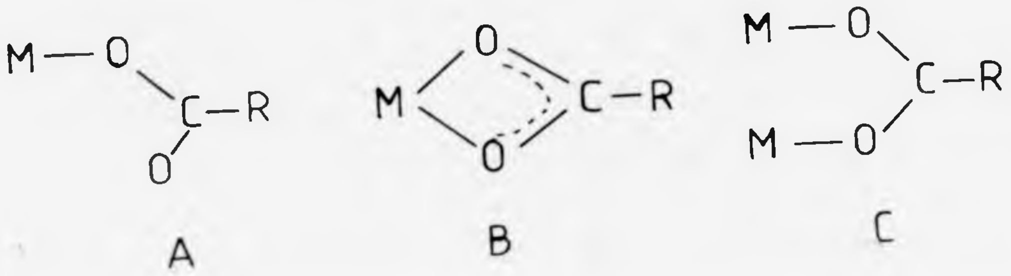
Stereochemical ASPECTS

Analytically pure samples of $[Co(tetren)O_2CR](ClO_4)_2$ ($R = H, CH_3, C_2H_5, CH_2Cl, CHCl_2$) were prepared by one of two methods. The first method, anation of isomerically pure αα-$[Co(tetren)H_2O](ClO_4)_3$ was performed by mixing the aquo complex with the appropriate carboxylic acid (RCO_2H). The second method was a silver (1) catalysed anation reaction of αα-$[Co(tetren)Cl](ClO_4)Cl$, which involved the in situ generation of $[Co(tetren)H_2O](ClO_4)_3$ in the presence of the carboxylic acid. In some cases αα-$[Co(tetren)H_2O](ClO_4)_3$ dissolved in aqueous RCO_2H was treated with dilute aqueous sodium hydroxide to raise the solution pH to the pK_a of the carboxylic acid and thereby ensure a supply of carboxylate anions for reaction with αα-$[Co(tetren)H_2O]^{3+}$. However, the carboxylato complexes were readily prepared by dissolving αα-$[Co(tetren)H_2O](ClO_4)_3$ in 98% solutions of RCO_2H although the solution pH was below the pK_a. This method succeeds because the pK_a's of the carboxylic acids are low, ranging from 1.48 for $CHCl_2COOH$ to 3.75 for HCO_2H, and because an excess of RCO_2H was used in each preparation.

The carboxylato complexes, $[Co(tetren)O_2CR](ClO_4)_2$ were characterised by ^{13}C NMR, ^1H NMR, i.r. and visible spectra. The structural information gained from each technique is discussed below.

I.r. spectra

The i.r. spectra are potentially useful for elucidating the nature of the bonding between O_2CR^- and the Co(111) ion and for determining the isomer geometry of the complexes. The carboxylato anion may coordinate to a transition metal ion by the modes shown in (11)A, B and C.



(11)

The bonding schemes can be differentiated by considering the vibrational frequencies of $\nu\ CO_2^-$ symmetric (denoted $\nu_sCO_2^-$) and $\nu\ CO_2^-$ asymmetric (denoted $\nu_aCO_2^-$) for the complexed carboxylato ions and comparing them with the vibrational frequencies of the free carboxylato ions[56]: For the unidentate structure (11)A ν C=O for the complex is higher than $\nu_aCO_2^-$ for the free ion and ν C-O for the complex is lower than $\nu_sCO_2^-$ for the free ion. As a result the separation between the 2 ν CO vibrations is much larger in unidentate complexes than in the free ion. For the bidentate structure (11)B the opposite trend is observed with the separation between the 2 ν CO vibrations smaller for the complexed ion than for the free ion. In the bridging complex (11)C, the 2 ν CO vibrations are close to the values found for the free ion.

The i.r. spectra of $[Co(tetren)O_2CR](ClO_4)_2$ ($R = H, CH_3, C_2H_5, CH_2Cl, CHCl_2$) show broad absorption bands in the range 1620 cm^{-1}-1650 cm^{-1} which are assigned to $\nu_aCO_2^-$. The vibrational frequencies for $\nu_aCO_2^-$ in the complexes are higher than those for $\nu_aCO_2^-$ in the free ion for example $[Co(tetren)O_2CH]^{2+}$ has $\nu_aCO_2^-$ at 1630 cm^{-1} while $\nu C=O$ for the free formate ion is at 1560 cm^{-1}. These data are consistent with the unidentate structure (11)A. The complexes $[Co(tetren)$-$O_2CR]^{2+}$ show additional absorption bands in the range 1300 cm^{-1}-1400 cm^{-1} due to $\nu_sCO_2^-$. However, unambiguous assignments of bands to $\nu_sCO_2^-$ are difficult as tetren displays strong absorptions in the same frequency range. Assignments of bands may be facilitated by observing frequency shifts resulting from deuteration of the amine protons.

Although the vibrational frequencies of $\nu_aCO_2^-$ are a useful indication of unidentate bonding of the carboxylato ligands these strong absorptions bands overlap with δ NH_2 for the asymmetric deformation of the tetren ligand in the range 1560 cm^{-1}-1600 cm^{-1}, thus, assignment of isomer geometry for $[Co(tetren)O_2CR]^{2+}$ on the basis of δ NH_2 frequencies is not possible.

^{13}C NMR

The ^{13}C F.T. NMR spectra for $[Co(tetren)O_2CR]^{2+}$ ($R = H, CH_3, C_2H_5, CH_2Cl, CHCl_2$) were recorded using a broad band frequency technique which eliminates all C-H couplings. In all cases, the complexes were dissolved in D_2O containing one drop of DCl to suppress base hydrolysis, NaTMS was used as an internal reference. The tetren carbon atoms resonate in the range δ40-δ70. The coordinated carboxylato groups affect the electronic shielding around the tetren carbon atoms and a correlation is found between the electron withdrawing ability of O_2CR^- and the lowest field resonance band $\delta_L(O_2CR)$ due to the tetren carbon atoms with $\delta_L(O_2CR) = 59.38(O_2CH)$, $60.69(O_2CCH_3)$, $60.80(O_2CC_2H_5)$, $66.58(O_2CCH_2Cl)$, $68.70(O_2CCHCl_2)$. As expected, the carbonyl carbon atoms of the O_2CR^- groups occur at *ca.* δ170 while the alkyl groups of O_2CR^- which are well shielded occur at *ca.* δ26. Although the complexes were prepared from isomerically pure αα-$[Co(tetren)H_2O](ClO_4)_3$, all samples of $[Co(tetren)O_2CR]^{2+}$ display a large number of ^{13}C signals, indicating the presence of mixtures of αβR-, αβS-, and αα-isomers.

Electronic spectra

The visible electronic spectra of the $[Co(tetren)O_2CR](ClO_4)_2$ complexes were determined using 0.1 mol dm^{-3} $(HClO_4)$ as solvent. The complexes all showed two d-d absorption bands with maxima at 351 ± 5 nm and 485 ± 3 nm. These absorption wavelengths are characteristic of a $Co^{III}N_5O$ chromophore and are comparable with αβS-$[Co(tetren)OH]^{2+}$ which has band maxima at 348 nm and 490 nm and αα-$[Co(tetren)CO_3]^+$ which has a band maximum at 492 nm. As ^{13}C NMR and kinetic studies indicated that these samples of $[Co(tetren)O_2CR]^{2+}$ are isomer mixtures accurate band maxima and extinction coefficients were not determined.

It can be concluded that the anation reactions of αα-$[Co(tetren)H_2O](ClO_4)_3$ with RCO_2H (R = H, CH_3, C_2H_5, CH_2Cl, $CHCl_2$) take place to give carboxylato complexes of the type

[Co(tetren)O_2CR]$(ClO_4)_2$ with O_2CR^- bound to Co(111) through one oxygen atom. The anation reaction proceeds without retention of configuration and results in isomer mixtures of αβR-, αβS- and αα-[Co(tetren)O_2CR]$(ClO_4)_2$. The difficulty in isolating these complexes in an isomerically pure form in solution may indicate that αβR-, αβS- and αα- isomers have very similar free energies.

Kinetics

Base hydrolysis of [Co(tetren)O_2CR]$(ClO_4)_2$ complexes was studied by the pH stat technique, at 25°C, under pseudo first order conditions. For the complexes with R = (CH_3, C_2H_5, CH_2Cl and $CHCl_2$) plots of $\log(V_\infty-V_t)$ versus time gave curved plots implying the presence of two isomers. Using extrapolation techniques these plots were resolved to give separate pseudo first order rate constants for the two reactions which are designated "fast" and "slow". Both the "fast" and "slow" reactions obey a rate law of the form rate = k_{OH}[[Co(tetren)-$O_2CR]^{2+}$][OH^-] with $k_{OH} = k_{obs}/[OH^-]$. For the complex [Co(tetren)OOCH]$(ClO_4)_2$ only one base hydrolysis reaction was observed as plots of $\log(V_\infty-V_t)$ versus time were linear over four half-lives. The rate of this reaction is comparable with the "slow" reactions for [Co(tetren)O_2CR]$(ClO_4)_2$ R = (CH_3, C_2H_5, CH_2Cl and $CHCl_2$) and is hereafter referred to as the [Co(tetren)OOCH]$(ClO_4)_2$ "slow" reaction.

TABLE 1.24

Base hydrolysis of "slow" $[Co(tetren)OOCH](ClO_4)_2$

pH stat kinetic data at 25°C and I = 0.1 mol dm^{-3} (KNO_3)

pH	$10^6[OH^-]$ (mol dm^{-3})	10^3k_{obs} (s^{-1})	$k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
8.41	3.35	0.51	153
8.70	6.54	0.99	152
8.89	10.13	1.60	158
8.99	12.76	1.95	152

The mean value for the overall second order rate constant $k_{OH} = k_{obs}/[OH^-]$ is 153 dm^3 mol^{-1} s^{-1}. By linear regression analysis k_{OH} = (155 ± 4.5) dm^3 mol^{-1} s^{-1}.

TABLE 1.25

Base hydrolysis of "slow" $[Co(tetren)O_2CCH_3](ClO_4)_2$

pH stat kinetic data at 25°C and I = 0.1 mol dm^{-3} (KNO_3)

pH	$10^5[OH^-]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
8.80	0.82	1.91	23.0
9.18	1.97	5.28	26.7
9.27	2.45	6.43	26.2
9.37^5	3.06	7.55	24.6
9.39	3.20	8.52	26.5

The mean value for the overall second order rate constant k_{OH} = 25.4 dm^3 mol^{-1} s^{-1}. By linear regression analysis k_{OH} = (26.4 ± 1.5) dm^3 mol^{-1} s^{-1}.

TABLE 1.26

Base hydrolysis of "slow" $[Co(tetren)O_2CC_2H_5](ClO_4)_2$

pH stat kinetic data at 25°C and I = 0.1 mol dm^{-3} (KNO_3)

pH	$10^5[OH^-]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
8.90_5	1.05	1.98	18.8
9.04	1.43	2.23	15.6
9.30	2.60	4.40	16.9
9.40	3.28	6.00	18.3
9.57	4.85	8.30	17.1
9.71	6.69	11.10	16.6

The mean value for the overall second order rate constant k_{OH} = 17.2 dm^3 mol^{-1} s^{-1}. By linear regression analysis k_{OH} = (16.6 ± 0.56) dm^3 mol^{-1} s^{-1}.

TABLE 1.27

Base hydrolysis of "slow" $[Co(tetren)O_2CCH_2Cl](ClO_4)_2$

pH stat kinetic data at 25°C and I = 0.1 mol dm^{-3} (KNO_3)

pH	$10^7[OH^-]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
7.29	2.54	0.38	149
7.70	6.54	1.12	171
8.20	20.69	3.45	165
8.49	40.35	6.60	163

The mean value for the overall second order rate constant k_{OH} = 162 dm^3 mol^{-1} s^{-1}. By linear regression analysis k_{OH} = (163 ± 1.7) dm^3 mol^{-1} s^{-1}.

Kinetic plot for the base hydrolysis reaction of an isomer mixture of $[Co(tetren)O_2CC_2H_5](ClO_4)_2$ at 25°C
$I = 0.1$ mol dm^{-3} (KNO_3) pH = 8.90_5

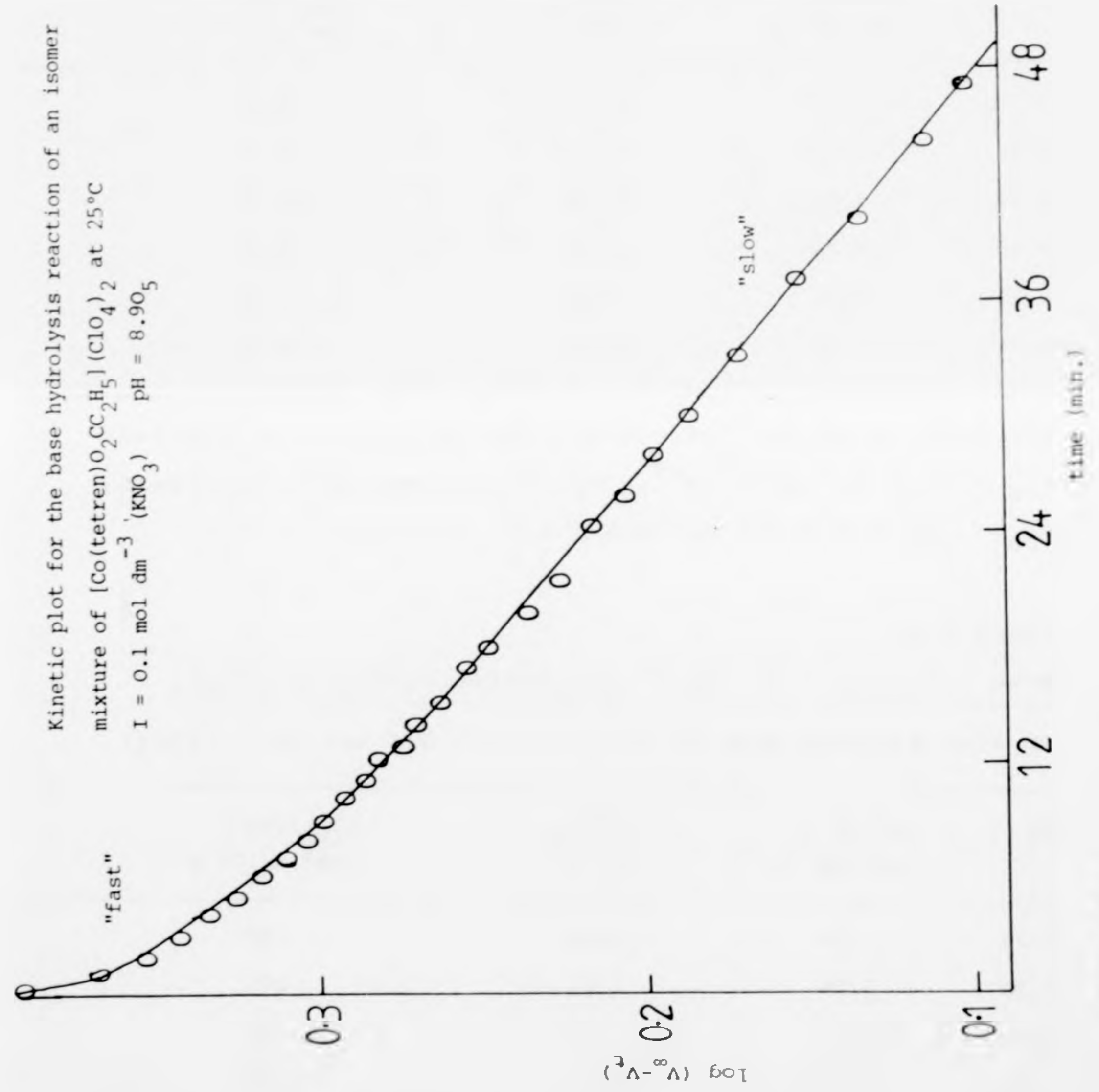


Figure 1.17

TABLE 1.28

Base hydrolysis of "slow" $[Co(tetren)O_2CCHCl_2](ClO_4)_2$

pH stat kinetic data at 25°C and I = 0.1 mol dm^{-3} (KNO_3)

pH	$10^7[OH^-]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$10^{-2}k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
7.65_5	5.89	4.32	7.33
7.85	9.24	7.30	7.90
7.97_5	12.32	8.82	7.15
8.00	13.05	9.62	7.35

The mean value for the overall second order rate constant $k_{OH} = 7.43 \times 10^2$ dm^3 mol^{-1} s^{-1}. By linear regression analysis $k_{OH} = (7.08 \pm 0.65) \times 10^2$ dm^3 mol^{-1} s^{-1}.

For the complexes $[Co(tetren)O_2CR](ClO_4)_2$ (R = CH_3, C_2H_5, CH_2Cl, $CHCl_2$) the overall second order rate constants for the "fast" reactions have been evaluated by resolving the curved plots of $\log(V_\infty - V_t)$ versus time by an extrapolation technique. The data are summarised in Table 1.29.

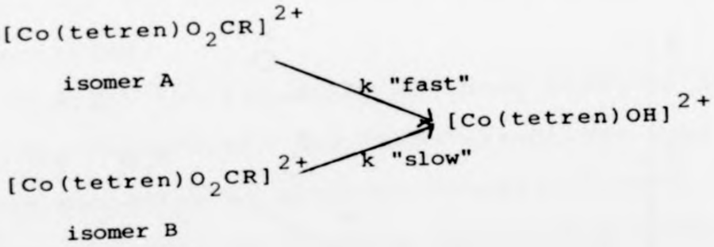
A plot of $\log(V_\infty - V_t)$ versus time for the base hydrolysis of $[Co(tetren)O_2CC_2H_5](ClO_4)_2$ is shown in Figure 1.17. The curvature is typical of plots drawn for the other $[Co(tetren)O_2CR](ClO_4)_2$ complexes and indicates that the sample contains a mixture of isomers. Base hydrolysis proceeds according to Scheme 3:

TABLE 1.29

Second order rate constants for base hydrolysis of $[Co(tetren)O_2CR](ClO_4)_2$ ($R = H, CH_3, C_2H_5, CH_2Cl, CHCl_2$)

Complex R	"fast" $k_{obs}/[OH^-]$ ($dm^3\ mol^{-1}\ s^{-1}$)		"slow" $k_{obs}/[OH^-]$ ($dm^3\ mol^{-1}\ s^{-1}$)		$\frac{k_{OH}\ \text{"fast"}}{k_{OH}\ \text{"slow"}}$
H	not detected		153	αα-	-
CH_3	4.3×10^3	αβS-	25.4		172
C_2H_5	1.0×10^3	αβR-	17.2		58
CH_2Cl	8.3×10^3		162		51
$CHCl_2$	3.6×10^4		743		48

SCHEME 3



where A is either the αβR- or αβS- isomer, B is the αα-isomer and both "fast" and "slow" reactions proceed by the same mechanism.

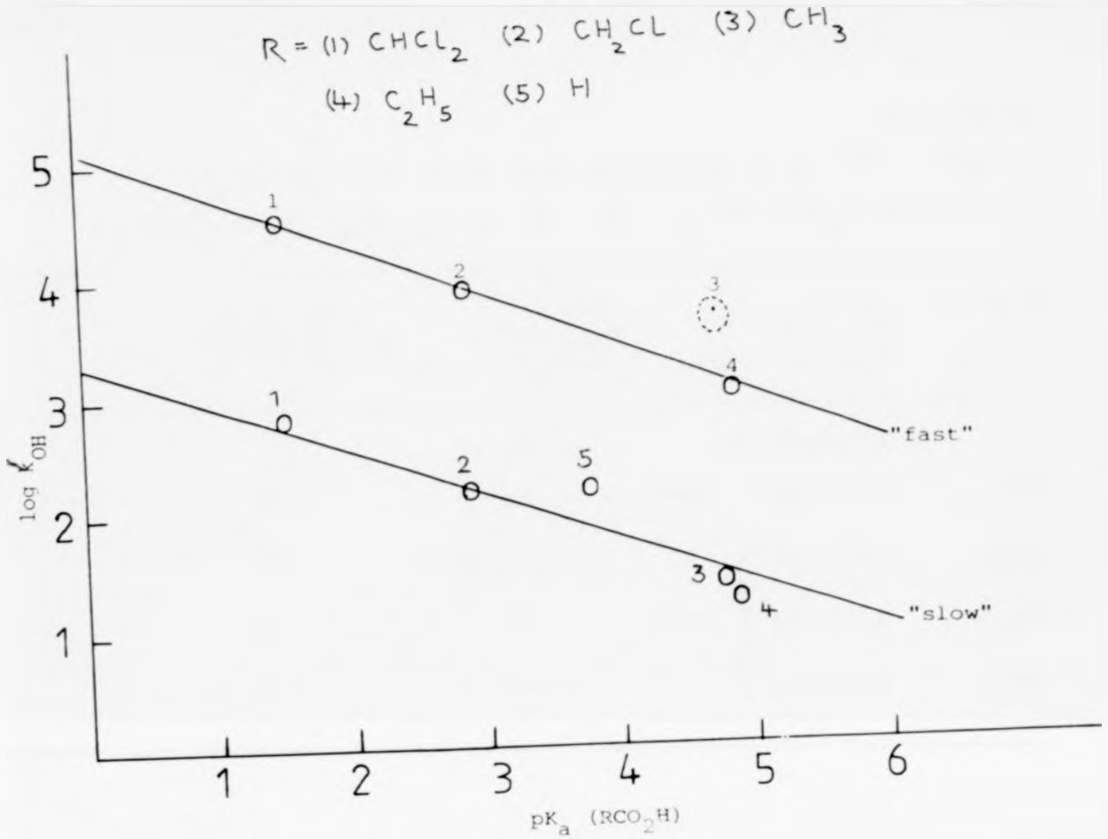


Figure 1.18

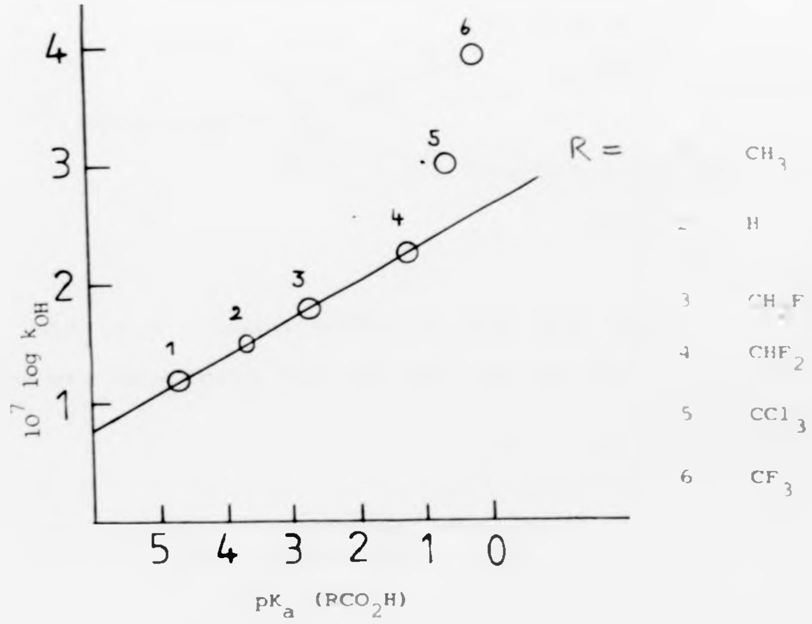


Figure 1.19

At the completion of the pH stat experiments on the "slow" reactions the pH was raised to monitor any further reaction. No additional base was consumed and the "slow" step assigned to base hydrolysis of the αα-isomers. In each pH stat run the weight of reactant complex is known and the volume of base consumed during hydrolysis was noted. A reaction stoichiometry for $[Co(tetren)O_2CR]^{2+}:OH^-$ of 1:1 was observed. The base consumption for the "slow" step in hydrolysis of $[Co(tetren)$-$O_2CR]^{2+}$ accounts for 40%-60% of the calculated value and thus the samples of $[Co(tetren)O_2CR]^{2+}$ appear to be ca. 50:50 mixtures of αβ- and αα-isomers.

A linear free energy relationship (LFER) is observed between k_{OH} for base hydrolysis of $[Co(tetren)O_2CR]^{2+}$ and the pK_a of RCOOH. Plots of k_{OH} versus pK_a for both "fast" and "slow" reactions are linear (Figure 1.18). Three possible mechanisms for base hydrolysis have been discussed in the introduction and the (LFER) can serve as a guide to assigning reaction mechanism.

Firstly, the linearity of these plots of log k_{OH} versus pK_a for both "fast" and "slow" reactions implies that the reaction mechanism is constant despite changes in the R group. A good example of a linear free energy relationship indicating a change in reaction mechanism is shown in the base hydrolysis of $[(NH_3)_5RhO_2CR]^{2+}$.[46] A plot of log k_{OH} versus pK_a (RCO_2H) is shown in Figure 1.19. Large deviations in the linear plot are found for the trifluoroacetato and trichloroacetato complexes $[(NH_3)_5RhO_2CCF_3]^{2+}$ and $[[(NH_3)_5RhO_2CCCl_3]^{2+}$. For the complexes $[(NH_3)_5RhO_2CR]^{2+}$

($R = CH_3$, H, CH_2F, CHF_2) base hydrolysis proceeds by cleavage of the Rh(III)-oxygen bond either by the SN1CB mechanism or by SN2 trans attack while for $[(NH_3)_5RhO_2CR]^{2+}$ ($R = CCl_3$,CF_3) base hydrolysis takes place by attack of OH^- at the carbonyl oxygen.

In the present work plots of log k_{OH} versus pK_a for both "fast" and "slow" base hydrolysis reactions give plots of equal slope (ρ) = 0.4. It is interesting to compare values of the reaction constant (ρ) found in the present work with those evaluated for base hydrolysis reactions of known reaction mechanism. Base hydrolysis of $[(NH_3)_5CoO_2CR]^{2+}$ ($R = CH_3$, CH_2Cl, $CHCl_2$) and $[(NH_3)_5RhO_2CR]^{2+}$ ($R = CH_3$, H, CH_2F) both have $\rho = 0.43$ [46] and are known to react by cleavage of the metal-oxygen bond as does $[Co(en)_2(OCOAr)_2]^{2+}$ with $\rho = 0.745$.[57] For the present complexes the reaction constant ($\rho = 0.4$) suggests that Co(III)-O bond cleavage is taking place. If base hydrolysis was taking place by hydroxyl ion attack on the carbonyl carbon then ρ would be expected to be ca. 2.0, comparable to the reaction constant found for the series $[(NH_3)_5RhO_2CR]^{2+}$ ($R = CH_2F$, CHF_2, CF_3) with $\rho = 1.80$ at 25°C.[46] Although the results for base hydrolysis of $[Co(tetren)O_2CR]^{2+}$ can be rationalised in terms of an SN1CB mechanism the alternative SN2 displacement reaction (trans attack) cannot be discarded, however, our experience of $[Co(tetren)X]^{n+}$ chemistry suggests that the SN1CB reaction mechanism is more likely to be operative.

Finally an examination of k_{OH} "fast"/k_{OH} "slow" ratios for base hydrolysis shows that for R = C_2H_5, CH_2Cl, $CHCl_2$ the ratio is constant ca. 52, Table 1.29, while for R = CH_3 k_{OH} "fast"/k_{OH} "slow" = 172. Examination of the linear free energy plot for the "fast" reaction shows that the experimental point for R = CH_3 lies above the best fit line. This result probably indicates that the "fast" hydrolysis reaction for $[Co(tetren)O_2CCH_3]^{2+}$ is due to the αβS-isomer while the "fast" reactions of $[Co(tetren)O_2CR]^{2+}$ (R = C_2H_5, CH_2Cl, $CHCl_2$) are due to base hydrolysis of the αβR-isomers. The "slow" reactions of $[Co(tetren)O_2CR]^{2+}$ are all assigned to base hydrolysis of the αα-isomers.

CHAPTER 3

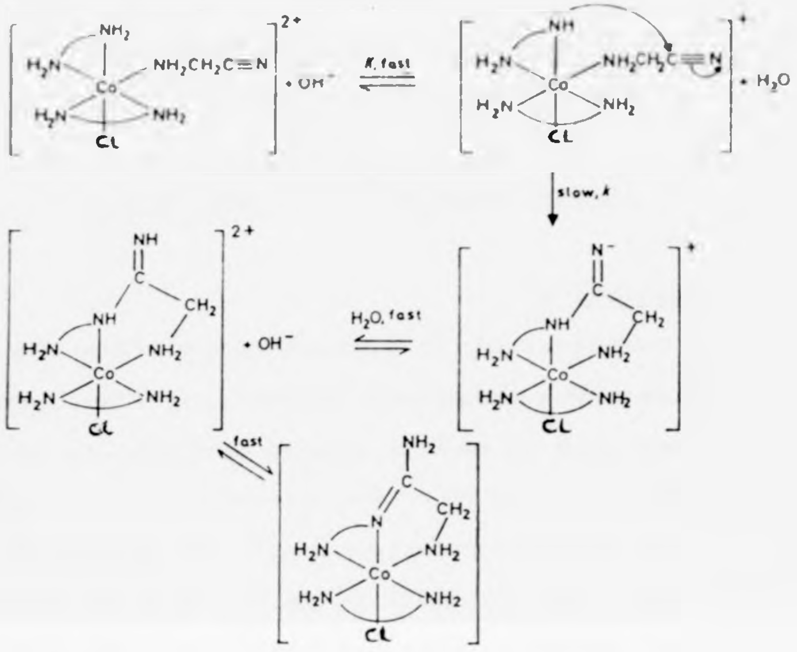
Synthesis and Kinetics of Complexes of the type $[Co(tetren)NCR]^{3+}$ $(R = CH_3, C_6H_5, p\text{-}MeOC_6H_4)$ and $[Co(tetren)N_4R]^{2+}$ $(R = CH_3, C_6H_5)$

3.1 Introduction

Coordination of organonitriles (RCN) to Co(III) pentaammines gives complexes of the type $[(NH_3)_5CoNCR]^{3+}$ in which the nitrile is end-on bonded through the nitrogen atom by σ donation to Co(III). Due to negligible π back bonding from Co(III) the coordinated nitrile is polarised by electron-donation such that the nitrile carbon becomes susceptible to nucleophilic attack. Base hydrolysis of $[(NH_3)_5CoNCR]^{3+}$ can proceed either by hydroxide ion attack on the coordinated nitrile to give the coordinated carboxamide $[(NH_3)_5CoNHCOR]^{2+}$ or by an S_N1CB displacement of NCR by OH^- to give $[(NH_3)_5CoOH]^{2+}$. Base hydrolysis studies undertaken for an extensive series of complexes of the type $[(NH_3)_5CoNCR]^{3+}$ reveal that hydroxide ion attack at the nitrile carbon atom does indeed take place leading to formation of coordinated carboxamides:[58,59,60,61]

$$[(NH_3)_5CoNCR]^{3+} \xrightarrow{OH^-} [(NH_3)_5CoNHCOR]^{2+}$$

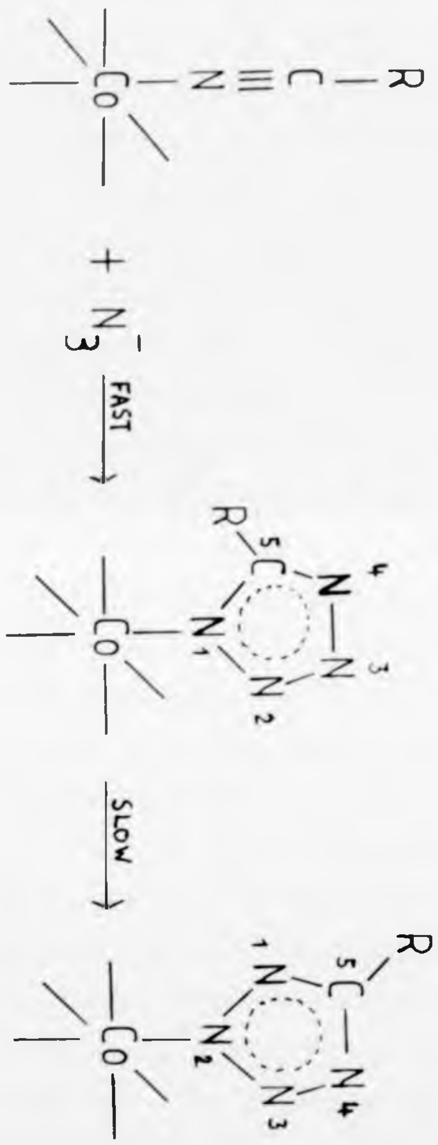
In most cases a simple second order rate law is found, with rate = $k[\text{Complex}][OH^-]$. Base hydrolysis of the coordinated nitrile is several orders of magnitude faster than that for the free nitrile. The usual conditions for hydrolysis of free nitriles to carboxamides involve concentrated acids or bases



(12)

at elevated temperatures, whereas the reactions of coordinated nitriles are virtually instantaneous in dilute base at room temperature. The rate enhancement with respect to hydrolysis of the free ligands ranges from 10^6 fold for the case of benzonitrile to 10^{11} fold for 2-cyano pyridine. The electron withdrawing influence of the $[(NH_3)_5Co]^{3+}$ group not only polarises the nitrile bond, making the carbon atom more susceptible to nucleophilic attack, but also stabilises the imino anion ($\bar{N} = C(R)OH$) which is formed by addition of hydroxide ion to the carbon atom. For coordinated nitriles having aromatic rings, electron withdrawing substituents on the ring have the same effect as the $[(NH_3)_5Co]^{3+}$ group and therefore accelerate the reaction. This point is illustrated in the base hydrolysis of $[(NH_3)_5CoNCR]^{3+}$ (R = $C_6H_4CN(3)$, $C_6H_4CN(4)$, $C_6H_4CHO(3)$, $C_6H_4CHO(4)$, $C_6H_4COCH_3(4)$) to give coordinated carboxamides. The rates are sensitive to substitution in the (3) and (4) positions on the aromatic ring.[60] Since substitution at these positions should not present any steric impediment to attack by the nucleophile, electronic effects must play a dominant role.

In near neutral or basic solution the ion $[Co(en)_2Cl(NH_2CH_2CN)]^{2+}$ undergoes rapid, base catalysed ring closure to give a tridentate amidine ligand.[62,74] This reaction shown in (12) takes place by attack of an amido group (formed by deprotonation of a nitrogen atom in (en)) on the coordinated nitrile carbon atom and results in intramolecular cyclization. However, for simple organonitriles bound to Co(III) this reaction is uncommon. One reason for studying



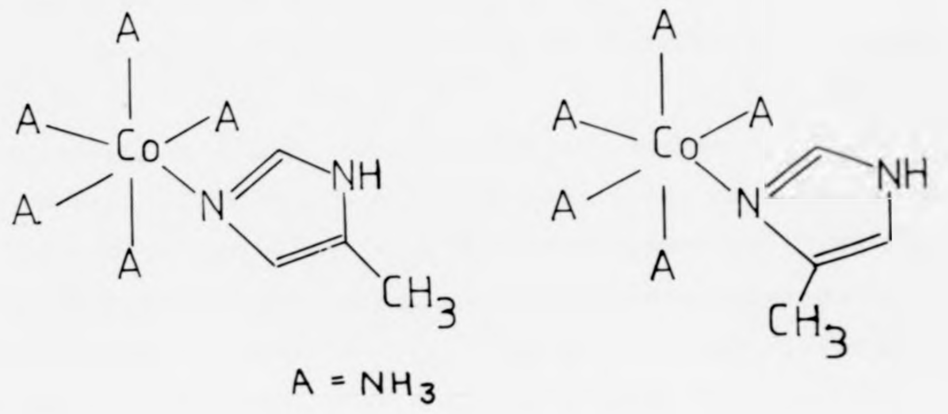
(13)

nitrile complexes of Co(III) pentaammines is that they may serve as models for the nitrilase enzymes. One such enzyme, ricinine nitrilase[63] catalyses the hydrolysis of several organic nitriles. While the mechanism of enzyme action is unknown the presence of metal ions may be necessary for catalytic activity.

A second reaction of metal bound organonitriles documented in the literature is nucleophilic attack by azide ion (N_3^-) on $[(NH_3)_5CoNCR]^{3+}$ (R = CH_3, C_6H_5) to give 5-substituted (tetrazolato)-pentamminecobalt(III) complexes bonded via the N_1 nitrogen. A slow linkage isomerisation of the N_1 species takes place to give N_2 bonded tetrazolato complexes[64,65]. The reaction scheme and ring numbering system is shown in (13).

Free tetrazoles with substituents at ring position 5 are conveniently prepared from organonitriles by nucleophilic attack by azide ion in a 1,3-dipolar cycloaddition.[66] As with nucleophilic attack by hydroxide ion on coordinated nitriles there is considerable rate enhancement for azide attack on a coordinated nitrile compared with an uncoordinated nitrile. The formation of 5-methyltetrazole from sodium azide and acetonitrile requires a reaction time of 25 hr. at 150°C compared to only 2 hr. at ambient temperature for coordinated acetonitrile. Similarly for benzonitrile the conditions are 3 hr. reaction time at 100°C in dimethylformamide versus 15 min. at ambient temperature for free and coordinated ligand, respectively.

The N_1 to N_2 linkage isomerisation reaction appears



(14)

to be driven by the steric congestion between the tetrazole ring substituent in the 5-position and the four *cis*-amines of the pentamminecobalt(111) unit, with congestion relieved in the N_2 bonding mode. The observation that the N_1-bonded 5-phenyltetrazolato complex isomerises some 6 times faster than the N_1-bonded 5-methyltetrazolato complex at 25°C in 0.01 mol dm^{-3} perchloric acid with rate constants of 1.17×10^{-4} s^{-1} and 2.8×10^{-5} s^{-1} respectively is consistent with a steric rather than electronic driving force. From consideration of ring nitrogen nucleophilicity N_1 coordination for 5-substituted tetrazolato complexes is favoured and hence electronic considerations alone would predict no isomerisation of the N_1-bonded complexes. A similar linkage isomerisation reaction occurs between the two isomeric forms of (4-methylimidazole) pentamminecobalt(111)[67] shown in (14).

In view of the interesting reactions presented above it was decided, in the present work, to prepare organonitrile complexes of Co(111) tetren and investigate the reactivity of the coordinated nitriles. Syntheses of $[Co(tetren)NCR]^{3+}$ (R = CH_3, C_6H_5, para-$MeOC_6H_4$) are described together with kinetic studies on their base hydrolysis reactions. The complexes $[Co(tetren)NCR]^{3+}$ (R = CH_3, C_6H_5) were reacted with sodium azide to give the corresponding tetrazolato complexes $[Co(tetren)N_4CCH_3]^{2+}$ and $[Co(tetren)N_4CC_6H_5]^{2+}$. Kinetic data have been collected for the reaction of the azide ion (N_3^-) with the complex $[Co(tetren)NCCH_3]^{3+}$.

3.2 Experimental

Preparations

$\alpha\alpha$-[Co(tetren)$NCCH_3$]$(ClO_4)_3$

A solution of $\alpha\alpha$-[Co(tetren)H_2O]$(ClO_4)_3$ (0.5g., 0.88 mmoles) in acetonitrile (20 cm^3) was heated at 60°C for 30 minutes. During this time a colour change from orange to yellow took place and yellow crystals deposited. The product was filtered off, washed with ethanol, ether and dried in vacuo. Calc. for $[Co(C_8H_{23}N_5)NCCH_3](ClO_4)_3$: C,20.43; H,4.46; N,14.30; Found: C,20.01; H,4.25; N,14.22%.

The i.r. spectrum (KBr) of the complex has sharp ν NH bands at 2865 and 3180 cm^{-1} with a broad ν NH in the range 3000-3150 cm^{-1}, δ NH at 1605 cm^{-1} is assigned to the NH_2 asymmetric deformations, ν C≡N is at 2320 cm^{-1} (cf. free acetonitrile ν C≡N at 2250 cm^{-1}). The visible spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 335 nm (ε = 72) and 464 (ε = 88). The synthesis of [Co(tetren)$NCCH_3$]$(ClO_4)_3$ from isomerically impure [Co(tetren)-H_2O]$(ClO_4)_3$ by the above method gave an isomer mixture of [Co(tetren)$NCCH_3$]$(ClO_4)_3$, indicated by the i.r. spectrum which shows a broad absorption band in the range 1560-1600 cm^{-1} assigned to the NH_2 asymmetric deformations.

$\alpha\alpha$-[Co(tetren)NCC_6H_5]$(ClO_4)_3$

A solution of $\alpha\alpha$-[Co(tetren)H_2O]$(ClO_4)_3$ (0.5g., 0.88 mmoles) in benzonitrile (20 cm^3) was heated at 60°C for 2 hours. During this time a colour change from orange to yellow took place with yellow crystals depositing: the product was filtered off, washed with ethanol, ether and dried in vacuo.

Calc. for $[Co(C_8H_{23}N_5)NCC_6H_5](ClO_4)_3$: C,27.73; H,4.34; N,12.93;

Found: C,26.04; H,4.03; N,12.94%.

The i.r. spectrum (KBr) of the complex has sharp ν NH bands at 2870 and 3240 cm^{-1} with a broad ν NH in the range 3000-3200 cm^{-1}. δ NH due to NH_2 asymmetric deformations is obscured by aromatic ν C=C absorptions, ν C≡N is at 2280 cm^{-1} (cf. free benzonitrile ν C≡N at 2230 cm^{-1}). The visible spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 330 nm (ε = 150) and 465 nm (ε = 145). Synthesis of [Co(tetren)-$NCC_6H_5](ClO_4)_3$ from isomerically impure $[Co(tetren)H_2O](ClO_4)_3$ leads to a mixed isomer sample of $[Co(tetren)NCC_6H_5](ClO_4)_3$.

αα-$[Co(tetren)NCC_6H_4OMe](ClO_4)_3$

Paramethoxybenzonitrile (0.17g., 1.30 mmoles) dissolved in the minimum volume of ethanol was added to a solution of αα-$[Co(tetren)H_2O](ClO_4)_3$ (0.5g., 0.88 mmoles) in 15 cm^3 of perchloric acid (0.1 mol dm^{-3}) and the mixture stirred at 60°C for three hours. At the end of this time all solvent ethanol was evaporated off. The aqueous solution was cooled, leading to precipitation of $[Co(tetren)NCC_6H_4OMe](ClO_4)_3$ and unreacted paramethoxybenzonitrile. This solid mixture was filtered off then stirred in ether to dissolve unreacted paramethoxybenzonitrile and leave product αα-$[Co(tetren)NCC_6H_4OMe]$-$(ClO_4)_3$ in the solid state. The product was filtered off, washed with ethanol, ether and dried in vacuo.

Calc. for $[Co(C_8H_{23}N_5)NCC_6H_4OMe](ClO_4)_3$: C,28.27; H,4.45; N,12.36;

Found: C,27.24; H,3.82; N,12.25%.

The i.r. spectrum (KBr) for the complex has a sharp ν NH band at 2875 cm^{-1} with a broad ν NH in the range 3000-3100 cm^{-1}. δ NH due to NH$_2$ asymmetric deformations is obscured by aromatic ν C$\overset{\cdots}{-}$C absorptions. ν C$\equiv$N is at 2275 cm^{-1} (cf. free para methoxybenzonitrile ν C$\equiv$N at 2220 cm^{-1}). The visible spectrum measured in 0.1 mol dm^{-3} HClO$_4$ has a band maximum at 466 nm.

[Co(tetren)N$_4$CCH$_3$](ClO$_4$)$_2$

The complex [Co(tetren)NCCH$_3$](ClO$_4$)$_3$ (1.0g., 1.7 mmoles) was dissolved in dilute perchloric acid and sodium azide (0.22g., 3.4 mmoles) added in small increments to the solution (fume cupboard). Throughout the addition the solution was kept at or below pH5 by adding drops of perchloric acid. The mixture was heated at 60°C for 2 hours resulting in a colour change from yellow to orange. Upon cooling, yellow crystals of product were obtained. The crystals were filtered off, washed with ethanol, ether and air dried. The crude product was recrystallised from 0.1 mol dm^{-3} HClO$_4$ to remove unreacted sodium azide.

Calc. for [Co(C$_8$H$_{23}$N$_5$)N$_4$CCH$_3$](ClO$_4$)$_2$: C,22.65; H,4.94; N,23.78;
Found: C,21.92; H,4.77; N,23.69%.

The i.r. spectrum (KBr) of the complex has a sharp ν NH at 2860 cm^{-1} with a broad ν NH in the range 3000-3200 cm^{-1}. The visible spectrum measured in 0.1 mol dm^{-3} HClO$_4$ has a broad maximum at 456 nm. A second crop of crystals from the mother liquors of this preparation is identified as [Co(tetren)-N$_3$](ClO$_4$)$_2$ with i.r. and visible spectrum parameters agreeing with literature values.[16]

$[Co(tetren)N_4CC_6H_5](ClO_4)_2$

The complex $[Co(tetren)NCC_6H_5](ClO_4)_3$ (0.4g., 0.61 mmoles) was dissolved in dilute perchloric and sodium azide (0.08g., 1.24 mmoles) added slowly (fume cupboard). The solution was kept at or below pH5 throughout the addition by occasional drops of perchloric acid. The mixture was heated at 60°C for four hours. During this time a colour change from yellow to orange took place. The solution volume was reduced under vacuum and ethanol added to precipitate yellow crystals. The product was filtered off, washed with ethanol, ether and air dried. The crude solid was recrystallised from 0.1 mol dm^{-3} $HClO_4$.

Calc. for $[Co(C_8H_{23}N_5)N_4CC_6H_5](ClO_4)_2$: C,30.42; H,4.77; N,21.88;

Found: C,29.77; H,4.70; N,21.03%.

The i.r. spectrum (KBr) of the complex has a sharp ν NH at 2880 cm^{-1} with a broad ν NH in the range 3080-3400 cm^{-1}. The visible spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has a band maximum at 468 nm.

Kinetics

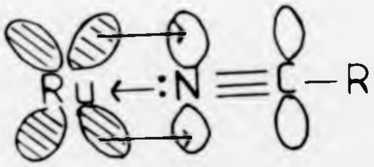
Kinetic studies were made on the base hydrolysis reactions of $[Co(tetren)NCR](ClO_4)_3$ (R = CH_3, C_6H_5, p-MeO-C_6H_4), under pseudo first order conditions, at 25°C and I = 0.1 mol dm^{-3} (KNO_3). The pH stat technique was used in the pH range 7-8.5. The possibility of carboxylation of the hydroxo complex $[Co(tetren)OH]^{2+}$ by CO_2 precluded the spectrophotometric technique for kinetic measurement. The pseudo first order rate constants were determined from the experimental data using the 16 point order programme and the Swinbourne calculation.

Spectrophotometric interval scans for the base hydrolysis reactions were obtained using freshly prepared buffers.

The kinetic study of the reaction of sodium azide with $[Co(tetren)NCCH_3](ClO_4)_3$ was made at 25°C using the spectrophotometric technique. Pseudo first order conditions were observed with $[NaN_3] > 10\ [[Co(tetren)NCCH_3](ClO_4)_3]$. Sodium azide solutions were made up in aqueous perchloric acid such that the final solution pH was ca. 5.7. When sodium azide solutions were prepared below pH 5.7, they rapidly discoloured, perhaps due to formation of HN_3 (HN_3 has pK_a = 4.7).

3.3 Results and Discussion

The reaction of $[Co(tetren)H_2O](ClO_4)_3$ with the organonitriles acetonitrile, benzonitrile and p-methoxybenzonitrile gave products which analyse as $[Co(tetren)NCCH_3](ClO_4)_3$, $[Co(tetren)NCC_6H_5](ClO_4)_3$ and $[Co(tetren)NCC_6H_4OMe](ClO_4)_3$ respectively. Visible electronic spectra for these complexes have band maxima at ca. 460 nm. characteristic of a CoN_6 chromophore. Two bonding modes are possible for Co-NCR, these are (a) end-on bonding through the nitrogen atom, or (b) side-on bonding through C≡N. The i.r. spectra of many metal-nitrile complexes of known structure have been studied and the stretching frequency of ν C≡N has been found to be characteristic of the type of bonding.[56] When NCR coordinates to the metal ion by side-on π bonding the stretching frequency ν C≡N tends to be lower than ν C≡N of the uncomplexed nitrile. When the nitrile is end-on bonded to the metal ion through the nitrile nitrogen atom, ν C≡N depends on the electronic nature of the metal ion. A bond is formed by sigma donation from the nitrile nitrogen to the metal ion but when the metal ion has strong π donation ability then back bonding of electrons from the metal to the ligand takes place and ν C≡N is shifted to a lower frequency than ν C≡N of uncoordinated RCN. For metal ions with little or no back donation ability the C≡N stretching frequency is shifted to a higher frequency than that of the uncoordinated RCN as a result of the inductive effect of the metal ion. To give an example, it is found that ν CN of benzonitrile (2231 cm^{-1}) shifts to a higher frequency (2267 cm^{-1}) when coordinated to the pentammine ruthenium(111), but to a lower frequency (2188 cm^{-1}) when coordinated to the pentammine ruthenium(11). A representation of the bonding is shown in structure (15).



(15)

The i.r. data for ν C≡N of $[Co(tetren)NCR]^{2+}$ are shown in Table 1.30.

TABLE 1.30

I.r. absorption bands (cm^{-1}) for ν C≡N of $[CoN_5NCR]^{3+}$.

R	$^a[Co(tetren)NCR]^{3+}$	$[(NH_3)_5CoNCR]^{3+}$	a free nitrile RCN
CH_3	2320	2320^b	2250
C_6H_5	2280	2270^c	2230
p-MeO-C_6H_4	2275	-	2220

All spectra were recorded as KBr discs.

a. present work; b. reference 68; c. reference 59.

Comparing ν C≡N for the free nitriles and the complexes $[Co(tetren)NCR]^{3+}$ the shift to higher frequency upon complexation is consistent with end-on bonding through the nitrogen atom with very little back-bonding from Co(III) to the nitrile taking place.

Although the samples prepared are analytically pure it was necessary to establish their isomeric purity. Purity was ascertained by kinetic studies of their base hydrolysis reactions and it was found that reaction of αα-$[Co(tetren)H_2O](ClO_4)_3$ with the corresponding organonitriles gave isomerically pure αα-$[Co(tetren)NCR](ClO_4)_3$ (R = CH_3, C_6H_5, p-MeO-C_6H_4) while isomerically impure $[Co(tetren)H_2O](ClO_4)_3$ gave $[Co(tetren)NCR](ClO_4)_3$ containing a mixture of isomers. The use of infra-red spectra for determining isomers by considering δ NH for the NH_2 asymmetric deformation is limited for $[Co(tetren)NCC_6H_5](ClO_4)_3$ and $[Co(tetren)NCC_6H_4OMe](ClO_4)_3$

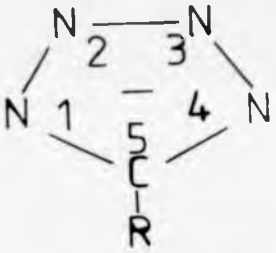
due to ν C$=$C absorptions from the aromatic rings occupying this region of the spectrum. However, $\alpha\alpha$-$[Co(tetren)NCCH_3](ClO_4)_3$ was found to have δ NH as a strong sharp band at 1600 cm^{-1} while isomerically impure $[Co(tetren)NCCH_3](ClO_4)_3$ had a broad absorption in the range 1550-1600 cm^{-1} due to NH_2 asymmetric deformations.

The collection of ^{13}C NMR data for the purposes of distinguishing between isomers and assessing the amount of electronic shielding on the nitrile carbon atom, and hence its susceptibility to nucleophilic attack proved difficult due to the insolubility of the complexes in most solvents. The complexes are freely soluble in dimethyl sulphoxide but undergo a rapid colour change suggesting formation of $[Co(tetren)$-$DMSO]^{3+}$.

The tetrazolato complexes $[Co(tetren)N_4CCH_3](ClO_4)_2$ and $[Co(tetren)N_4CC_6H_5](ClO_4)_2$ were isolated by reaction of sodium azide in acidic solution with $[Co(tetren)NCCH_3](ClO_4)_3$ and $[Co(tetren)NCC_6H_5](ClO_4)_3$ respectively. An acidic reaction medium is required to suppress base hydrolysis. The yellow crystalline tetrazolato complexes were found to be free of unreacted $[Co(tetren)NCR]^{3+}$ with i.r. spectra showing the absence of ν C$\equiv$N.

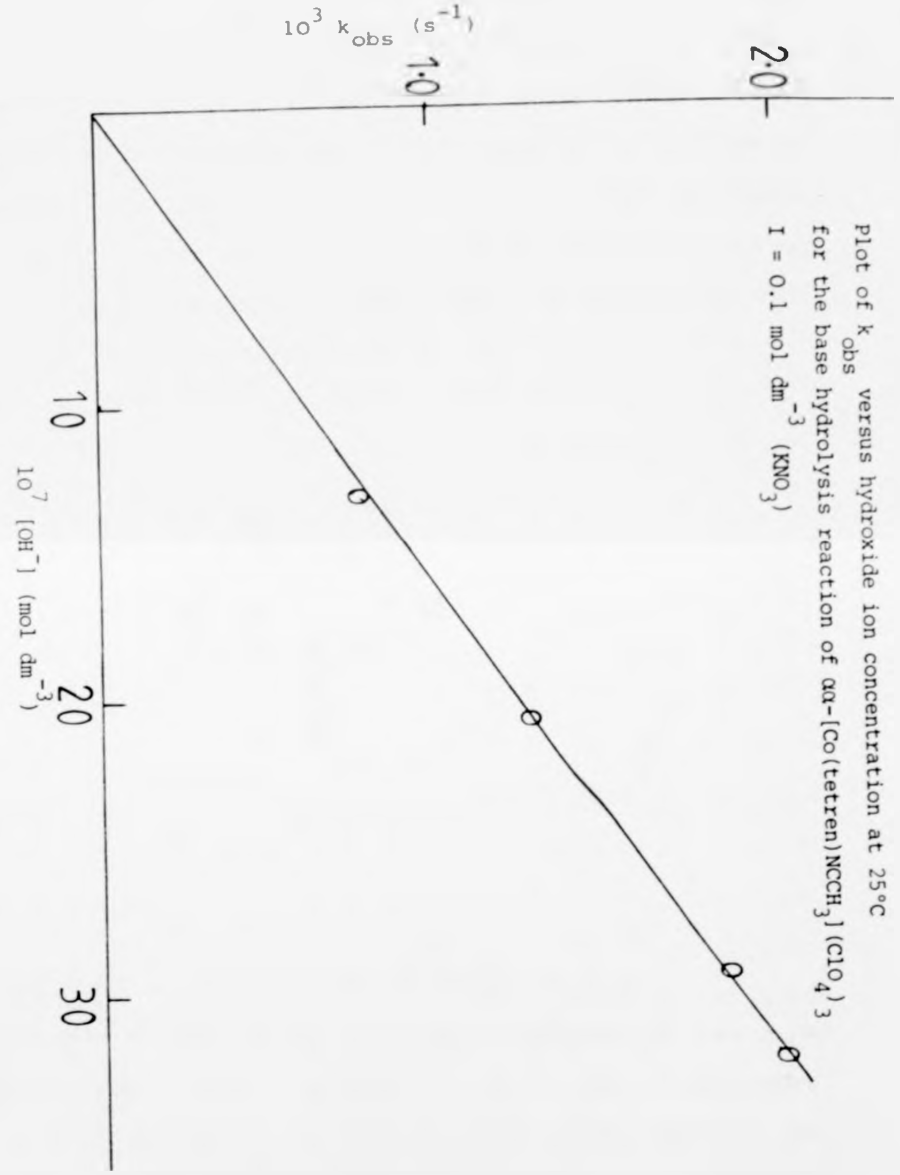
While the preparative methods given resulted in isolation of the tetrazolato complexes subsequent crops of product from the mother liquors of these reactions were identified as $[Co(tetren)N_3]^{2+}$, formed by direct replacement of NCR with N_3^-.

Although several isomeric forms are possible for the tetrazolato complexes (arising from folding of the tetren ligand) a second type of isomerism can occur depending on the mode of bonding of the tetrazolato ligand to Co(III). The tetrazolato anion could function as an n^5 π-bonding ligand, however, no evidence for this bonding mode has been found. Sigma bonding possibilities exist for the ligand, with the non-equivalent ring nitrogens serving as donor atoms. The tetrazolato ring numbering scheme is shown in (16).



(16)

For 5-substituted tetrazolato complexes both N_1- and N_2-bonded complexes are possible and have been identified for $[(NH_3)_5CoN_4CCH_3]^{2+}$ and $[(NH_3)_5CoN_4CC_6H_5]^{2+}$. By analogy with these complexes it seems likely that the tetrazolato complexes of Co(III) tetren prepared in the present work consist of mixtures of N_1 and N_2 bonded isomers.



Plot of k_{obs} versus hydroxide ion concentration at 25°C for the base hydrolysis reaction of αα-[Co(tetren)NCCH$_3$](ClO$_4$)$_3$ I = 0.1 mol dm^{-3} (KNO$_3$)

Figure 1.20

Kinetics

The base hydrolysis of αα-[Co(tetren)NCCH$_3$](ClO$_4$)$_3$ was studied by pH stat and the kinetic data obtained are summarised in Table 1.31.

TABLE 1.31

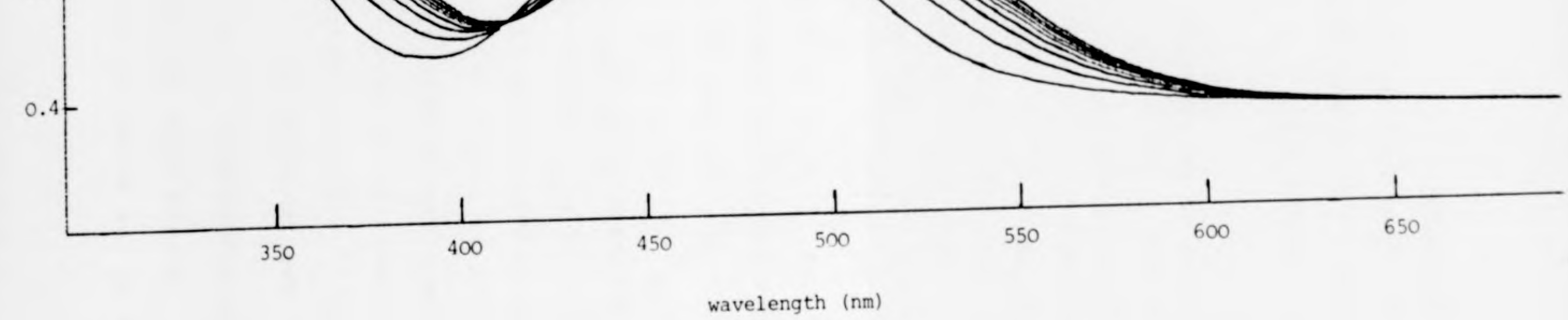
Base hydrolysis of αα-[Co(tetren)NCCH$_3$](ClO$_4$)$_3$ by pH stat at 25°C and I = 0.1 mol dm^{-3} (KNO$_3$)

pH	10^6[OH^-] (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})	$10^{-2} k_{obs}$/[OH^-] (dm^3 mol^{-1} s^{-1})
8.00	1.30	0.78	6.00
8.20	2.07	1.28	6.18
8.35	2.92	1.85	6.33
8.39	3.20	2.00	6.25

The mean value for the overall second order rate constant at 25°C is k_{OH} = 6.19 x 10^2 dm^3 mol^{-1} s^{-1}. A linear regression analysis gives k_{OH} = (6.48 ± 0.1) x 10^2 dm^3 mol^{-1} s^{-1}. The plot of k_{obs} versus [OH^-] is shown in Figure 1.20 and a typical interval scan spectrum of the base hydrolysis is shown in Figure 1.21. Isosbestic points are observed at 412 and 465 nm. The visible spectrum of the product of the reaction is identical to that of an authentic sample of [Co(tetren)OH]$^{2+}$ with band maxima of equal intensity at 350 and 490 nm. The reaction is:

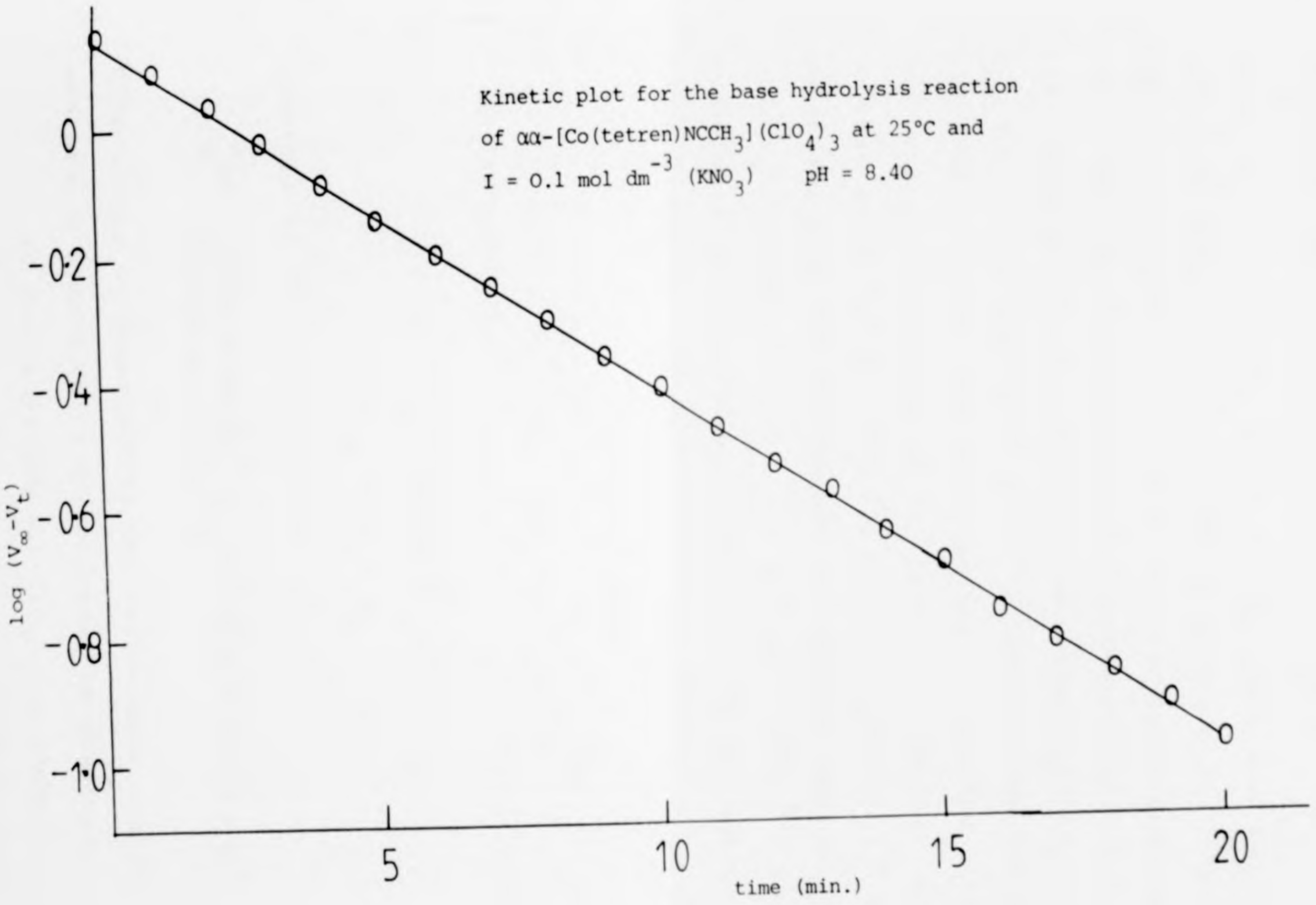
$$[Co(tetren)NCCH_3]^{3+} + OH^- \rightarrow [Co(tetren)OH]^+ + CH_3CN.$$

The results indicate that the sample of αα-[Co(tetren)NCCH$_3$]-(ClO$_4$)$_3$ used in the study is isomerically pure with plots of



Absorbance changes for the base hydrolysis reaction of αα-[Co(tetren)$NCCH_3$]$(ClO_4)_3$ at 25°C I = 0.1 mol dm^{-3} ($NaClO_4$) pH = 7.81

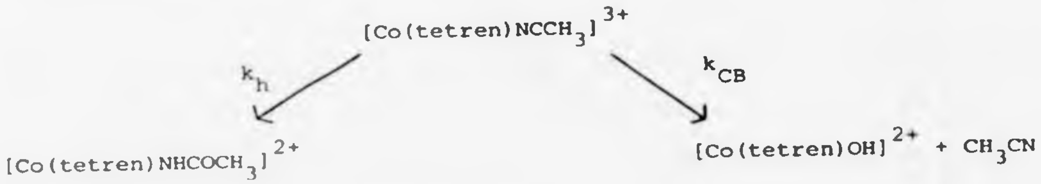
Figure 1.21



Kinetic plot for the base hydrolysis reaction of αα-[Co(tetren)$NCCH_3$]$(ClO_4)_3$ at 25°C and I = 0.1 mol dm^{-3} (KNO_3) pH = 8.40

Figure 1.22

$\log(V_\infty - V_t)$ versus time giving linear plots over four half-lives. A typical plot is shown in Figure 1.22. Close agreement was found between experimental and calculated base consumption for a reaction stoichiometry $[Co(tetren)NCCH_3](ClO_4)_3:OH^-$ of 1:1. Base hydrolysis of αα-$[Co(tetren)NCCH_3](ClO_4)_3$ has $k_{OH} = 6.2 \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$. If the reaction was taking place by hydroxide ion attack at the coordinated nitrile then the rate constant would be expected to be smaller, similar to that found for the reaction of $[(NH_3)_5CoNCCH_3]^{3+}$ with OH^- which leads to the coordinated carboxamido complex $[(NH_3)_5CoNHCOCH_3]^{2+}$ ($k_{OH} = 3.5\ dm^3\ mol^{-1}\ s^{-1}$).[61] For base hydrolysis of the $[Co(tetren)NCCH_3]^{3+}$ complex Scheme 4 can be considered.



Scheme 4

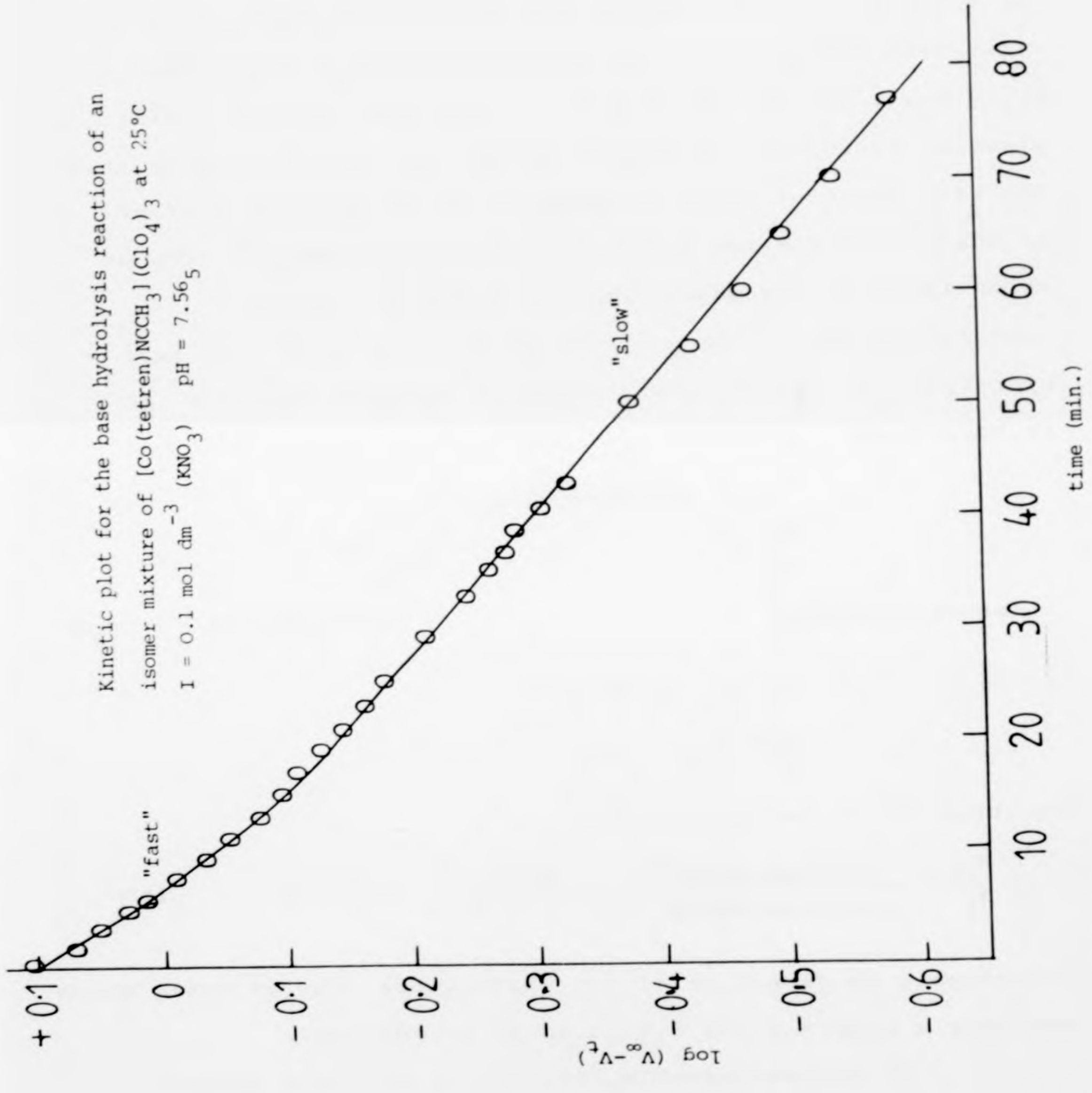
$$\text{with } k_{OH} = k_{CB} + k_h \qquad (11)$$

Equation 12 can be estimated:

$$\frac{k_{CB}}{k_h} = \frac{[[Co(tetren)OH]^{2+}]}{[[Co(tetren)NHCOCH_3]^{2+}]} \approx \frac{6.2 \times 10^2}{3.5} \approx 1.77 \times 10^2 \qquad (12)$$

Effectively no formation of the carboxamido complex takes place and only a simple SN1CB displacement is observed.

If $[Co(tetren)NCCH_3](ClO_4)_3$ is prepared from an isomerically impure sample of $[Co(tetren)H_2O](ClO_4)_3$ the pH stat measurements give indications of a mixture of isomeric



Kinetic plot for the base hydrolysis reaction of an isomer mixture of $[Co(tetren)NCCH_3](ClO_4)_3$ at 25°C

$I = 0.1$ mol dm^{-3} (KNO_3) pH = 7.56_5

Figure 1.23

nitrile complexes. A typical pH stat plot is shown in Figure 1.23 indicating a "fast" and "slow" reaction. These plots were resolved by extrapolation to give separate rate constants for base hydrolysis of the two isomers designated "fast" and "slow". An approximate second order rate constant for the "fast" reaction is 1.95×10^4 dm^3 mol^{-1} s^{-1}, while for the "slow" reaction the mean value of k_{OH} is 6.93×10^2 dm^3 mol^{-1} s^{-1}. A linear regression analysis gave k_{OH} "slow" = $(6.72 \pm 0.15) \times 10^2$ dm^3 mol^{-1} s^{-1}. The value for k_{OH} "slow" is in reasonable agreement with k_{OH} found for base hydrolysis of αα-$[Co(tetren)NCCH_3]$-$(ClO_4)_3$ ($k_{OH} = 6.2 \times 10^2$ dm^3 mol^{-1} s^{-1}). The slight variation is assigned to the difficulty of evaluating accurate rate constants in systems where two reactions are overlapping. The "fast" reaction is probably due to base hydrolysis of αβR- or αβS-$[Co(tetren)NCCH_3](ClO_4)_3$. Similar experiments were carried out for the complexes $[Co(tetren)NCC_6H_5](ClO_4)_3$ and $[Co(tetren)NCC_6H_4\text{-}OMe](ClO_4)_3$. The kinetic results are summarised in Tables 1.32 and 1.33.

TABLE 1.32

Base hydrolysis of αα-$[Co(tetren)NCC_6H_5](ClO_4)_3$ by pH stat at 25°C and $I = 0.1$ mol dm^{-3} (KNO_3)

pH	$10^7[OH^-]$ (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})	$10^{-3} k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
7.35	2.92	0.66	2.26
7.56	4.50	1.04	2.31
7.70	6.54	1.53	2.34
7.80	8.24	1.86	2.25

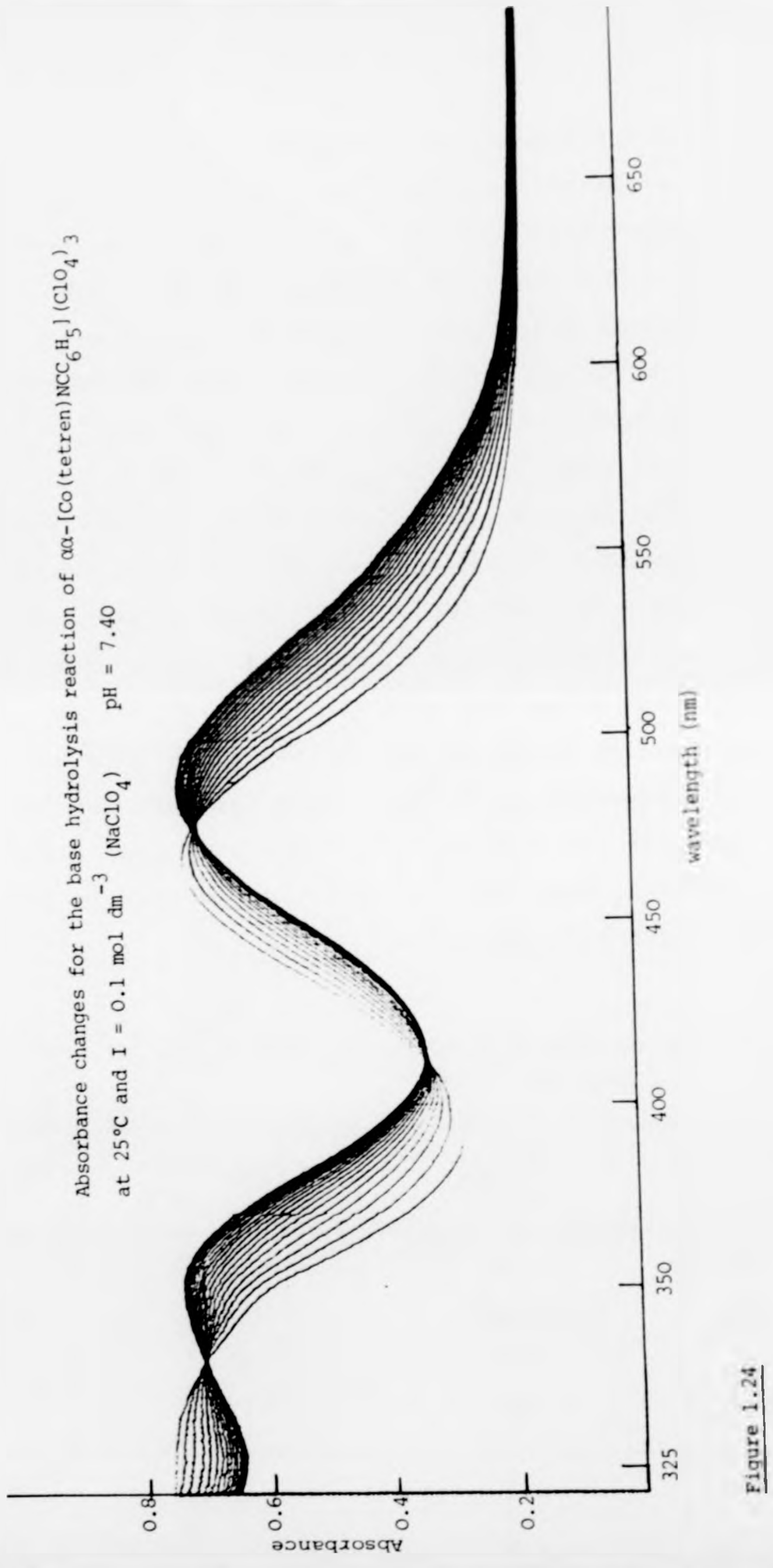
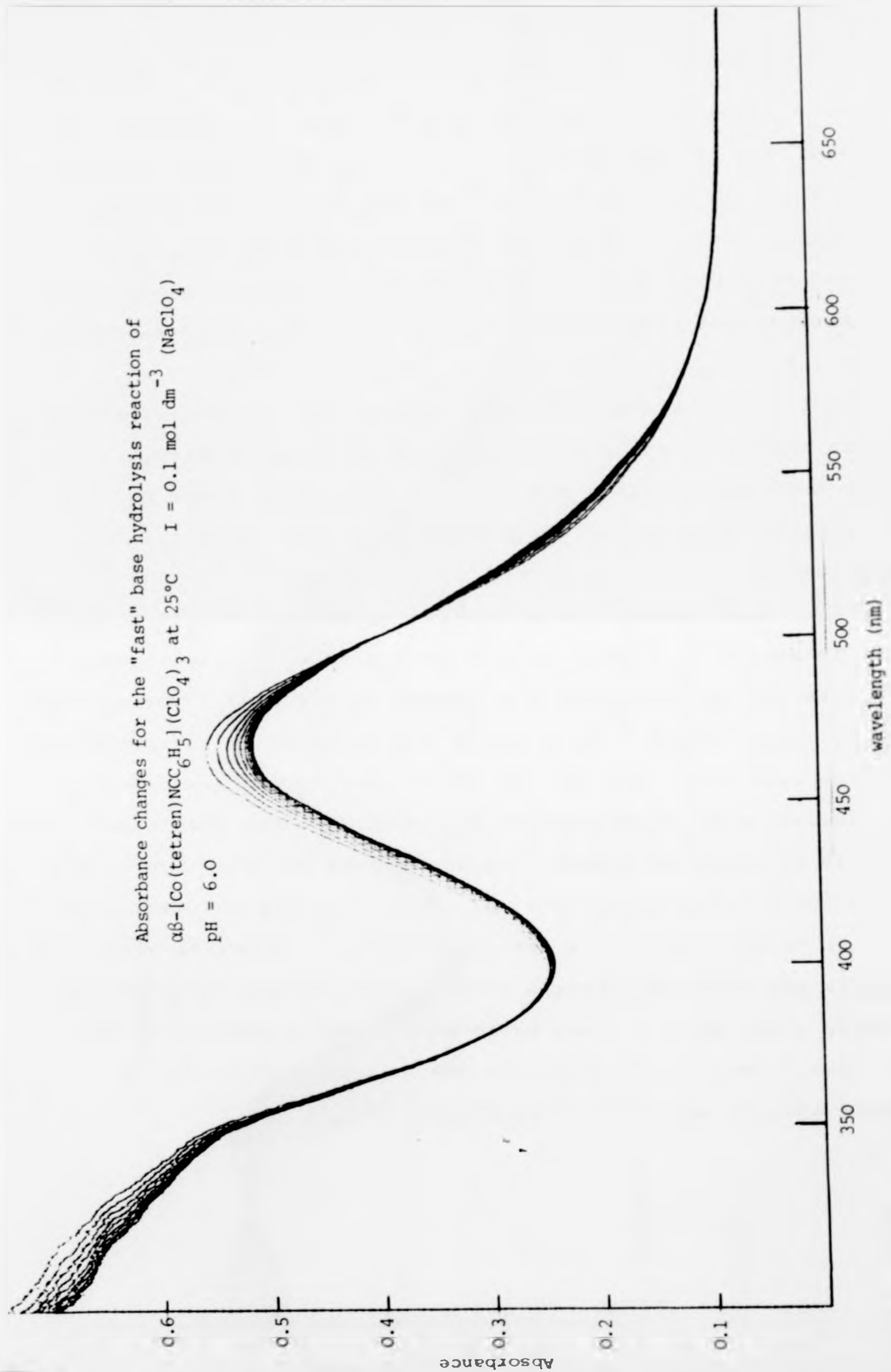


Figure 1.24

Absorbance changes for the base hydrolysis reaction of αα-$[Co(tetren)NCC_6H_5](ClO_4)_3$ at 25°C and I = 0.1 mol dm^{-3} $(NaClO_4)$ pH = 7.40

The mean value for the overall second order rate constant is $k_{OH} = 2.29 \times 10^3$ dm^3 mol^{-1} s^{-1}. A linear regression analysis gives $k_{OH} = (2.27 \pm 0.07) \times 10^3$ dm^3 mol^{-1} s^{-1}. The kinetic data imply that the sample of $[Co(tetren)NCC_6H_5](ClO_4)_3$ is isomerically pure with experimental base consumption equal to the theoretical base consumption for a reaction stoichiometry $[Co(tetren)NCC_6H_5](ClO_4)_3:OH^-$ of 1:1. Plots of $\log(V_\infty - V_t)$ versus time are linear over four half-lives. A spectrophotometric interval scan for the reaction is shown in Figure 1.24. Clean isosbestic points are found at 340, 412 and 476 nm. The visible spectrum of the product from base hydrolysis is identical to that of authentic $[Co(tetren)OH]^{2+}$.

Base hydrolysis of $[Co(tetren)NCC_6H_5](ClO_4)_3$ prepared from isomerically impure $[Co(tetren)H_2O](ClO_4)_3$ reveals the presence of two reactions with graphs of $\log(V_\infty - V_t)$ versus time giving curved plots. These plots are resolved by extrapolation to give rate constants for the "fast" and "slow" reactions. The second order rate constant k_{OH} evaluated for the "slow" step is in close agreement with that found for base hydrolysis of αα-$[Co(tetren)NCC_6H_5](ClO_4)_3$. While k_{OH} was not evaluated for the "fast" reaction a spectrophotometric interval scan reveals the spectral changes taking place during the reaction (Figure 1.25) with a clean isosbestic point found at 503 nm. The "fast" reaction is probably due to base hydrolysis of either αβR- or αβS-$[Co(tetren)NCC_6H_5](ClO_4)_3$.



Absorbance changes for the "fast" base hydrolysis reaction of $\alpha\beta$-[Co(tetren)NCC$_6$H$_5$](ClO$_4$)$_3$ at 25°C I = 0.1 mol dm^{-3} (NaClO$_4$)

pH = 6.0

Figure 1.25

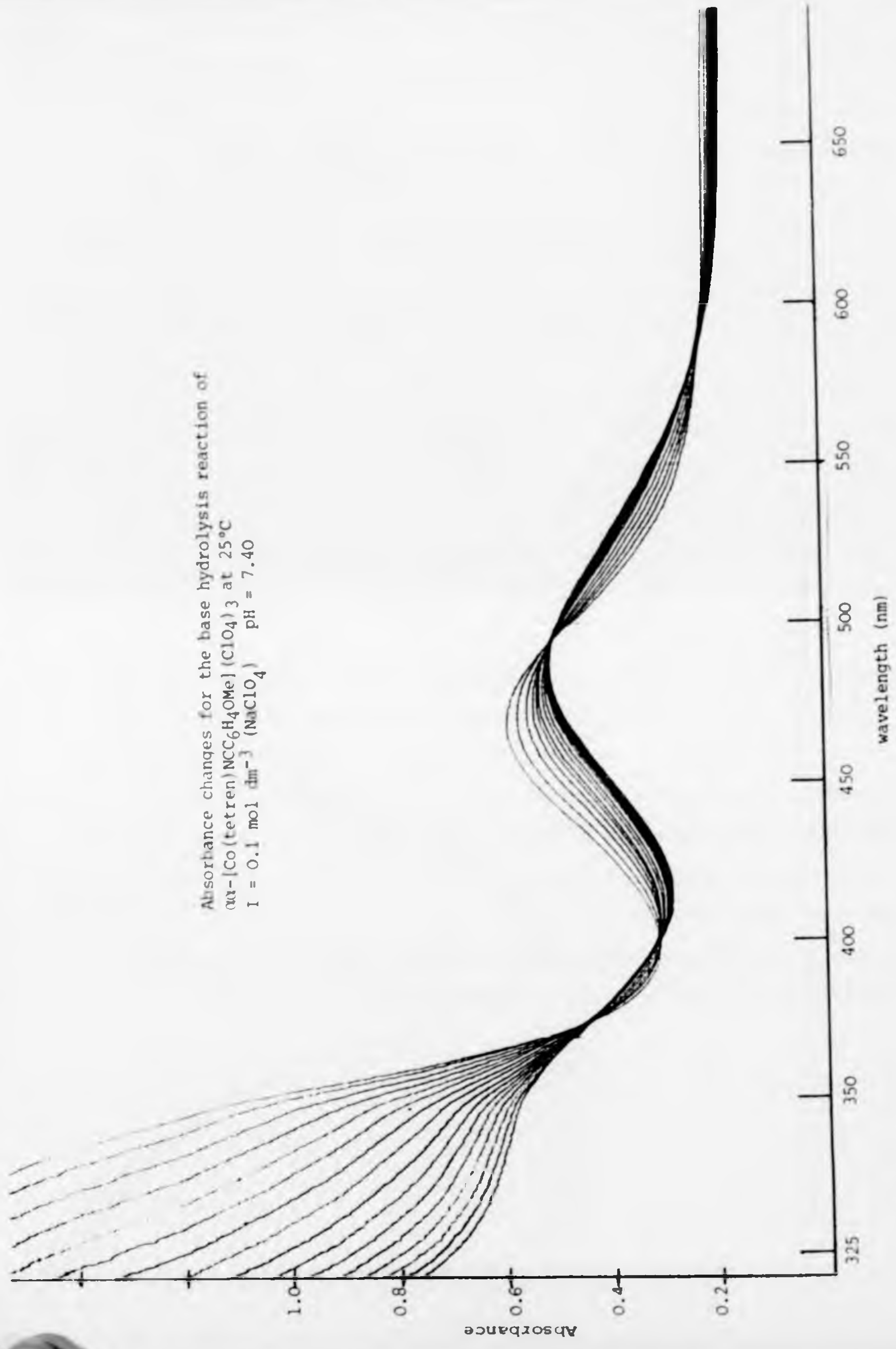
TABLE 1.33

Base hydrolysis of $\alpha\alpha$-[Co(tetren)NCC$_6$H$_4$OMe](ClO$_4$)$_3$ by pH stat at 25°C and I = 0.1 mol dm^{-3} (KNO$_3$)

pH	10^7[OH$^-$] (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})	$10^{-2} k_{obs}$/[OH$^-$] (dm^3 mol^{-1} s^{-1})
7.30	2.60	0.17	6.53
7.51	4.22	0.27	6.39
8.07	15.61	1.01	6.47
8.20	20.69	1.33	6.43

The mean value for the second order rate constant is k_{OH} = 6.45 x 10^2 dm^3 mol^{-1} s^{-1}. A linear regression analysis gives k_{OH} = (6.43 ± 0.02) x 10^2 dm^3 mol^{-1} s^{-1}. The kinetic data indicate that the complex is isomerically pure with plots of log($V_\infty - V_t$) versus time giving straight lines over four half-lives. A spectrophotometric interval scan for the reaction is shown in Figure 1.26. Isosbestic points are found at 374, 400 and 494 nm. The visible spectrum of the hydrolysed product is identical to that of an authentic sample of [Co(tetren)OH]$^{2+}$.

The base hydrolysis kinetics for the complexes [Co(tetren)NCR](ClO$_4$)$_3$ are summarised in Table 1.34.



Absorbance changes for the base hydrolysis reaction of $\alpha\alpha$-[Co(tetren)NCC_6H_4OMe]$(ClO_4)_3$ at 25°C
I = 0.1 mol dm^{-3} ($NaClO_4$) pH = 7.40

Figure 1.26

TABLE 1.34

Base hydrolysis kinetics of [Co(tetren)NCR]$(ClO_4)_3$. (SN1CB)

Complex	k_{OH} ($dm^3\ mol^{-1}\ s^{-1}$)
$\alpha\alpha$-[Co(tetren)$NCCH_3$]$^{3+}$	6.2×10^2
$\alpha\beta$-[Co(tetren)$NCCH_3$]$^{3+}$	2×10^4
$\alpha\alpha$-[Co(tetren)NCC_6H_5]$^{3+}$	2.3×10^3
$\alpha\alpha$-[Co(tetren)NCC_6H_4OMe]$^{3+}$	6.5×10^2

Base hydrolysis of [Co(tetren)NCR]$^{3+}$ (R = CH_3, C_6H_5, p-MeO-C_6H_4) gives [Co(tetren)OH]$^{2+}$, probably by an SN1CB reaction mechanism.

An infra-red spectral comparison of ν C≡N for [Co(tetren)NCR]$^{3+}$, [$(NH_3)_5$CoNCR]$^{3+}$ and RCN shows that electron withdrawal from the nitrile bond takes place to a similar extent for [$(NH_3)_5$CoNCR]$^{3+}$ and [Co(tetren)NCR]$^{3+}$. The i.r. data are shown in Table 1.30. By analogy, as [$(NH_3)_5$CoNCR]$^{3+}$ hydrolyzes to give the coordinated carboxamido complexes, [$(NH_3)_5$CoNHCOR]$^{2+}$, then the nitrile group in [Co(tetren)NCR]$^{3+}$ should be sufficiently electrophilic to allow attack of OH^- to give [Co(tetren)NHCOR]$^{2+}$, however, a comparison of kinetic data for base hydrolysis of [Co(tetren)NCR]$^{3+}$ (Table 1.34) and [$(NH_3)_5$CoNCR]$^{3+}$ (Table 1.35) reveals that carboxamide formation does not take place in the tetren system. SN1CB displacement of coordinated NCR by OH^- is much more rapid. This result is not surprising in view of the extremely fast displacement of the substituent X by OH^- in all $[Co(tetren)X]^{n+}$ systems studied so far.

TABLE 1.35

Base hydrolysis rates of $[(NH_3)_5CoNCR]^{2+}$ and free RCN

R	$[(NH_3)_5CoNCR]^{2+}$ k_{OH} ($dm^3\ mol^{-1}\ s^{-1}$)	free nitriles k_{OH} ($dm^3\ mol^{-1}\ s^{-1}$)
CH_3	3.4 [a]	1.6×10^{-6} [a]
C_6H_5	18.8 [b]	8.2×10^{-6} [b]

a. taken from reference 61 T = 25°C I = 1.0 mol dm^{-3} ($NaClO_4$)

b. taken from reference 61 T = 25.6°C

A kinetic study of the reaction of αα-$[Co(tetren)NCCH_3](ClO_4)_3$ with sodium azide was undertaken under conditions where displacement of NCR by OH^- was excluded (pH 5.7).

Interval scan spectra for the reaction in 0.068 mol dm^{-3} (NaN_3) indicated that two reactions were occurring. The final spectrum had a band maximum at 465 nm consistent with a CoN_6 chromophore. A kinetic study allowed rate constants to be evaluated for the two reactions designated "fast" and "slow". The kinetic data for the "fast" reaction are summarised in Table 1.36.

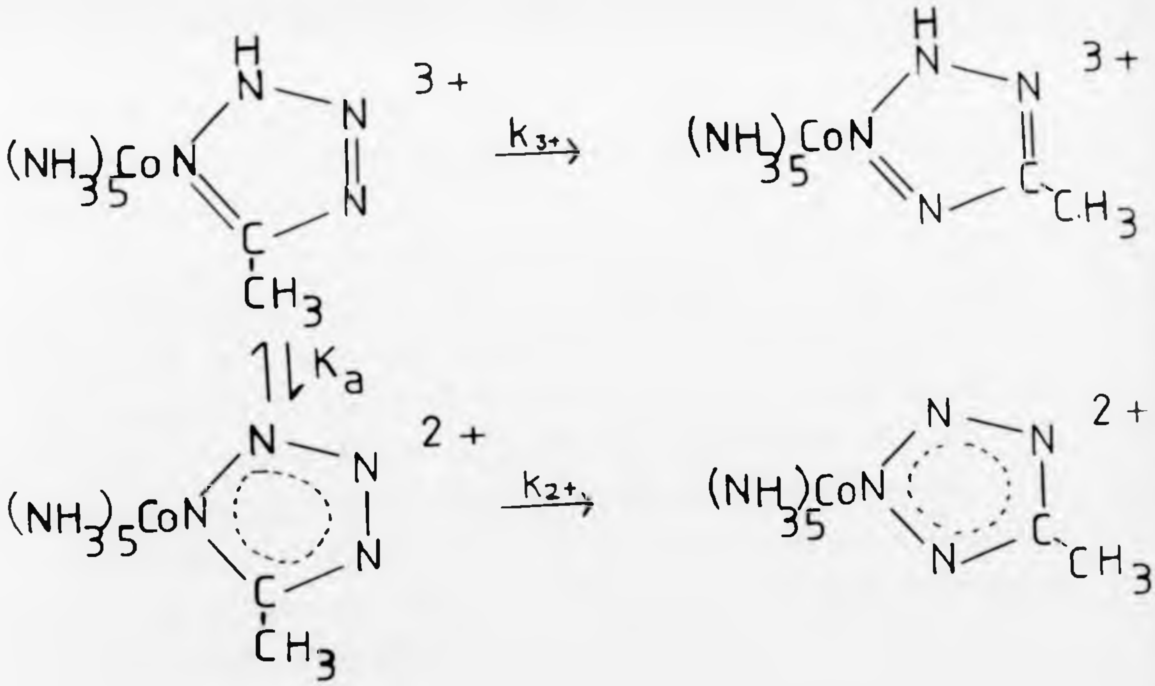
TABLE 1.36

Kinetic data for the "fast" reaction of sodium azide with αα-[Co(tetren)NCCH$_3$](ClO$_4$)$_3$ [a] at 25°C

[NaN$_3$] mol dm^{-3}	$10^3 k_{obs}$ (s^{-1})	$10^3 k_{obs}$/[NaN$_3$] (dm^3 mol^{-1} s^{-1})
0.068	1.06	15.6
0.154	2.27	14.7
0.184	3.99	21.7

a. the absorbance change was monitored at 320 nm.

While it was difficult to measure k_{obs} with a high degree of precision for the "fast" reaction the rate law was found to take the form, rate = k_{N_3}[αα-[Co(tetren)NCCH$_3$](ClO$_4$)$_3$][N$_3^-$] with the mean value of k_{N_3} = 1.72 x 10^{-2} dm^3 mol^{-1} s^{-1}. By a linear regression analysis k_{N_3} = (2.27 ± 0.9) x 10^{-2} dm^3 mol^{-1} s^{-1}. The "slow" reaction has a rate which is independent of the sodium azide concentration. The monitoring of absorbance changes due to this reaction allow k_{obs} to be evaluated, k_{obs} "slow" = 3.5 x 10^{-5} s^{-1}. Interval scan spectra for the "slow" process shows increases in absorbance at all wavelengths with very little change in band maxima. These data suggest that the "fast" reaction is azide ion attack on coordinated nitrile to give the tetrazolato complex while the "slow" reaction is a linkage isomerisation in which the donor atom of the tetrazolato ring to Co(lll) changes as shown in (13). The tetrazolato complex [Co(tetren)N$_4$CCH$_3$](ClO$_4$)$_2$ is readily isolated in the solid state from reaction of sodium azide with $[Co(tetren)NCCH_3](ClO_4)_3$. The literature shows that the rate of N_1 to N_2 linkage isomerisation for (5-methyltetrazolato) pentammine cobalt(111) is very pH dependent with the rate most rapid at low pH and slowing considerably as neutral solution is approached.[65] The mechanistic interpretation of this behaviour is to attribute different rate constants for isomerisation to the protonated and deprotonated (3^+ and 2^+) complexes (17).



(17)

The linkage isomerisation reaction of $[Co(tetren)N_4CCH_3]^{2+}$ is extremely slow at pH 5.7 with $k_{obs} = 3.5 \times 10^{-5}\ s^{-1}$. The pH dependence of the reaction was not studied, as the sodium azide solutions prepared below pH 5.7 rapidly become yellow, perhaps due to formation of HN_3 (HN_3 has $pK_a = 4.7$).

A useful comparison can be made of the second order rate constants for OH^- and N_3^- reaction with αα-$[Co(tetren)NCCH_3](ClO_4)_3$ $k_{OH} = 6.2 \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$, $k_{N_3} = 1.72 \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$. The enormous rate difference found for the reaction of these two strong nucleophiles with the same substrate αα-$[Co(tetren)NCCH_3](ClO_4)_3$ is further evidence that both reactions proceed by different mechanisms. If hydroxide was attacking the coordinated nitrile to give the coordinated carboxamide, k_{OH} would be expected to be similar to the value found for azide ion attack on coordinated nitrile to give the tetrazolato complexes.

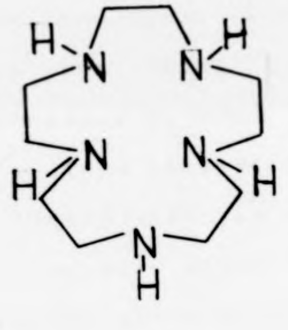
Activation parameters for the reaction of N_3^- and OH^- with $[Co(tetren)NCR]^{3+}$ were not determined. However, base hydrolysis of $[Co(tetren)NCR]^{3+}$, by an SN1CB process, to give $[Co(tetren)OH]^{2+}$ would be expected to have a large positive $\Delta S^{\neq}$ value, while the value found for base hydrolysis of $[(NH_3)_5CoNCC_6H_5]^{3+}$ to give the coordinated carboxamide has $\Delta S^{\neq} = -63.5\ J\ K^{-1}\ mol^{-1}$.[59] A substantial negative $\Delta S^{\neq}$ is also expected for azide ion attack on $[Co(tetren)NCR]^{3+}$ to give $[Co(tetren)N_4CR]^{2+}$.

CHAPTER 4

Synthesis and Base Hydrolysis Kinetics of $[Co(tetren)DMF](ClO_4)_3$

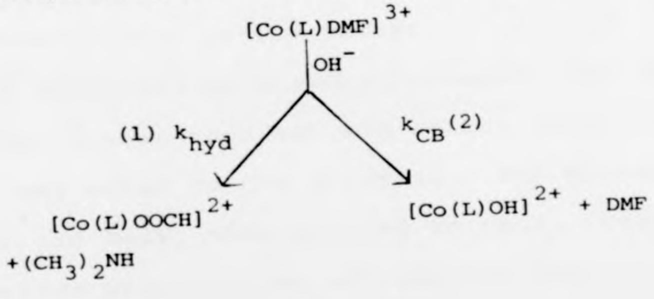
4.1 Introduction

Coordination of dimethylformamide (DMF) via the carbonyl oxygen atom to Co(III), in complexes of the type $[Co(L)DMF]^{3+}$ where L = $(NH_3)_5$ and L = $[15]aneN_5$, see structure (18), leads to a significant rate acceleration for base hydrolysis of coordinated DMF [69,70] compared with the free ligand.



(18)

Two reaction pathways have been detected (Scheme 5):



Scheme 5

The major pathway labelled (1) corresponds to hydroxide ion attack at the carbonyl centre leading to $[Co(L)OOCH]^{2+}$ and $(CH_3)_2NH$ while the minor pathway (2) leads to direct SN1CB displacement of DMF by OH^- giving $[Co(L)OH]^{2+}$ and DMF. The second order rate constants (k_{hyd}) determined at 25°C, for formation of $[Co(L)OOCH]^{2+}$ are as follows; for L = $(NH_3)_5$, $k_{hyd} = 1.3$ dm^3 mol^{-1} s^{-1},[69] for L = [15]aneN_5, $k_{hyd} = 3.2 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}.[70] Compared with hydrolysis of uncoordinated dimethylformamide,[71] amide cleavage in $[(NH_3)_5CoDMF]^{3+}$ is accelerated > 10^4 fold, a rate acceleration due solely to the entropy term. The rate of DMF cleavage is also dependent on (L) the "inert" ligand, with the rate acceleration for $[Co[15]aneN_5\ DMF]^{2+}$ being less than that for $[(NH_3)_5CoDMF]^{3+}$. This rate difference is probably due to the macrocyclic ligand with its more basic secondary nitrogen atoms donating more sigma electron density to Co(111) and thereby reducing the Lewis acidity of the central metal ion.

4.2 Experimental

The complex αα-$[Co(tetren)Cl](ClO_4)Cl$ (3.0g., 7.16 mmoles) was dissolved in dimethylformamide (10 cm^3, dried over BDH molecular sieves type 4A) and silver perchlorate (3.1g., 15 mmoles) was added to the solution. The mixture was heated at 60°C for one hour, then allowed to cool. Precipitated silver chloride was filtered off and the red filtrate was treated with ethanol to give a red oil which solidified upon trituration with ethanol. Upon standing a fine red powder settled to the bottom of the beaker. The supernatant was decanted off leaving the product which was washed twice with ethanol, ether and dried in vacuo.

Calc. for $[Co(C_8H_{23}N_5)OCHN(CH_3)_2](ClO_4)_3$: C,21.35; H,4.72; N,13.58;

Found: C,22.39; H,5.01; N,13.80%.

The i.r. spectrum (KBr) of this complex has a strong band at 1660 cm^{-1} assigned to ν C=0. The electronic spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 358 and 492 nm. A ^1H NMR spectrum of the complex was recorded in $Me_2SO\text{-}D_6$ using NaTMS as an internal reference. Two signals due to non-equivalent N-bonded methyl groups $N(CH_3)_2$ occur at 2.71δ and 2.87δ with the formyl singlet seen at 7.88δ. A ^{13}C NMR spectrum of the complex in $Me_2SO\text{-}D_6$ shows an extremely complex spectrum with forty peaks of measurable intensity.

Kinetics

The pH stat technique was used to monitor the base hydrolysis reaction of $[Co(tetren)DMF](ClO_4)_3$ at 25°C in the pH range 8.6-9.0. The ionic strength was maintained at I = 0.1 mol dm^{-3} (KNO_3). The pseudo first order rate constants were determined from the experimental data using the Swinbourne calculation.

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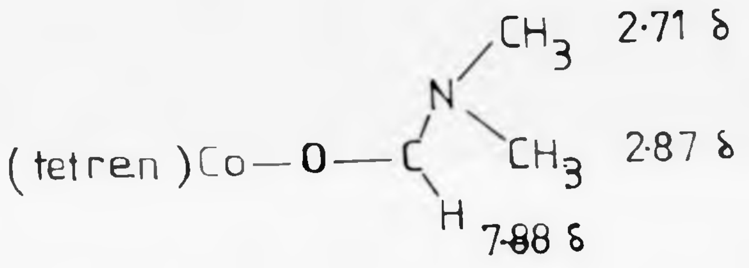

(19)

4.3 Results and Discussion

Synthesis and Stereochemistry

Analytically pure $[Co(tetren)DMF](ClO_4)_3$ was prepared by silver catalysed anation of isomerically pure αα-$[Co(tetren)Cl](ClO_4)Cl$. The DMF complex which could contain either N-bonded or O-bonded dimethyformamide was characterised by consideration of i.r., electronic and ^1H NMR spectra.

The i.r. spectrum (KBr) has ν C=0 at 1660 cm^{-1} and this stretching frequency is in close agreement with ν C=0 for similar O-bonded DMF complexes ($[(NH_3)_5CoDMF]^{3+}$ with ν C=0 at 1655 cm^{-1} and $[Co[15]aneN_5\ DMF]^{3+}$ with ν C=0 at 1660 cm^{-1}).

The visible spectrum measured in 0.1 mol dm^{-3} perchloric acid has the lowest energy ligand field band at 492 nm, identical to that for αβS-$[Co(tetren)OH]^{2+}$ and is therefore characteristic of the CoN_5O chromophore.

The O-bonded DMF structure of $[Co(tetren)DMF](ClO_4)_3$ is supported by ^1H NMR (Me_2SO-D_6 solvent). The ^1H NMR of uncoordinated DMF has <u>two</u> signals for the methyl groups on the nitrogen atom. The methyl groups are non-equivalent due to restricted rotation about the N-CO bond as a result of partial double bonding involving the lone pair on nitrogen. Two methyl signals are also seen in $[Co(tetren)DMF](ClO_4)_3$ at 2.71 and 2.87δ, with a singlet at 7.88δ which can be assigned to the formyl proton, (19). The possibility that the nitrogen atom is coordinated to Co(111) and that the two methyl signals arise from coupling to the formyl proton can be excluded as the formyl resonance occurs as a sharp singlet. The ^1H NMR data for $[Co(tetren)DMF](ClO_4)_3$ and similar systems are given in Table 1.37.

TABLE 1.37

^{1}H NMR data^{a} for [Co)L)DMF]$^{3+}$

L	formyl proton δ(ppm)	methyl protons (1) δ(ppm)	methyl protons (2) δ(ppm)
$(NH_3)_5$ ^{b}	7.43	2.88	3.03
tetren ^{c}	7.88	2.71	2.87
[15]aneN_5 ^{d}	7.96	2.73	2.90

a. data recorded in Me_2SO-D_6 with Na TMS as an internal reference;

b. taken from reference 69;

c. from present work;

d. taken from reference 70.

The ^{13}C NMR of [Co(tetren)DMF]$(ClO_4)_3$ in Me_2SO-D_6 is extremely complicated having 40 peaks of measurable intensity.

The product appears to contain several isomers of [Co(tetren)DMF]$(ClO_4)_3$. The presence of more than one isomer is confirmed by the kinetic study of base hydrolysis.

Kinetics

Interval scan spectra for base hydrolysis of [Co(tetren)DMF]$(ClO_4)_3$ show that the hydrolysed product reacts rapidly with carbon dioxide to give [Co(tetren)CO_3]$^{+}$. The large spectral changes associated with the carboxylation reaction preclude spectrophotometry as a suitable method for kinetic monitoring, and the pH stat method was therefore used.

Analysis of the kinetic data shows that two reactions are taking place with plots of $\log(V_{\infty}-V_t)$ versus time giving curved plots. These plots were resolved by extrapolation to give separate rate constants for the two reactions designated "fast" and "slow". An approximate second order rate constant for the "fast" reaction is $k_{OH} = 1.2 \times 10^4$ dm^3 mol^{-1} s^{-1}. The data for the "slow" reaction are given in Table 1.38.

TABLE 1.38

Base hydrolysis of $[Co(tetren)DMF](ClO_4)_3$. "Slow" reaction. pH stat kinetic data at 25°C and I = 0.1 mol dm^{-3} (KNO_3).

pH	$10^6[OH^-]$ mol dm^{-3}	$10^3 k_{obs}$ s^{-1}	$10^{-2} k_{obs}/[OH^-]$ dm^3 mol^{-1} s^{-1}
8.60	5.20	0.97	1.86
8.72	6.85	1.29	1.88
8.80	8.24	1.63	1.98
8.89	10.13	1.87	1.84
8.95_5	11.77	2.32	1.97

The mean value for the overall rate constant for the "slow" reaction is $k_{OH} = 1.90 \times 10^2$ dm^3 mol^{-1} s^{-1}. A linear regression analysis gives $k_{OH} = (1.99 \pm 12) \times 10^2$ dm^3 mol^{-1} s^{-1}.

Two pathways are observed for base hydrolysis of $[(NH_3)_5Co\ DMF]^{3+}$ leading to a mixture of $[(NH_3)_5CoOOCH]^{2+}$ and $[(NH_3)_5Co\ OH]^{2+}$. In the base hydrolysis of $[Co(tetren)DMF]^{3+}$ two steps are indeed observed, labelled "fast" and "slow". Both steps obey the rate law, rate = $k[[Co(tetren)DMF]^{3+}][OH^-]$, however, from our general experience of $[Co(tetren)X]^{n+}$ systems it is unlikely that hydroxide ion attack on coordinated DMF is taking place. The two steps are most probably due to SN1CB displacement of DMF in two different isomers of $[Co(tetren)DMF](ClO_4)_3$. The presence of an isomer mixture in the sample of $[Co(tetren)DMF](ClO_4)_3$ is indicated by ^{13}C NMR. For the complex, the ratio k_{OH} "fast"/k_{OH} "slow" = 63. This ratio is comparable to k_{OH} "fast"/k_{OH} "slow" found for base hydrolysis of $[Co(tetren)O_2CR]^{2+}$ (Table 1.39) and supports the view that k_{OH} "fast" corresponds to base hydrolysis of αβR-$[Co(tetren)DMF]^{3+}$ while k_{OH} "slow" corresponds to base hydrolysis of αα-$[Co(tetren)DMF]^{3+}$.

TABLE 1.39

Base hydrolysis data for $[Co(tetren)X]^{n+}$ at 25°C and $I = 0.1$ mol dm^{-3} (KNO_3)

X	k_{OH} "fast" ($dm^3 mol^{-1} s^{-1}$)	Isomer assignment	k_{OH} "slow" ($dm^3 mol^{-1} s^{-1}$)	Isomer assignment	k_{OH} "fast"/ k_{OH} "slow"
DMF	1.2×10^4	αβR-	190	αα-	63
O_2CCH_3	4.3×10^3	αβS-	25	αα-	172
$O_2CC_2H_5$	1.0×10^3	αβR-	17.2	αα-	58
O_2CCH_2Cl	8.3×10^3	αβR-	162	αα-	51
O_2CCHCl_2	3.6×10^4	αβR-	7.43×10^2	αα-	48

In some respects $[Co(tetren)DMF]^{3+}$ and $[Co(tetren)NCR]^{3+}$ are comparable systems in that both DMF and NCR are potentially susceptible to nucleophilic attack. Studies on $[Co(tetren)NCR]^{3+}$

have shown that while azide ion directly attacks the coordinated nitrile to give the coordinated tetrazole, hydroxide ion does not give the carboxamido complex. In the latter case direct displacement of NCR by OH^- occurs to give $[Co(tetren)OH]^{2+}$. By analogy, it is not surprising that base hydrolysis of $[Co(tetren)DMF]^{3+}$ takes place with displacement of DMF by OH^- to give $[Co(tetren)OH]^{2+}$ to the exclusion of hydroxide ion attack on coordinated DMF to give $[Co(tetren)OOCH]^{2+}$. If OH^- was directly attacking coordinated DMF to give $[Co(tetren)OOCH]^{2+}$ then the rate constant for the process would be expected to be of a similar magnitude to that found for azide ion attack on coordinated nitrile in $[Co(tetren)NCR]^{3+}$. The observation that the rate constants for base hydrolysis of $[Co(tetren)DMF]^{3+}$ are several orders of magnitude greater than the rate constant for azide ion attack on the coordinated nitrile in $[Co(tetren)NCCH_3]^{3+}$ ($k_{N_3} = 1.72 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}) is further support for the view that base hydrolysis of $[Co(tetren)DMF]^{3+}$ takes place by an SN1CB mechanism to give $[Co(tetren)OH]^{2+}$.

CHAPTER 5

Synthesis and Base Hydrolysis Kinetics of [Co(tetren)DMSO]$(ClO_4)_3$

5.1 Introduction

Several cobalt (111) complexes containing the dimethylsulphoxide ligand (DMSO) have been prepared including cis-[Co(en)$_2$(X)DMSO]$^{2+}$ [75,76] (X = Cl^-, Br^-, NO_2^-) and [$(NH_3)_5$CoDMSO]$^{3+}$.[77] Cobalt (111) coordinates to DMSO via the oxygen atom. In such complexes DMSO functions as a good leaving group. Reactions of [$(NH_3)_5$CoDMSO]$^{3+}$ include the oxidation of coordinated DMSO to dimethyl sulphone, using potassium permanganate.[78] The dimethyl sulphone is a poor ligand and leaves the coordination sphere of Co(111). This reaction carried out in the presence of competing ligands H_2O and Cl^- has provided evidence for the existence of the five coordinate pentammine Co(111) complex.

Base hydrolysis studies have been undertaken on pentamminecobalt(111) complexes containing neutral leaving groups,[79] that is [$(NH_3)_5$Co(L)]$^{3+}$ where L = $(NH_2)_2C{=}O$, $(CH_3)_2S{=}O$ and $(CH_3O)_3P{=}O$. The results support the SN1CB mechanism.

In the present work, the complex [Co(tetren)DMSO]$(ClO_4)_3$ has been prepared and the base hydrolysis kinetics studied.

5.2 Experimental

[Co(tetren)DMSO]$(ClO_4)_3$

The complex αα-[Co(tetren)H_2O]$(ClO_4)_3$ (0.5g., 0.88 mmoles) was dissolved in dimethylsulphoxide (DMSO) (10 cm^3) and the solution heated at 60°C for 1 hour. Upon cooling, ethanol was added to precipitate a sticky red solid. The mixture was allowed to settle and the supernatant decanted leaving the hygroscopic product which was scrubbed with ethanol then ether and dried <u>in vacuo</u>.

Calc. for $[Co(C_8H_{23}N_5)OS(CH_3)_2](ClO_4)_3$: C,19.23; H,4.68; N,11.21;

Found: C,20.52; H,4.98; N,10.07%.

The i.r. spectrum (KBr) of the complex has ν S-O at 940 cm^{-1}. The visible electronic spectrum measured in dimethylsulphoxide has band maxima at 350 and 500 nm. A ^1H NMR spectrum of the complex was recorded in D_2O containing 1 drop of DCl, Na TMS was used as an internal reference. The sulphur bonded methyl groups display a singlet at 2.70δ. ^{13}C NMR spectra of the complex, $[Co(tetren)DMSO](ClO_4)_3$ show a large number of peaks of measurable intensity and suggest that the sample is composed of a mixture of isomers.

Kinetics

Base hydrolysis of $[Co(tetren)DMSO](ClO_4)_3$ was studied spectrophotometrically at 25°C, using freshly prepared succinic acid buffer solutions. The ionic strength was maintained at $I = 0.1$ mol dm^{-3} $(NaClO_4)$.

5.3 Results and Discussion

Preparation and Stereochemical

$[Co(tetren)DMSO](ClO_4)_3$ was prepared by warming pure αα-$[Co(tetren)H_2O](ClO_4)_3$ in dimethylsulphoxide. The i.r. visible-electronic and ^1H NMR spectra recorded for the

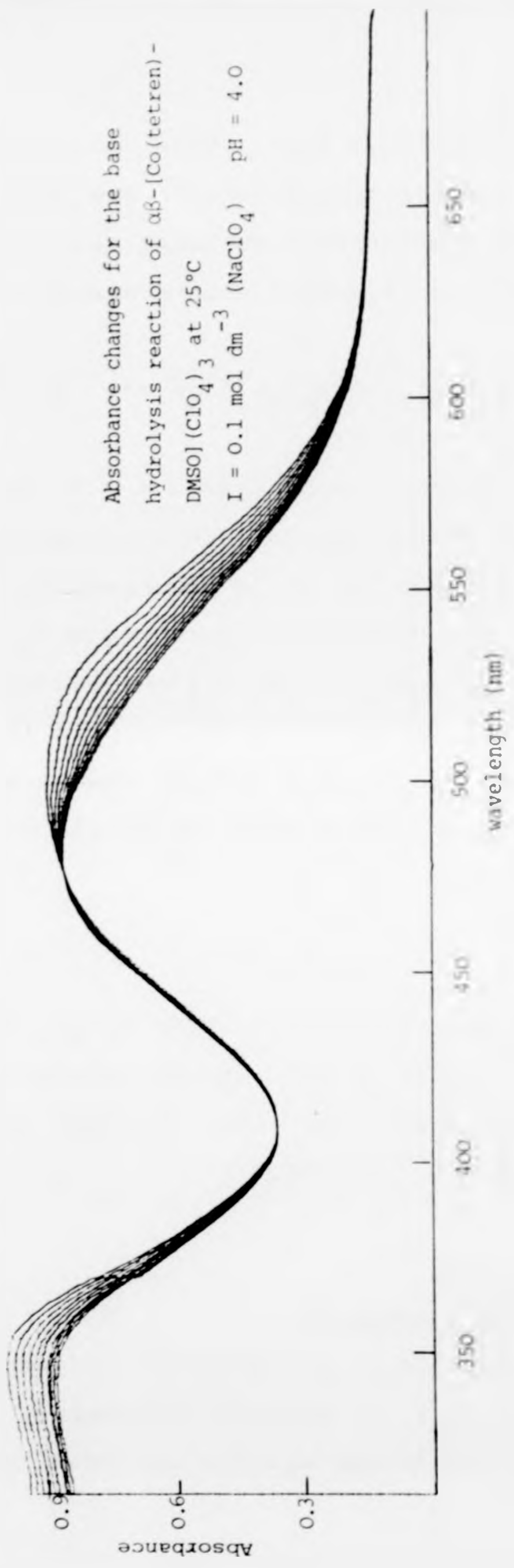

Figure 1.27

Absorbance changes for the base hydrolysis reaction of αβ-[Co(tetren)DMSO](ClO$_4$)$_3$ at 25°C

I = 0.1 mol dm^{-3} (NaClO$_4$) pH = 4.0

product are consistent with a complex having DMSO coordinated to Co(111) through the oxygen atom. The i.r. spectrum (KBr) of the complex has ν S=O at 940 cm^{-1}. This value is comparable to that for [(NH$_3$)$_5$CoDMSO]$^{3+}$ with ν S-O at 937 cm^{-1}. Uncoordinated DMSO has ν S-O at 1055 cm^{-1} while a DMSO molecule of crystallisation has ν S-O ca. 1116 cm^{-1}. The visible electronic spectrum of [Co(tetren)DMSO]$^{3+}$ has two d-d ligand field bands with maxima at 350 and 500 nm, consistent with a CoN$_5$O chromophore. The ^{1}H NMR of the complex [Co(tetren)DMSO]$^{3+}$ implies that both of the methyl groups of coordinated DMSO are equivalent, giving a singlet at 2.70δ. The ^{13}C NMR spectrum of the compound is complex. The large number of signals indicating a mixture of isomers.

Kinetics

Interval scan spectra of [Co(tetren)DMSO](ClO$_4$)$_3$ were recorded at pH 4.0. The spectral changes accompanying base hydrolysis are shown in Figure 1.27. An isosbestic point occurs at 477 nm. While the initial spectrum of [Co(tetren)-DMSO](ClO$_4$)$_3$ has a band maximum at 500 nm the spectrum of the hydrolysed product has a band maximum at 472 nm. The final spectrum is identical to that of αβR-[Co(tetren)H$_2$O]-(ClO$_4$)$_3$. Kinetic data are summarised in Table 1.40.

TABLE 1.40

Spectrophotometric data for base hydrolysis of $[Co(tetren)DMSO](ClO_4)_3$ [a] at 25°C and I = 0.1 mol dm^{-3} ($NaClO_4$)

pH	$10^{10}[OH^-]$ (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})	$10^{-6} k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
4.23	2.22	0.52	2.34
4.42_5	3.47	0.73	2.10
4.72_5	6.93	1.45	2.09
5.03_5	14.15	2.76	1.95

a. the reaction was monitored at 310 nm.

The mean value for the overall second order rate constant is $k_{OH} = 2.12 \times 10^6$ dm^3 mol^{-1} s^{-1}. Linear regression analysis gives $k_{OH} = (1.89 \pm 0.04) \times 10^6$ dm^3 mol^{-1} s^{-1}. Plots of $\log(A_\infty - A_t)$ versus time are linear for four half lives. The constant, k_{OH}, evaluated for base hydrolysis of $[Co(tetren)DMSO](ClO_4)_3$ is extremely fast relative to base hydrolysis rate constants measured for other $[Co(tetren)X]^{n+}$ systems suggesting that the reaction monitored is base hydrolysis of αβR- or αβS-$[(tetren)DMSO]^{3+}$ rather than the αα-isomer. This view is supported by the visible spectrum of the product of base hydrolysis which has a band maximum at 472 nm. Authentic αβR-$[Co(tetren)H_2O]^{3+}$ has λ_{max} 472 nm, while αα-$[Co(tetren)H_2O]^{3+}$ has λ_{max} 494 nm.

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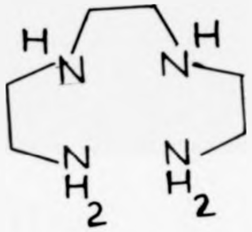
SECTION II

Syntheses and Kinetics of $[Co(trien)(A)Cl]^{2+}$ (A = unidentate amine)

Introduction

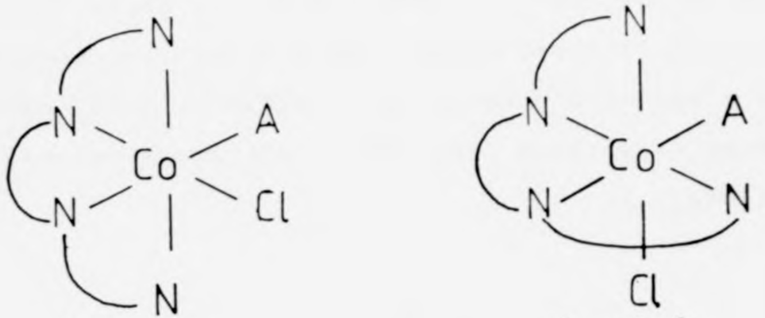
The study of the base hydrolysis reactions of Co(111) halopentaamines is continued in this Section with complexes of the type $[Co(trien)(A)Cl]^{2+}$, where trien is the quadridentate nitrogen donor ligand triethylenetetramine (1) and A is a unidentate amine (A = imidazole (ImH) n-butylamine ($BuNH_2$) pyridine (py) and 2,2-dimethoxyethylamine $NH_2CH_2CH(OCH_3)_2$).



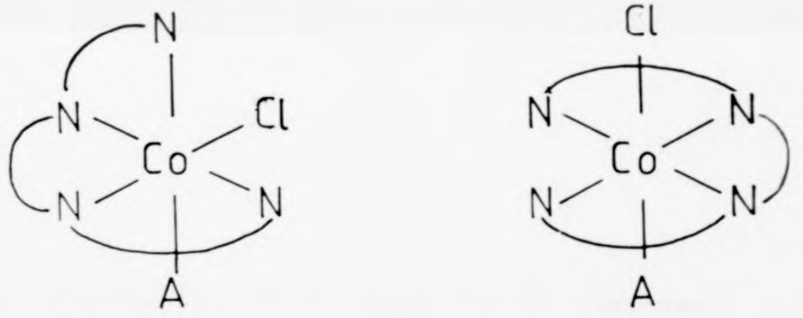
(1)

Complexes of the type $[Co(trien)(A)Cl]^{2+}$ can exist in the topological forms shown in (2)A, B, C and D. While the cis-α-isomer (2)A can exist in only one form, the trans isomer (2)D has several possible diastereoisomers. The cis-β_1 (2)C and cis-β_2 (2)B geometrical isomers have two possible diastereoisomers arising from different arrangements of the chiral nitrogen centre present in the mer ring of the trien ligand. These forms are shown in structures (3)A, B, C and D.

The cis-α-, cis-β_1- and cis-β_2- isomers are known for $[Co(trien)(H_2O)_2]^{3+}$, but for $[Co(trien)Cl_2]^+$ and all known $[Co(trien)(A)Cl]^{2+}$ complexes the cis-β_1-isomers have not been

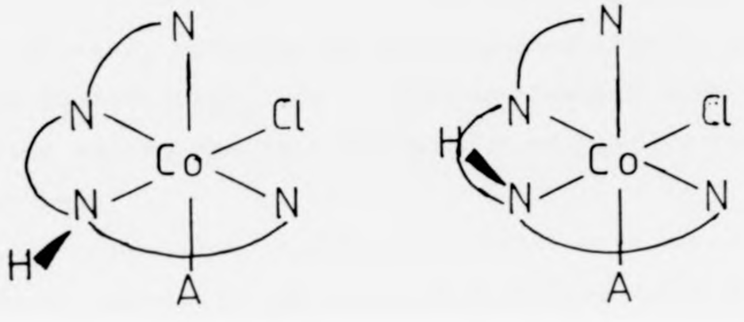


A cis-α B cis-β_2



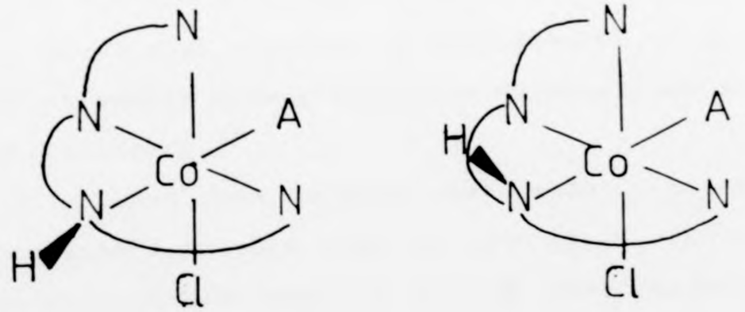
C cis-β_1 D trans

(2)



A B

cis-β_1



C D

cis-β_2

(3)

detected and the *cis*-isomers are found only in the *cis*-α- and *cis*-β_2- forms. Non-bonded interactions are responsible for the greater stability of the *cis*-β_2- form over the *cis*-β_1- form.[1]

In the literature, and in the present work, reactions of $[Co(trien)Cl_2]^+$ with amines have been confined to the *cis*-isomers of $[Co(trien)Cl_2]^+$. The complex, *trans*-$[Co(trien)Cl_2]^+$ was not used, although in an analogous system, the reaction of *trans*-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine) with a series of primary amines has been shown to give *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$ complexes.

Reaction of $[Co(trien)Cl_2]^+$ with an amine has several possible outcomes. An amine with strong donor properties will displace Cl^- to give $[Co(trien)(A)Cl]^{2+}$ but a strongly basic amine will generate hydroxide ion which may displace Cl^- to give $[Co(trien)(OH)Cl]^+$. Weak bases may lead to disproportionation of the dichloro complex to give $[Co(trien)]^{3+}$, however, it is found that reaction of $[Co(trien)Cl_2]^+$ with a wide range of amines allows isolation of complexes of the type $[Co(trien)(A)Cl]^{2+}$.

Dash[4] has reported that crude *cis*-β-$[Co(trien)Cl_2]^+$ reacts with imidazole (ImH) to give *cis*-β_2-$[Co(trien)(ImH)Cl]^{2+}$ while *cis*-α-$[Co(trien)Cl_2]^+$ reacts with imidazole to GIVE *cis*-α-$[Co(trien)(ImH)Cl]^{2+}$. Moharty and Nanda[5] found that *cis*-α-$[Co(trien)(aniline)Cl]^{2+}$ was the product from reaction of aniline with crude $[Co(trien)Cl_2]^+$ while *cis*-β_2-$[Co(trien)(aniline)Cl]^{2+}$ was synthesised from *cis*-β_2-$[Co(trien)Cl_2]^+$ and aniline. The complex *cis*-β_2-$[Co(trien)(benzimidazole)Cl]^{2+}$ was found to be the only product from reaction of either crude, cis-α- or cis-β$_2$-[Co(trien)Cl$_2$]$^+$ with benzimidazole.[5] Cis-α-[Co(trien)(glyOEt)Cl]$^{2+}$ [7] was prepared in good yield by triturating cis-α-[Co(trien)(H$_2$O)Cl]$^{2+}$ and glycine ethyl ester hydrochloride in basic medium while cis-β$_2$-[Co(trien)(glyOEt)-Cl]$^{2+}$ [8] was prepared by reaction of cis-β$_2$[Co(trien)Cl$_2$]$^+$ with glycine ethyl ester hydrochloride. Gainsford et al.[9] reported that cis-α-[Co(trien)(NH$_2$CH$_2$CH(OCH$_3$)$_2$)Cl]$^{2+}$ was the product from reaction of 2,2-dimethoxyethylamine with either cis-α- or cis-β$_2$-[Co(trien)Cl$_2$]$^+$. From the above results the relationship between the isomer geometry of the reactant [Co(trien)Cl$_2$]$^+$ and the product [Co(trien)(A)Cl]$^{2+}$ seemed worthy of further investigation.

The intention of the present work was to expand the range of known cis-[Co(trien)(A)Cl]$^+$ complexes and investigate their base hydrolysis kinetics as a function of (a) the isomer geometry of the complex and (b) the unidentate amine ligand (A). Kinetic studies have been reported on the spontaneous aquation reactions of [Co(trien)(A)Cl]$^{2+}$ complexes at elevated temperatures with rate constants for base hydrolysis obtained by extrapolation of the aquation rate data.[4,5,6,10] No independent base hydrolysis rate constants have been evaluated directly and it was hoped to rectify this position in the present work.

Experimental

Preparations

Isomerically pure samples of cis-α-[Co(trien)Cl_2]Cl and cis-β_2-[Co(trien)Cl_2]Cl were prepared and characterised by the method of Sargeson and Searle.[1]

cis-α-[Co(trien)(ImH)Cl](ClO_4)Cl

The complex cis-α-[Co(trien)(ImH)Cl]$^{2+}$ was obtained if cis-α-[Co(trien)Cl_2]Cl or cis-β-[Co(trien)Cl_2]Cl were used as the starting materials.

Method A

By the method of Dash,[10] cis-β_2-[Co(trien)Cl_2]Cl (6.23g., 20 mmoles) and imidazole (1.5g., 22 mmoles) were suspended in 10 cm^3 of water in a mortar containing a few drops of 0.1 mol dm^{-3} perchloric acid. The mixture was ground continually for 24 hours, during which time it coagulated and became purple-red. The paste was scraped out, filtered under vacuum, washed with ethanol, ether and air dried to give a crystalline solid. The crude product was dissolved in warm 0.1 mol dm^{-3} perchloric acid and left to stand. The red solid which crystallised, was filtered off, washed with ethanol, ether and air dried. An i.r. spectrum of this material shows it to be a mixture of unreacted cis-β_2-[Co(trien)Cl_2]Cl and the desired product cis-α-[Co(trien)(ImH)Cl]Cl_2. A second crop of crystals came out of the filtered solution upon further standing, these were filtered off, washed with ethanol, ether and air dried. A visible electronic spectrum shows the second crop product to be isomerically pure cis-α-[Co(trien)(ImH)Cl]-(ClO_4)Cl.

Calc. for $[Co(C_6H_{18}N_4)C_3H_4N_2Cl](ClO_4)Cl$: C,24.36; H,4.99; N,18.94;

Found: C,24.28; H,5.24; N,18.63%.

An i.r. spectrum (KBr) of the complex has two strong absorption bands at 1570 cm^{-1} and 1600 cm^{-1}. The visible electronic spectrum of the complex measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 535 nm (ε = 109) and 365 nm (ε = 111) with a shoulder at 480 nm (ε = 71). The literature[10] reports band maxima at 532 nm (ε = 105) and 360 nm (ε = 107) with a shoulder at 480 nm (ε = 76).

Method B

Cis-α-[Co(trien)Cl_2]Cl (6.23g., 20 mmoles) was suspended in 10 cm^3 water and imidazole (1.5g., 22 mmoles) added. This purple mixture was stirred at room temperature for ca. two hours during which time the supernatant became red in colour. Unreacted cis-α-[Co(trien)Cl_2]Cl was filtered off and addition of a few crystals of sodium perchlorate to the filtrate resulted in immediate crystallisation of the red-purple product. The product was filtered off, washed with ethanol, ether and recrystallised from 0.1 mol dm^{-3} perchloric acid.

Cis-β_2-[Co(trien)(py)Cl]$(ClO_4)_2$

Cis-α-[Co(trien)Cl_2]Cl (0.7g., 2 mmoles) and pyridine (py) (0.17g., 2.2 mmoles) were suspended in 1 cm^3 of water in a mortar. The mixture was ground continually for several hours until a colour change from purple to red took

place and the mixture coagulated. The paste was scraped out, filtered under vacuum and washed with ethanol and ether, giving a crystalline solid. This crude product was recrystallised from the minimum volume of 0.1 mol dm^{-3} perchloric acid.
Calc. for $[Co(C_6H_{18}N_4)C_5H_5NCl](ClO_4)_2$: C,25.47; H,4.47; N,13.50; Found: C,25.86; H,4.41; N,13.30%.
An i.r. spectrum (KBr) of the complex has a broad absorption band between 1560 cm^{-1} and 1590 cm^{-1} with a sharp absorption band at 1610 cm^{-1}. The visible electronic spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 371 nm (ε = 111) and 484 nm (ε = 113) with a shoulder at 540 nm (ε = 78) indicating the sample to be *cis*-β_2-[Co(trien)(py)Cl]$(ClO_4)_2$.

The preparation was repeated several times using both *cis*-α-[Co(trien)Cl_2]Cl and *cis*-β_2-[Co(trien)Cl_2]Cl, but in all cases the product was found to be *cis*-β_2-[Co(trien)(py)Cl]$(ClO_4)_2$.

Cis-α-[Co(trien)($BuNH_2$)Cl](ClO_4)Cl

Cis-α-[Co(trien)Cl_2]Cl (0.62g., 2 mmoles) and n-butylamine (0.16g., 2.2 mmoles) were suspended in 1 cm^3 of water in a mortar. These reagents were ground continually for three hours during which time a colour change from purple to red took place and the mixture coagulated. The paste was scraped out, filtered under vacuum and washed with ethanol giving a crystalline solid. The i.r. and electronic visible spectra identified the solid as unreacted *cis*-α-[Co(trien)Cl_2]Cl. The red ethanolic washings from the above filtration were treated with a few drops of 60% perchloric acid and left to stand until a red-violet solid crystallised out from solution. This crude product $[Co(trien)(BuNH_2)Cl]Cl_2$ was filtered off, washed with ethanol, ether and recrystallised from 0.1 mol dm^{-3} perchloric acid giving cis-α-$[Co(trien)(BuNH_2)Cl](ClO_4)Cl$.

Calc. for $[Co(C_6H_{18}N_4)(C_4H_{11}N)Cl](ClO_4)Cl$: C,26.77; H,6.51; N,15.61;

Found: C,26.90; H,6.58; N,15.65%.

An i.r. spectrum (KBr) of the complex has a sharp, strong absorption band at 1570 cm^{-1} and a broad absorption band between 1595 cm^{-1} and 1615 cm^{-1}. The visible electronic spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 366 nm (ε = 101) and 530 nm (ε = 91) with a shoulder at 490 nm (ε = 75) indicating the sample to be cis-α-$[Co(trien)(BuNH_2)Cl](ClO_4)Cl$.

Cis-α-$[Co(trien)NH_2CH_2CH(OCH_3)_2Cl]Br_2$

By the method of Gainsford et al.[9] cis-α-$[Co(trien)Cl_2]Cl$ (4.65g., 15 mmoles) was suspended in methanol (200 cm^3) containing 2,2-dimethoxyethylamine (1.57g., 15 mmoles). The mixture was refluxed for ca. 90 minutes during which time the violet starting material dissolved to form an intense red-violet solution from which violet platelets of cis-α-$[Co(trien)NH_2CH_2CH(OCH_3)_2Cl]Cl_2$ gradually deposited. After the solution was cooled the product was filtered off, washed with ethanol, ether and air dried. The crude product was recrystallised from water (90 cm^3) by the slow addition of aqueous sodium bromide (7g. in 30 cm^3 water).

Calc. for $[Co(C_6H_{18}N_4)NH_2CH_2CH(OCH_3)Cl]Br_2$: C,23.74; H,5.78; N,13.91;

Found: C,24.08; H,6.07; N,13.96%.

The i.r. spectrum (KBr) of the complex has a strong, sharp absorption band at 1560 cm^{-1} with weaker bands at 1578 cm^{-1} and 1590 cm^{-1}.

The visible electronic spectrum measured in water has band maxima at 367 nm (ε = 102) and 533 nm (ε = 103). The literature[9] reports absorption bands at 367 nm (ε = 102) and 535 nm (ε = 105).

Kinetic Measurements

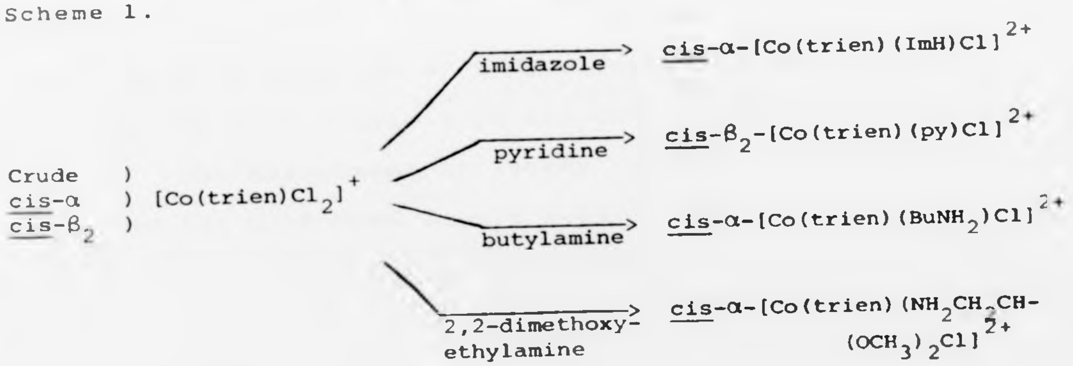
Kinetic studies were made on the base hydrolysis reactions of $[Co(trien)(amine)Cl]^{2+}$ (amine = imidazole, pyridine, n-butylamine, and 2,2-dimethoxyethylamine) under pseudo first order conditions, at 25°C and I = 0.1 mol dm^{-3} ($NaClO_4$). The spectrophotometric technique was used, monitoring absorbance changes at a pre-selected wavelength. The pseudo first order rate constants (k_{obs}) were determined from the experimental data using both the Swinbourne method and the 16 point first order programme. The variation of k_{obs} with hydroxide ion concentration allowed evaluation of overall second order rate constants for base hydrolysis ($k_{OH} = k_{obs}/[OH^-]$).

The mercury (11) assisted aquation reaction of cis-β_2-$[Co(trien)(py)Cl]^{2+}$ was studied at 25°C, using pseudo first order conditions, with $[Hg^{2+}]$ > 10[complex]. Mercury (11) solutions of varying concentrations were prepared by dissolving appropriate amounts of $Hg(NO_3)_2.H_2O$ in aqueous nitric acid

(2.0 mol dm^{-3}) and adding KNO_3 to bring the solutions to a total ionic strength of I = 2.0 mol dm^{-3}. After preliminary spectral scans to establish isosbestic points kinetic data were obtained by adding a small amount of *cis*-β_2-[Co(trien)-(py)Cl]$(ClO_4)_2$ to the mercury (11) solution and monitoring the absorbance change with time, at a pre-set wavelength.

Results and Discussion

In the present work, *cis*-α-[Co(trien)(ImH)Cl]$^{2+}$, *cis*-α-[Co(trien)$(BuNH_2)$Cl]$^{2+}$, *cis*-α-[Co(trien)$(NH_2CH_2CH(OCH_3)_2$-Cl]$^{2+}$ and *cis*-β_2-[Co(trien)(py)Cl]$^{2+}$ were prepared from crude, *cis*-α-, and *cis*-β-[Co(trien)Cl_2]$^{+}$. The isomer geometry of the products [Co(trien)(A)Cl]$^{2+}$ was independent of the stereochemistry of the reactant complex [Co(trien)Cl_2]$^{+}$ but was dependent on the nature of the amine (A) used in the preparation. The reaction stereochemistries are summarised in Scheme 1.



Scheme 1

The result for (A) = imidazole is in contrast to that found by Dash[4] who reports that while crude or *cis*-α-[Co(trien)Cl_2]$^{+}$

reacts with imidazole to give *cis*-α-[Co(trien)(ImH)Cl]$^{2+}$, *cis*-β-[Co(trien)Cl_2]$^{+}$ reacts with imidazole giving *cis*-$β_2$-[Co(trien)(ImH)Cl]$^{+}$.

For [Co(trien)X_2]$^{+}$ (X = Cl, NO_2, H_2O), Sargeson and Searle[1] found that the relative stabilities of the *cis*-α- and *cis*-β-isomers of [Co(trien)X_2]$^{+}$ are a function of the substituent X rather than of the possible strain associated with coordination of the secondary nitrogen atoms in the two configurations. The dichloro and dinitro complexes appear to favour the *cis*-α- form. A concentrated solution of *cis*-β-[Co(trien)Cl_2]$^{+}$ in hydrochloric acid slowly changes to *cis*-α-[Co(trien)Cl_2]$^{+}$. The diaquo ion [Co(trien)$(H_2O)_2$]$^{3+}$ favours the *cis*-β-configuration and there appears to be no obvious correlation between either the size or the electronic properties of these substituents to account for the variation in stability of the geometrical forms. Extrapolating this result to the present work, the isomer of [Co(trien)(A)Cl]$^{2+}$ resulting from reaction of [Co(trien)Cl_2]$^{+}$ with an amine is probably the most stable form for the particular amine (A).

The assignment of isomer geometry [Co(trien)(A)Cl]$^{2+}$ complexes has been made from a consideration of i.r., visible electronic spectra and ^1H NMR spectra.

I.r. data

In general, in these systems, the isomer geometry can be elucidated from the NH vibrations of the (trien) ligand.[11] Two potentially useful areas in the i.r. spectrum are (a) the NH_2 asymmetric deformations *ca*. 1500 cm^{-1}-1600 cm^{-1}

and (b) the NH stretching at ca. 3300 cm^{-1}. The folding of (trien) in the cis-α-isomer is such that the two NH_2 groups on trien are effectively equivalent and only one absorption band is observed for the NH_2 asymmetric deformations. In the cis-β_2-isomers the folding of trien ensures that both NH_2 groups are non-equivalent and this is manifested in the appearance of two strong absorption bands in the region 1500 cm^{-1}-1600 cm^{-1}. For example, cis-α-$[Co(trien)(ImH)Cl]^{2+}$ has one strong band at 1572 cm^{-1} due to NH_2 asymmetric deformations. Dash reports that cis-β_2-$[Co(trien)(ImH)Cl]^{2+}$ has two bands, assigned to NH_2 asymmetric deformations of the trien ligand at 1540 cm^{-1} and 1575 cm^{-1} reflecting the different site symmetries for the primary amine groups of trien in the cis-α- and cis-β_2-isomers. The lesser symmetry of the cis-β_2-isomer is also reflected in the NH stretching region of the spectrum ca. 3300 cm^{-1} with the cis-β_2-isomers showing greater complexity than the cis-α-isomers. The i.r. data collected in the present work for the $[Co(trien)(A)Cl]^{2+}$ complexes are summarised in Table 2.1. Where (A) = n-$BuNH_2$ and $NH_2CH_2CH(OCH_3)_2$ the absorption bands due to the primary NH_2 groups of (A) will occur in the range 1500-1600 cm^{-1} obscuring the bands due to asymmetric deformation of the NH_2 groups on (trien) thus impeding assignment of isomer geometry. For cis-β_2-$[Co(trien)(py)Cl]^{2+}$, complexities in the i.r. spectrum in the region 1500-1610 cm^{-1} are attributed to the splitting of the asymmetric deformation mode of NH_2 on (trien) and the ring stretching vibrations (C-H) of pyridine.

TABLE 2.1

Infra-red absorption bands (in cm^{-1}) for complexes of the type $[Co(trien)(A)Cl]^{2+}$

Complex	Absorption		
cis-α-$[Co(trien)(ImH)Cl]^{2+}$	1572(s)	1600(s)	
cis-α-$[Co(trien)(BuNH_2)Cl]^{2+}$	1570(s)	1600(m)	1612(m)
cis-α-$[Co(trien)NH_2CH_2CH(OCH_3)_2Cl]^{2+}$	1560(s)	1578(m)	1590(w)
cis-β_2-$[Co(trien)(py)Cl]^{2+}$	broad 1560(m)-1590(m)		1610(s)

The absorption bands due to NH groups in the range 3000-3500 cm^{-1} for these complexes are not clearly resolved and do not allow unequivocal assignment of cis-α- and cis-β-isomers. Examination of visible electronic spectral data facilitates isomer assignment.

Electronic spectra

The electronic spectra of the [Co(trien)-(A)Cl]$^{2+}$ complexes were measured in 0.1 mol dm^{-3} perchloric acid. The isomer geometries were assigned on the basis of a comparison with the spectral parameters of cis-α- and cis-β_2-isomers of $[Co(trien)(A)Cl]^{2+}$ reported in the literature. The data obtained are summarised in Table 2.2. Both cis-α- and cis-β_2-isomers of $[Co(trien)(A)Cl]^{2+}$ show two d-d bands as expected for octahedral Co(111) (low spin, d^6). The highest energy band for both isomers is found ca. 360 nm and is assigned to the transition $^1A_1 \rightarrow {}^1T_{2g}$. The absorption band at lower energy is unsymmetrical in appearance and is significantly different for *cis*-α- and *cis*-β_2-isomers thus allowing differentiation between the two isomers. *Cis*-α-isomers of $[\mathrm{Co(trien)(A)Cl}]^{2+}$ have band maxima *ca*. 535 nm with a shoulder *ca*. 490 nm while *cis*-β_2-isomers have a band maximum *ca*. 490 nm with a shoulder *ca*. 540 nm.

TABLE 2.2

Visible absorption spectra of $[\mathrm{Co(trien)(A)Cl}]^{2+}$ in aqueous solution. Numbers in parentheses are the extinction coefficients in $M^{-1}\ cm^{-1}$.

Complex	λ,nm	λ,nm	λ,nm
cis-α-$[\mathrm{Co(trien)(ImH)Cl}]^{2+}$ [a,f]	365_{max} (111)	480_{sh} (71)	535 (109)
cis-α-$[\mathrm{Co(trien)(PhNH_2)Cl}]^{2+}$ [b,f]			525_{max} (124)
cis-α-$[\mathrm{Co(trien)(NH_3)Cl}]^{2+}$ [c]			530 (95)
cis-α-$[\mathrm{Co(trien)(BuNH_2)Cl}]^{2+}$ [a,f]	366_{max} (101)	490_{sh} (75)	530_{nm} (91)
cis-α-$[\mathrm{Co(trien)NH_2CH_2CH(OCH_3)_2Cl}]^{2+}$ [a,g]	367_{max} (102)		533_{max} (103)
cis-β_2-$[\mathrm{Co(trien)(ImH)Cl}]^{2+}$ [d,f]	360_{max} (111)	480_{max} (110)	540_{sh} (79)
cis-β_2-$[\mathrm{Co(trien)(PhNH_2)Cl}]^{2+}$ [b,f]		490_{max} (114)	
cis-β_2-$[\mathrm{Co(trien)(BzH)Cl}]^{2+}$ [e]	370_{sh} (148)	495 (126)	540_{sh} (93)
cis-β_2-$[\mathrm{Co(trien)(NH_3)Cl}]^{2+}$ [c]		475 (93)	
cis-β_2-$[\mathrm{Co(trien)(py)Cl}]^{2+}$ [a,f]	371_{max} (111)	484_{max} (113)	540_{sh} (78)

a. present work,

b. taken from reference 5,

c. taken from reference 9,

d. taken from reference 4,

e. taken from reference 6,

f. measured in 0.1 mol dm^{-3} perchloric acid,

g. measured in water.

Cis-β-[Co(trien)(py)Cl]$^{2+}$ prepared in the present work has been assigned the cis-β_2- rather than the cis-β_1-configuration. This assignment is based on the observation that the cis-β_1-isomer has not been found for any analogous system and studies show that on the basis of non-bonded interactions the cis-β_2-form is favoured over the cis-β_1-configuration.

Finally cis-α- and cis-β-isomers of [Co(trien)(A)Cl]$^{2+}$ can be differentiated on the basis of rate constants evaluated for their base hydrolysis reactions to give [Co(trien)(A)OH]$^{2+}$ with the rate constants for base hydrolysis of cis-β_2-[Co(trien)-(A)Cl]$^{2+}$ several orders of magnitude greater than the rate constants for the corresponding cis-α-isomers. These kinetic results are now presented and discussed.

Kinetics

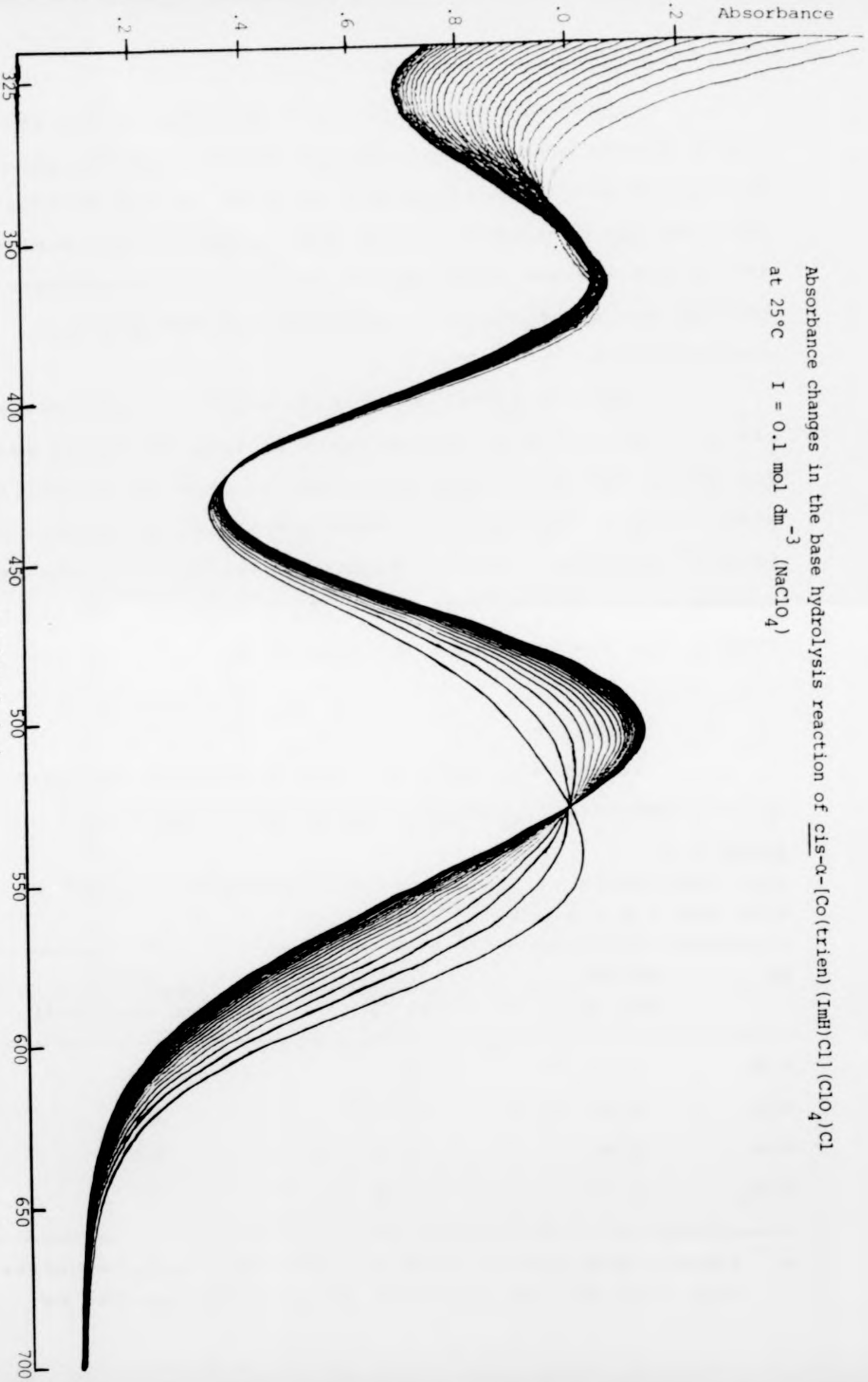
The kinetic data for base hydrolysis of cis-α-[Co(trien)(ImH)Cl](ClO$_4$)Cl are summarised in Table 2.3.

TABLE 2.3

Base hydrolysis of cis-α-[Co(trien)(ImH)Cl](ClO$_4$)Cl^a at 25°C and I = 0.1 mol dm^{-3} (NaClO$_4$)

pH	10^6[OH$^-$] (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})	k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
8.38	3.13	0.82	262
8.60	5.20	1.47	282
8.66	5.96	1.38	231
8.85_5	9.35	2.22	237

a. Freshly prepared trishydroxymethylaminomethane buffers were used and the reaction was monitored at 540 nm.



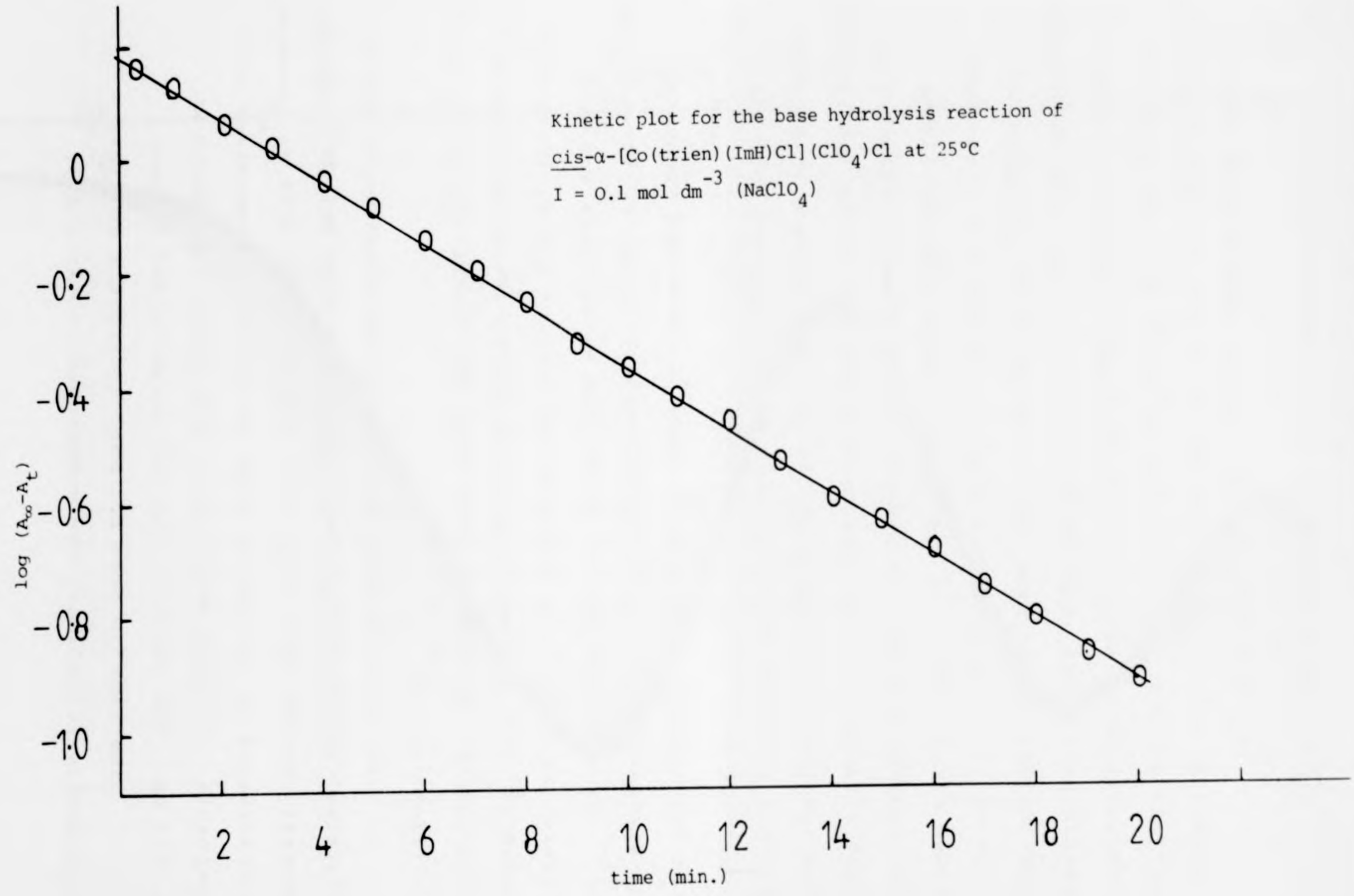
Absorbance changes in the base hydrolysis reaction of cis-α-[Co(trien)(ImH)Cl](ClO$_4$)Cl at 25°C I = 0.1 mol dm^{-3} (NaClO$_4$)

Figure 2.1

The mean value of the overall second order rate constant at 25°C is k_{OH} = 253 dm^3 mol^{-1} s^{-1}. A linear regression analysis gives k_{OH} = (218 ± 30) dm^3 mol^{-1} s^{-1}. An interval scan spectrum of this reaction is shown in Figure 2.1. Isosbestic points are observed at 410 and 519 nm. The absorption band maximum shifts from 535 to 490 nm consistent with the chromophore changing from a weak ligand field to a stronger ligand field. Plots of log(A_∞-A_t) versus time are linear over four half-lives. A sample plot is shown in Figure 2.2. While isosbestic points are seen at 410 and 519 nm the interval scan spectrum shows that at ca. 350 nm there appears to be more than one reaction taking place. It is suggested that this second reaction could be the release of coordinated imidazole from the complex [Co(trien)(ImH)OH]$^{2+}$. Dash and Mohapatra[6] who studied the base hydrolysis reaction of cis-β$_2$-[trien)(BzH)-Cl]$^{2+}$ (Bz = benzimidazole) found that while there was no evidence of release of BzH from the complex cis-β$_2$-[Co(trien)-(BzH)Cl]$^{2+}$, the hydroxide group in cis-β$_2$-[Co(trien)(BzH)OH]$^{2+}$ labilised the release of (BzH) from the Co(111) centre to yield [Co(trien)(H$_2$O)$_2$]$^{3+}$.

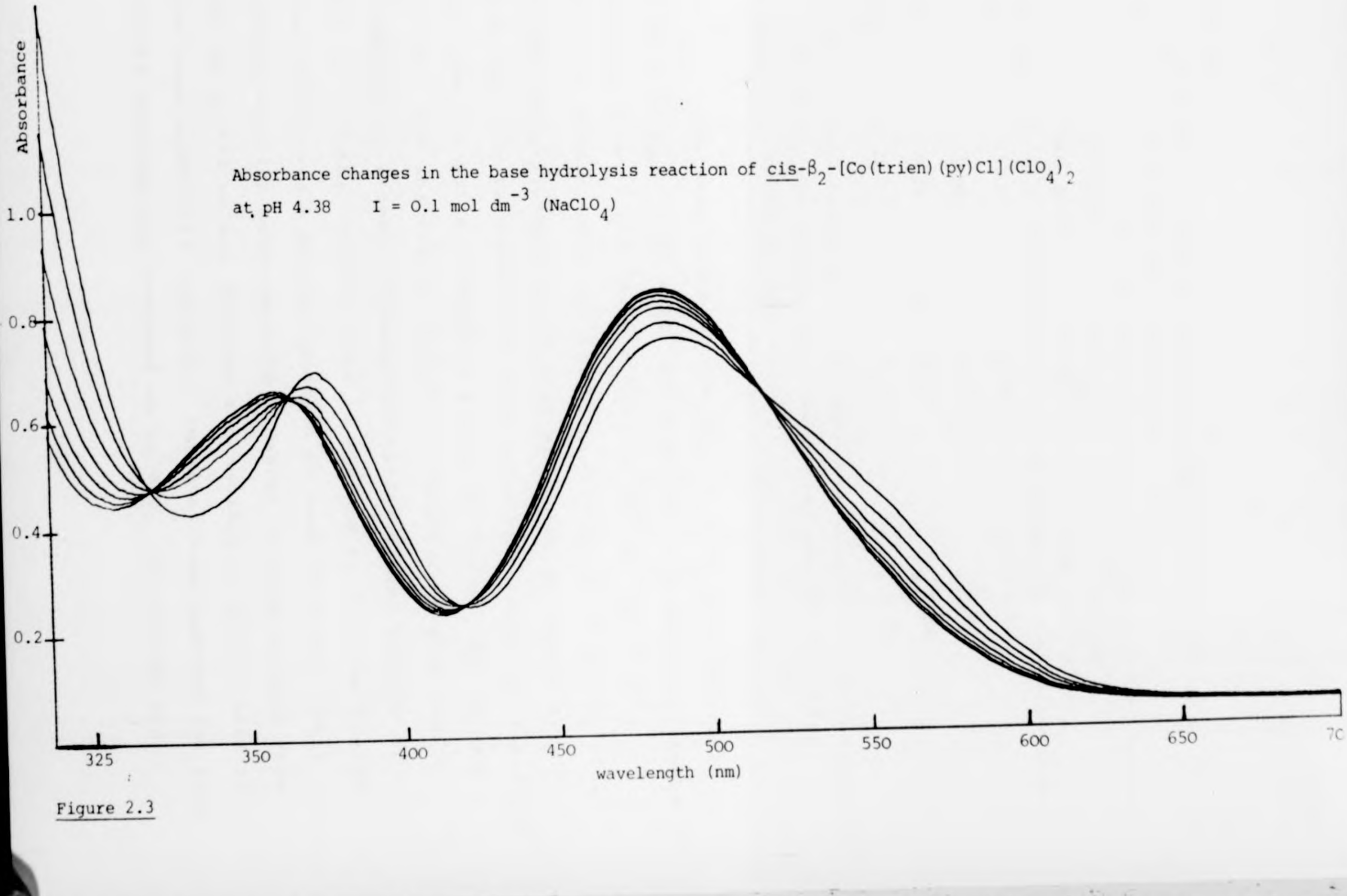
An interval scan spectrum of the reaction of cis-α-[Co(trien)(ImH)Cl](ClO$_4$)$_2$ was recorded in 0.01 mol dm^{-3} (NaOH). Spectral changes took place over several hours with an increase in absorbance at 490 nm but with no change in absorption band wavelength. A large decrease in absorbance took place at ca. 325 nm. The reaction was not investigated further.

The kinetic data for base hydrolysis of cis-β$_2$-[Co(trien)(py)Cl](ClO$_4$)$_2$ are summarised in Table 2.4.



Kinetic plot for the base hydrolysis reaction of
cis-α-[Co(trien)(ImH)Cl]$(ClO_4)Cl$ at 25°C
$I = 0.1$ mol dm^{-3} $(NaClO_4)$

Figure 2.2



Absorbance changes in the base hydrolysis reaction of cis-β_2-[Co(trien)(py)Cl]$(ClO_4)_2$
at pH 4.38 $I = 0.1$ mol dm^{-3} $(NaClO_4)$

Figure 2.3

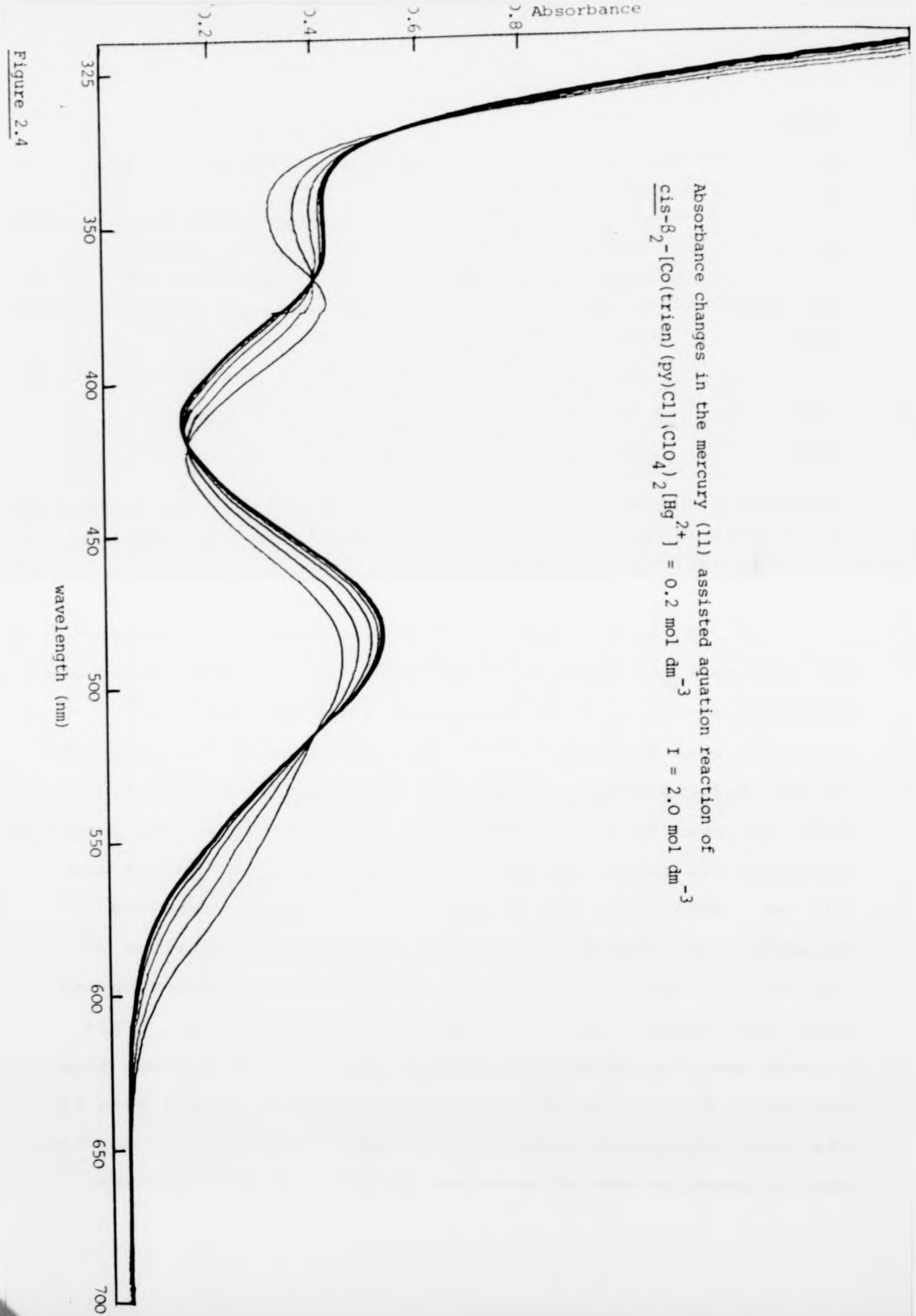
TABLE 2.4

Base hydrolysis of cis-β_2-[Co(trien)(py)Cl]$(ClO_4)_2$ [a] at 25°C and I = 0.1 mol dm^{-3} ($NaClO_4$)

pH	$10^{11}[OH^-]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$10^{-6}k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
3.20_5	2.09	1.45	6.93
3.37	3.06	1.97	6.43
3.58	4.96	3.47	6.99
3.82_5	8.72	5.45	6.25

a. Fresh formic acid buffers were used and the reaction was monitored at 320 nm.

The mean value of the second order rate constant at 25°C is k_{OH} = 6.65 x 10^6 dm^3 mol^{-1} s^{-1}. Linear regression analysis gives k_{OH} = (6.10 ± 0.37) x 10^6 dm^3 mol^{-1} s^{-1}. Interval scan spectra for the base hydrolysis of cis-β_2-[Co(trien)(py)Cl]$(ClO_4)_2$ at pH 4.38 are shown in Figure 2.3. When the scan is terminated after four half-lives the resultant spectrum has three isosbestic points at 334 nm, 360 nm and 512 nm. The absorbance changes are consistent with the formation of a CoN_5O chromophore having a band maximum at 480 nm. If the interval scan is allowed to continue beyond four half-lives a second reaction is seen to occur. This second reaction proceeds with a change in band maximum from 480 nm to 495 nm and destroys the isosbestic points seen in the base hydrolysis reaction. Interval scan spectra for this second reaction was recorded at pH 8.8. At this pH base



Absorbance changes in the mercury (11) assisted aquation reaction of cis-β_2-[Co(trien)(py)Cl](ClO$_4$)$_2$ [Hg^{2+}] = 0.2 mol dm^{-3} I = 2.0 mol dm^{-3}

Figure 2.4

hydrolysis is complete before the scan commences. Isosbestic points are observed at 400 and 470 nm. This reaction, following base hydrolysis of cis-β_2-[Co(trien)(py)Cl]$^{2+}$ may be due to loss of coordinated pyridine from [Co(trien)(py)OH]$^{2+}$ by an SN1CB process to give [Co(trien)(H$_2$O)$_2$]$^{3+}$. The spectrum of the final product has band maxima at 356 and 495 nm and is consistent with a mixture of cis-α- and cis-β_2-[Co(trien)(H$_2$O)$_2$]$^{3+}$. An authentic sample of cis-α-[Co(trien)(H$_2$O)$_2$]$^{3+}$ has band maxima at 359 nm (ε = 57) and 500 nm (ε = 87) while cis-β_2-[Co(trien)(H$_2$O)$_2$]$^{3+}$ has band maxima at 357 nm (ε = 85) and 487 nm (ε = 122).[10] An approximate rate constant was evaluated for the second reaction by monitoring absorbance changes in the pH range 8 - 9.5. The rate constant was found to be independent of hydroxide ion concentration and has $k = 7 \times 10^{-4}\ s^{-1}$.

Kinetic studies on the mercury (11) assisted aquation of cis-β_2-[Co(trien)(py)Cl](ClO$_4$)$_2$ confirm that there is only one species in the sample undergoing hydrolysis. Interval scan spectra of the aquation displayed isosbestic points at 331, 359, 413 and 505 nm, Figure 2.4. There is no indication of a second reaction following aquation. Kinetic data for the Hg(11) assisted aquation of cis-β_2-[Co(trien)(py)Cl](ClO$_4$)$_2$ are collected in Table 2.5.

TABLE 2.5

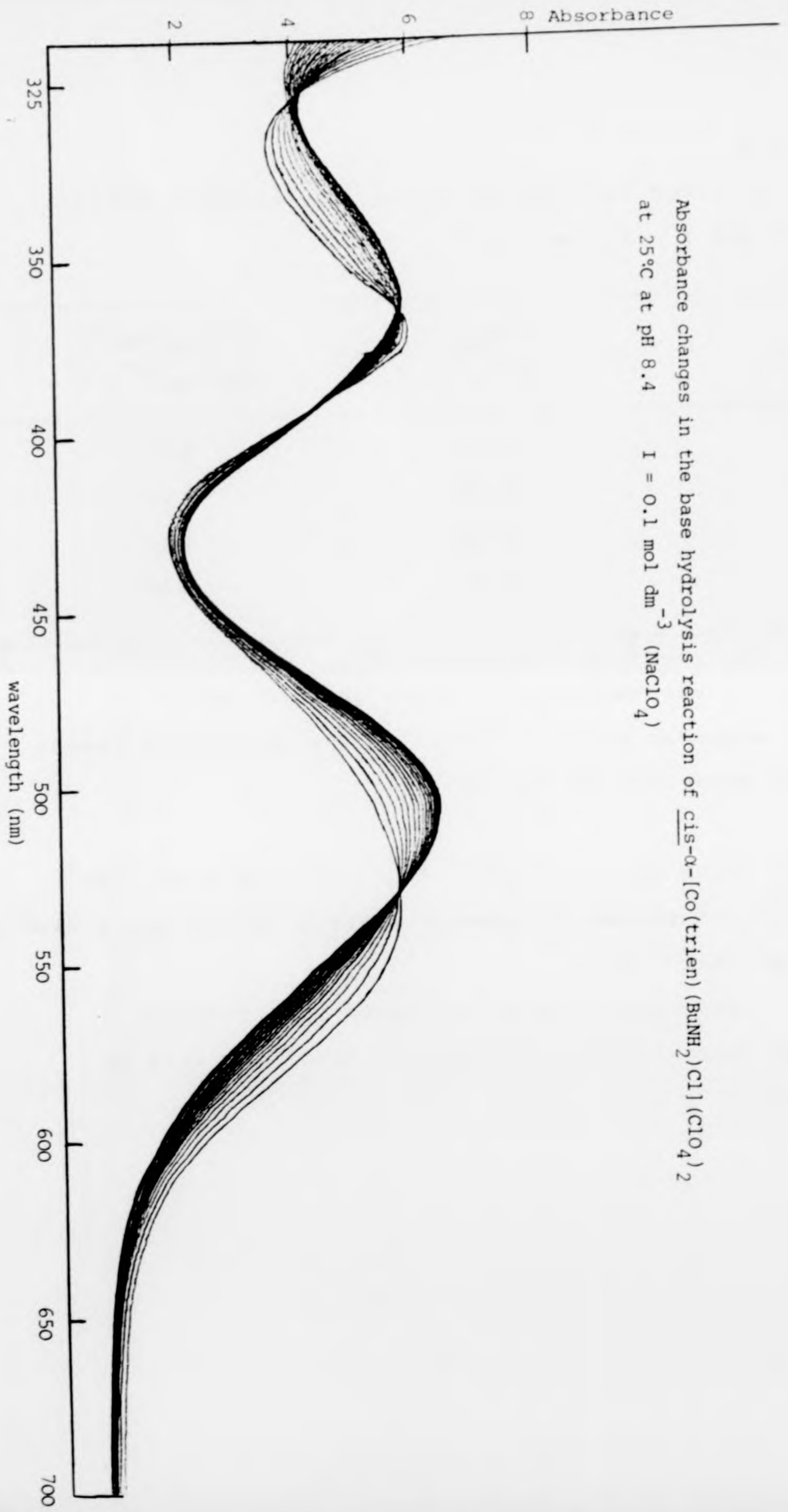
Hg(11) assisted aquation of cis-β_2-[Co(trien)(py)Cl]$(ClO_4)_2$[a] at 25°C and I = 2.0 mol dm^{-3}

$[Hg^{2+}]$ (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})	$10^2 k_{obs}/[Hg^{2+}]$ (dm^3 mol^{-1} s^{-1})
0.05	1.17	2.34
0.1	2.10	2.10
0.2	4.31	2.15
0.3	5.93	1.97

a. Hg(11) solutions are 1.0 mol dm^{-3} in (HNO_3) to suppress base hydrolysis. The absorbance change was monitored at 342 nm.

The mean value of $k_{obs}/[Hg^{2+}]$ (k_{Hg}) is 2.14×10^{-2} dm^3 mol^{-1} s^{-1}. A linear regression analysis gives $k_{Hg} = (1.93 \pm 0.09) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}.

The kinetic data for base hydrolysis of cis-α-[Co(trien)$(BuNH_2)$Cl](ClO_4)Cl are summarised in Table 2.6.



Absorbance changes in the base hydrolysis reaction of cis-α-[Co(trien)(BuNH$_2$)Cl](ClO$_4$)$_2$ at 25°C at pH 8.4 I = 0.1 mol dm^{-3} (NaClO$_4$)

Figure 2.5

TABLE 2.6

Base hydrolysis of cis-α-[Co(trien)(BuNH$_2$)Cl](ClO$_4$)Cl[a] at 25°C and I = 0.1 mol dm^{-3} (NaClO$_4$)

pH	10^6[OH$^-$] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})	k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
8.48	3.94	2.81	71
8.50	4.13	3.10	75
8.60$_5$	5.26	3.84	73
8.79$_5$	8.14	5.94	73

a. Fresh trishydroxymethylaminomethane buffers were used and the reaction was monitored at 490 nm.

The mean value of the second order rate constant at 25°C is k_{OH} = 73 dm^3 mol^{-1} s^{-1}. Linear regression analysis gives k_{OH} = (72.8 ± 2.2 dm^3 mol^{-1} s^{-1}). The kinetic measurements indicate that only one reaction is taking place in this pH range. Plots of log(A$_\infty$-A$_t$) versus time are linear over four half-lives. Interval scan spectra for base hydrolysis of cis-α-[Co(trien)(BuNH$_2$)Cl](ClO$_4$)Cl at pH 8.4 are shown in Figure 2.5. Isosbestic points are observed at 370 nm and 530 nm. The absorption band maximum shifts from 535 nm to 495 nm consistent with a change in chromophore from CoN$_5$Cl to CoN$_5$O. Interval scan spectra of cis-α-[Co(trien)(BuNH$_2$)Cl]$^{2+}$ in 0.01 mol dm^{-3} NaOH established that spectral changes took place over several hours with an increase in absorbance at 490 nm but occurring with no shift in the absorption band

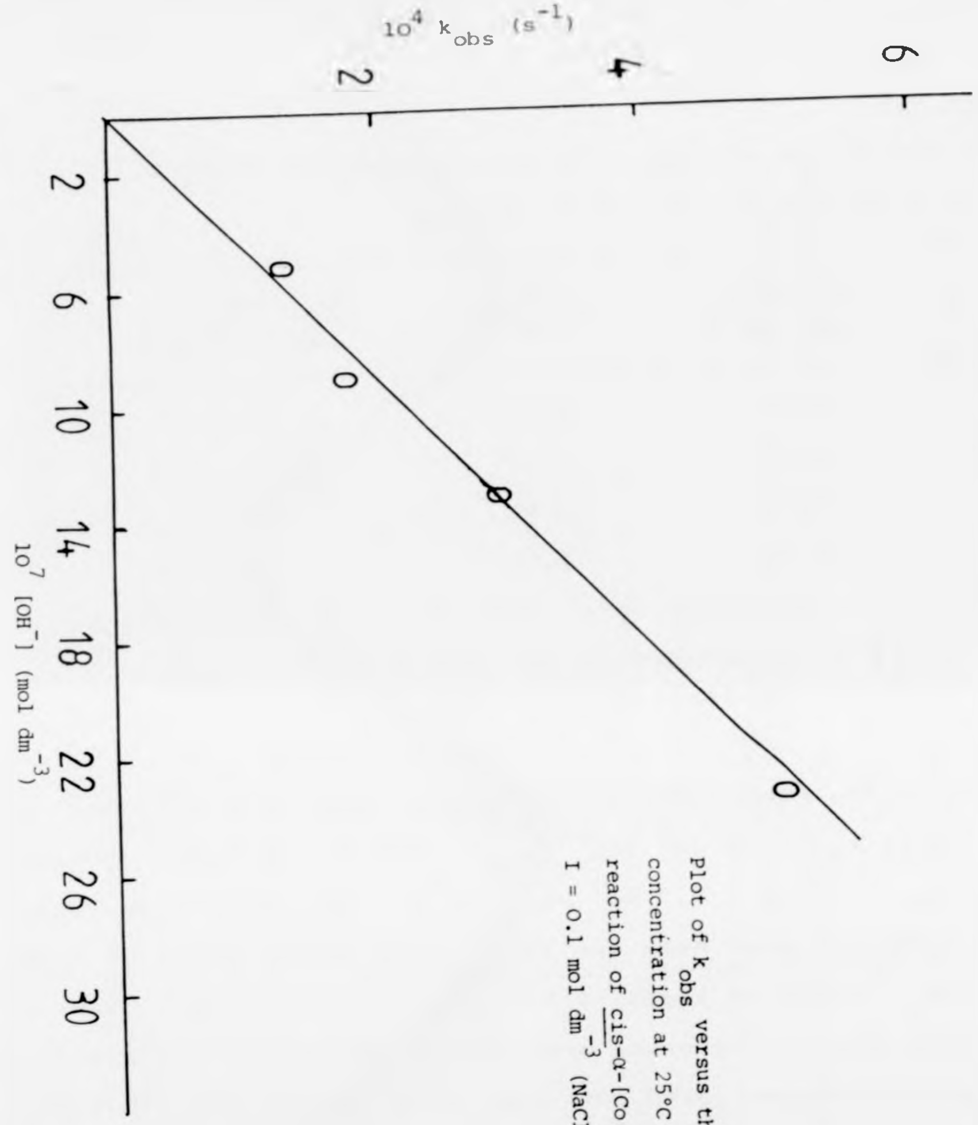


Figure 2.6

Plot of k_{obs} versus the hydroxide ion concentration at 25°C for the base hydrolysis reaction of cis-α-[Co(trien)$NH_2CH_2CH(OCH_3)_2Cl]Br_2$ I = 0.1 mol dm^{-3} ($NaClO_4$)

maximum wavelength. This subsequent reaction was not investigated further.

The kinetic data for base hydrolysis of cis-α-[Co-(trien)$NH_2CH_2CH(OCH_3)_2Cl]Br_2$ are summarised in Table 2.7.

TABLE 2.7

Base hydrolysis of cis-α-[Co(trien)$NH_2CH_2CH(OCH_3)_2Cl]Br_2$[a] at 25°C and I = 0.1 mol dm^{-3} ($NaClO_4$)

pH	$10^7[OH^-]$ (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})	$k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
7.67	6.10	1.34	219
7.84	9.03	1.93	213
8.00	13.05	2.84	217
8.25	23.22	5.02	216

a. Fresh trishydroxymethylaminomethane buffers were used and the reaction was monitored at 490 nm.

The mean value for the second order rate constant at 25°C is k_{OH} = 216 dm^3 mol^{-1} s^{-1}. Linear regression analysis gives k_{OH} = (215 ± 1.9) dm^3 mol^{-1} s^{-1}. A plot of k_{obs} versus the hydroxide ion concentration is shown in Figure 2.6. Interval scan spectra for base hydrolysis (over four half-lives) are shown in Figure 2.7. Isosbestic points are observed at 374 and 528 nm. The absorbance maximum shifts from 533 to 500 nm. If the spectrum is allowed to run beyond four half lives a second reaction is seen to take place with a shift in absorption band maximum from 500 nm to 515 nm. Interval scan

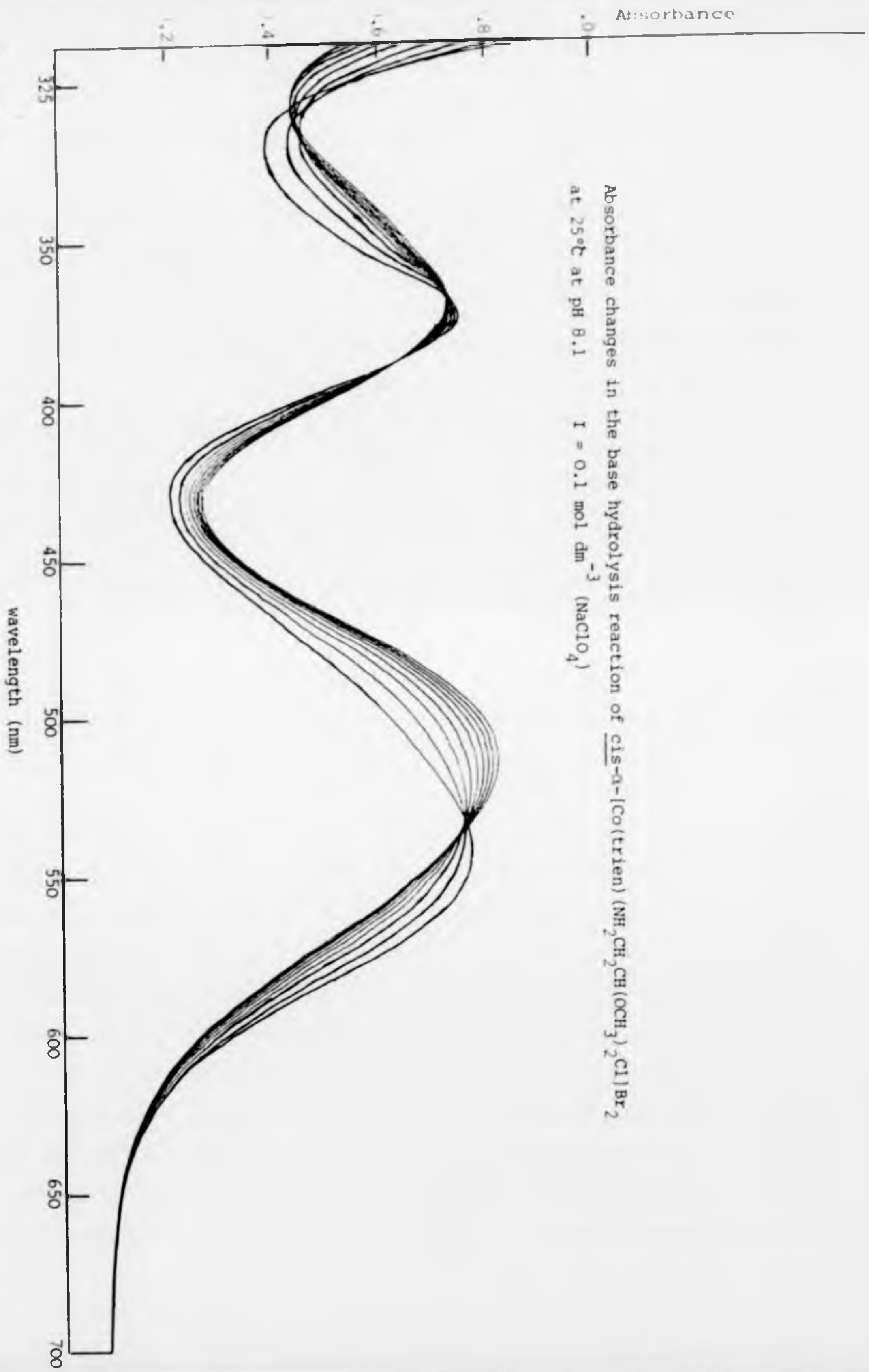


Figure 2.7

Absorbance changes in the base hydrolysis reaction of cis-α-[Co(trien)($NH_2CH_2CH(OCH_3)_2$Cl]Br_2 at 25°C at pH 8.1 I = 0.1 mol dm^{-3} ($NaClO_4$)

spectra were run for this second reaction by dissolving the complex in 0.1 mol dm^{-3} sodium hydroxide. In this reaction medium base hydrolysis is complete before measurement commenced. The resultant spectra display isosbestic points at 354 nm, 405 nm and 504 nm (Figure 2.8).

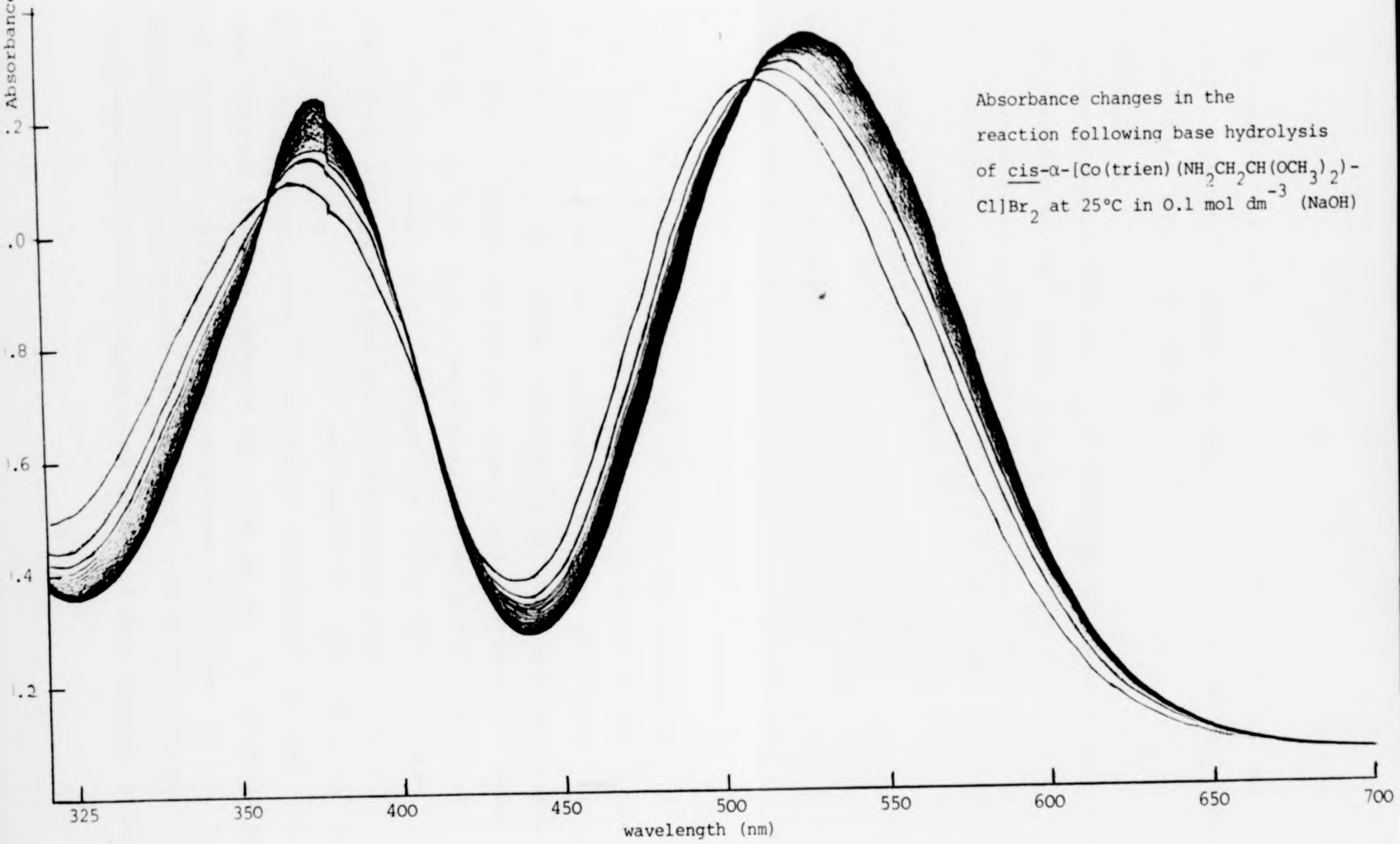
Base hydrolysis of the four complexes studied, cis-α-[Co(trien)(A)Cl]$^{2+}$ (A = ImH, $BuNH_2$, $NH_2CH_2CH(OCH_3)_2$ and cis-β_2-[Co(trien)(py)Cl]$^{2+}$ all obey a second order rate law of the form -d[complex]/dt = k_{OH}[complex][OH^-]. Plots of k_{obs} versus hydroxide ion concentration are linear passing through the origin and show no indication of spontaneous aquation. The second order rate constants are collected in Table 2.8.

TABLE 2.8

Base hydrolysis rate data for [Co(trien)(A)Cl]$^{2+}$, collected in the present work at 25°C and I = 0.1 mol dm^{-3}.

Complex	k_{OH} (dm^3 mol^{-1} s^{-1})
cis-α-[Co(trien)(ImH)Cl]$^{2+}$	253
cis-α-[Co(trien)($BuNH_2$)Cl]$^{2+}$	73
cis-α-[Co(trien)$NH_2CH_2CH(OCH_3)_2$Cl]$^{2+}$	216
cis-β_2-[Co(trien)(py)Cl]$^{2+}$	6.6×10^6

Interval scan spectra for these base hydrolysis reactions all show a shift in absorption maximum from higher to lower wavelength as expected for an increase in ligand field strength in moving from a CoN_5Cl chromophore to CoN_5O. The absorption maxima of the products of base hydrolysis are given



Absorbance changes in the reaction following base hydrolysis of cis-α-[Co(trien)($NH_2CH_2CH(OCH_3)_2$)-Cl]Br_2 at 25°C in 0.1 mol dm^{-3} (NaOH)

Figure 2.8

in Table 2.9. The reactions following the formation of $[Co(trien)(A)OH]^{2+}$ impede the determination of the λ_{max} for the products $[Co(trien)(A)OH]^{2+}$.

TABLE 2.9

Absorption maxima for the first products of base hydrolysis of $[Co(trien)(A)Cl]^{2+}$ ions

$[Co(trien)(A)Cl]^{2+}$	Hydrolysis product λ_{max} (nm)
cis-α-$[Co(trien)(ImH)Cl]^{2+}$	490
cis-β_2-$[Co(trien)(py)Cl]^{2+}$	480
cis-α-$[Co(trien)(BuNH_2)Cl]^{2+}$	495
cis-α-$[Co(trien)(NH_2CH_2CH(OCH_3)_2)Cl]^{2+}$	500

Previous studies of the base hydrolysis of $[Co(trien)(A)Cl]^{2+}$ ions have been interpreted on the basis of an SN1CB mechanism. Deprotonation of a secondary nitrogen atom on the trien ligand could lead to the conjugate base, however, in complexes of the type $[Co(trien)(A)Cl]^{2+}$ where A is an "acidic" amine, deprotonation of A can contribute to the conjugate base. A study has shown that the base hydrolysis of cis-α- and cis-β_2-$[Co(trien)(aniline)Cl]^{2+}$ at 50°C have k_{OH} = 3.3 x 10^5 dm^3 mol^{-1} s^{-1} and 138 x 10^5 dm^3 mol^{-1} s^{-1} respectively.[5] The small difference in reaction rate between the two isomers led Dash et al. to conclude that the conjugate bases in these complexes are formed mainly by deprotonation of coordinated aniline with the additional deprotonation site (secondary-NH group of the (trien) ligand trans to aniline) probably accounting for the slightly higher base hydrolysis rate of the cis-β_2-isomer relative to the cis-α-isomer.

In the present work rate constants for the base hydrolysis for the three cis-α-isomers $[Co(trien)(A)Cl]^{2+}$ where A = (ImH, $BuNH_2$, $NH_2CH_2CH(OCH_3)_2$ have been obtained. These constants are collected in Table 2.10 together with base hydrolysis rate constants for other Co(111) halopentaamines.

TABLE 2.10

Base hydrolysis kinetic data for $[CoN_5Cl]^{2+}$ complexes at 25°C

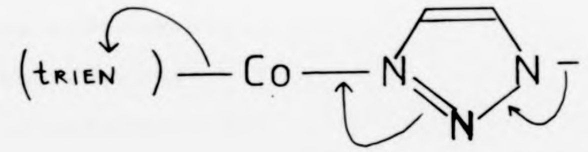
Complex	k_{obs} ($dm^3\ mol^{-1}\ s^{-1}$	I ($mol\ dm^{-3}$)
cis-α-$[Co(trien)(ImH)Cl]^{2+}$ [a]	253	0.1
cis-α-$[Co(trien)(BuNH_2)Cl]^{2+}$ [a]	73	0.1
cis-α-$[Co(trien)NH_2CH_2CH(OCH_3)_2Cl]^{2+}$ [a]	216	0.1
cis-α-$[Co(trien)(glyOEt)Cl]^{2+}$ [b]	74	1.0
cis-α-$[Co(trien)(NH_3)Cl]^{2+}$ [b]	10	1.0
$\alpha\alpha$-$[Co(tetren)Cl]^{2+}$ [a]	116	0.1
π-$[Co(en)(dien)Cl]^{2+}$ [c]	26.6	0.1

a. present work,

b. taken from reference 7,

c. taken from reference 12.

All of the complexes shown in Table 2.10 have one important structural feature in common. Folding of the polydentate amines (trien, tetren and (en)(dien)) is such that no "flat" nitrogen atom (that is, the middle member of a meridional set of three donor nitrogen atoms) is available to form the amido group of the conjugate base. These complexes have similar "slow" base hydrolysis rates and the data support the view that for base hydrolysis of the three cis-α-[Co(trien)-(A)Cl]$^{2+}$ complexes studied in the present work, the conjugate bases are formed by deprotonation of the secondary NH group on the trien ligand, trans to (A). "Minor" variations in base hydrolysis rates take place with variations in ligand (A). Ligand (A) can influence the reaction in two ways. First, if A is bulky and causes steric strain in the reactant molecule it can provide a driving force towards formation of the five coordinate intermediate. Second, if A is readily deprotonated it can labilise the secondary NH groups on the trien ligand, (4).



(4)

Base hydrolysis of one cis-β_2-isomer has been studied in the present work (cis-β_2-[Co(trien)(py)Cl]$^{2+}$). The large rate acceleration for the base hydrolysis of this cis-β_2-complex relative to the cis-α-isomers may be due either to the change in chelate geometry or to the presence of pyridine.

Both factors probably contribute to the rate acceleration but the unavailability of cis-α-$[Co(trien)(py)Cl]^{2+}$ makes it difficult to assess the individual contributions. Kinetic data for base hydrolysis of several cis-β_2-$[Co(trien)(A)Cl]^{2+}$ complexes are collected in Table 2.11.

TABLE 2.11

Base hydrolysis data for cis-β_2-$[Co(trien)(A)Cl]^{2+}$ complexes at 25°C

Complex	k_{OH} ($dm^3\ mol^{-1}\ s^{-1}$)	I ($mol\ dm^{-3}$)
cis-β_2-$[Co(trien)(ImH)Cl]^{2+}$ [a]	1.1×10^5	0.1
cis-β_2-$[Co(trien)(BzH)Cl]^{2+}$ [b]	2.4×10^6	0.1
cis-β_2-$[Co(trien)(NH_3)Cl]^{2+}$ [c]	2.3×10^5	1.0
cis-β_2-$[Co(trien)(py)Cl]^{2+}$ [d]	6.6×10^6	0.1
cis-β_2-$[Co(trien)(glyOEt)Cl]^{2+}$ [e]	2.2×10^5	1.0

a. taken from reference 4,

b. taken from reference 6,

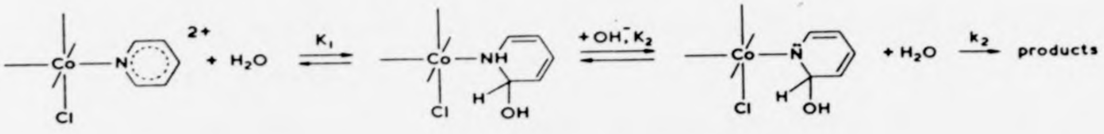
c. taken from reference 7,

d. present work,

e. taken from reference 7.

The similarity in base hydrolysis rates for these cis-β_2-$[Co(trien)(A)Cl]^{2+}$ complexes despite changes in (A) again suggests that isomer geometry is the major factor influencing reaction rate. Studies of the base hydrolysis of cis-β_2-$[Co(trien)(glyOEt)Cl]^{2+}$ [7] have shown that the preferred site of deprotonation is the planar secondary NH group on trien trans to the glycine ester (the exchange rate for this NH group in D_2O is $k_H = 2.5 \times 10^8$ dm^3 mol^{-1} s^{-1} at 25°C). It seems likely that the conjugate base which contributes significantly to the base hydrolysis of the cis-β_2-[Co(trien)(A)Cl]$^{2+}$ complexes is generated at the planar secondary NH groups of trien lying trans to A. If this is the case, then the rapid base hydrolysis of cis-β_2-isomers relative to cis-α-isomers can be rationalised in terms of the steric requirements for rapid base hydrolysis[13] described in Section I of this thesis. Cis-α-[Co(trien)(A)Cl]$^{2+}$ is fac-fac, with both secondary nitrogen atoms on the trien ligand "orthogonal". Deprotonation of either of the NH groups to form the conjugate base would result in poor overlap between the filled p-π orbital on N^- and the empty orbital on Co(111) in the trigonal bipyramidal intermediate. The complex cis-β_2-[Co(trien)(A)Cl]$^{2+}$ has a mer ring, and the "flat" secondary NH group on trien trans to A will form a conjugate base having favourable overlap between the filled p-π orbital on N and the empty orbital on Co(111), in the trigonal bipyramidal intermediate. This effect is believed to be responsible for the large rate constant found for base hydrolysis of cis-β_2-[Co(trien)(py)Cl]$^{2+}$.

The second factor affecting the base hydrolysis of cis-β_2-[Co(trien)(py)Cl]$^{2+}$ is the presence of pyridine. Rapid base hydrolysis has been observed in many other complexes where a pyridine or pyridyl ligand is present,[14] (either as a monodentate or as part of a multidentate ligand system). Gillard has suggested that "covalent hydration"[15] involving the addition of water to the pyridine ligand generates a new amine of higher acidity (Scheme 2).



Scheme 2

If as a result of "covalent hydration" the pyridine nitrogen provides the labilising amido group, it would be expected to follow the rules regarding the stereochemical requirements for rapid base hydrolysis. Rapid base hydrolysis requires the amido group in the trigonal bipyramidal intermediate to have its lone pair lying in the trigonal plane, so that good overlap between the p-π orbital containing the nitrogen lone pair and the empty orbital on Co(111) occurs. The observation that the base hydrolysis rates of pyridine complexes are independent of this criterion is regarded as strong evidence against the "covalent hydration" theory. In his review, Tobe[14] concludes that "the question as to why pyridine labilises the system is not yet answered and the definitive experiment remains to be done."

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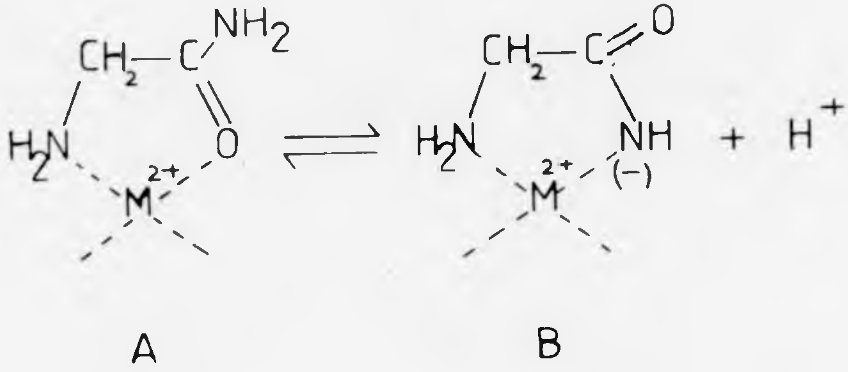
SECTION III

Transition Metal Complexes of Open Chain Amide Ligands

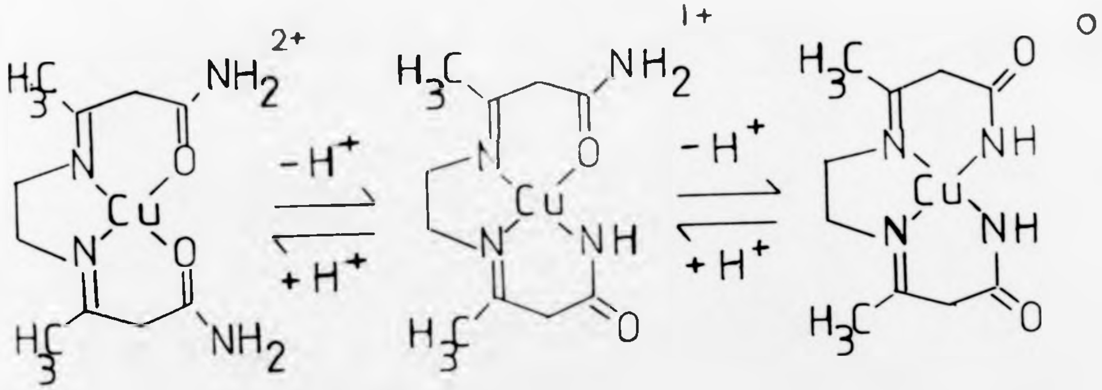
Introduction

The coordinating properties of the amide group in a number of open chain and macrocyclic amides have been investigated for transition metal ions including Cu(ll), Ni(ll), Co(ll) and Pd(ll) and some aspects of the topic have been reviewed.[1] The amide group can coordinate via (a) the carbonyl oxygen atom, (b) the protonated nitrogen atom, or (c) the deprotonated nitrogen atom. The ions Cu(ll), Ni(ll), Co(ll) and possibly Zn(ll)[2] facilitate the deprotonation of the nitrogen bound amide hydrogen atom. Second and third row transition metal ions such as Pd(ll) and Pt(ll) can induce amide ionisation at quite low pH (ca. 4.0 for Pd(ll)).[3] It is generally believed that the site of coordination in the complexes prior to deprotonation is the carbonyl oxygen atom,[1,4,5,6,7] for example glycinamide chelates weakly with metal ions via the amino nitrogen and carbonyl oxygen, Structure (1)A, but a stronger chelation occurs upon ionisation of an amide nitrogen bound hydrogen by some metal ions such as Cu(ll) and Ni(ll) to give structure (1)B, and the reaction shown in (1) occurs in neutral solutions with Cu(ll) and in more basic solutions with Ni(ll).[8] The complexes formed between Cu(ll) and 3,8-dimethyl-4,7-diazadeca-3,7-dienediamide in solution at different pH's have been investigated and the equilibria established,[7] are shown in (2).

Claims have been made that the protonated amide nitrogen atom can also serve as a donor[9,10], however recent e.s.r. data[7] on Cu(ll) complexes provide strong evidence for carbonyl oxygen coordination prior to amide deprotonation.



(1)



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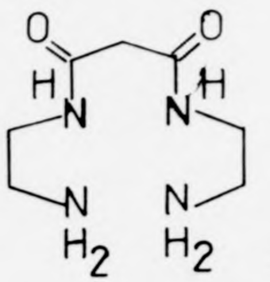
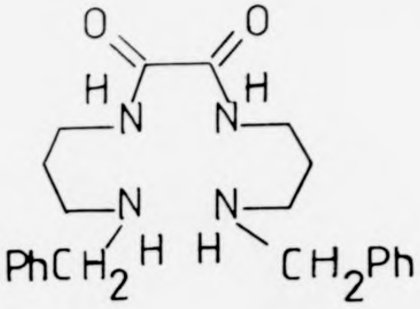


L_1H_2 ref.11



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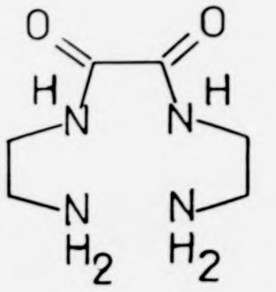

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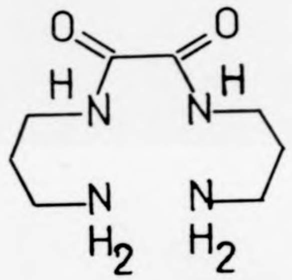
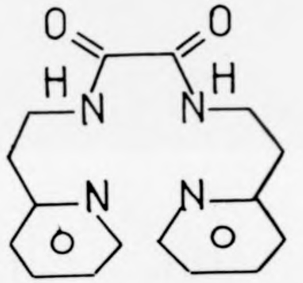
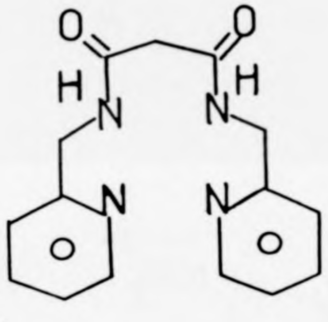


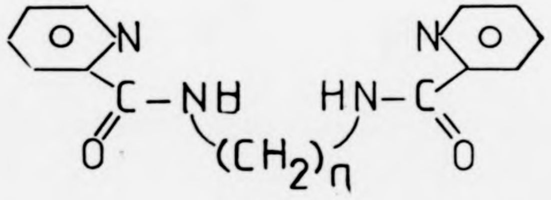
L_4H_2 ref.13



L_5H_2 ref.13

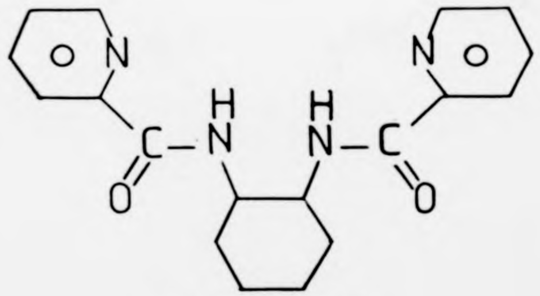


L_6H_2 ref.13



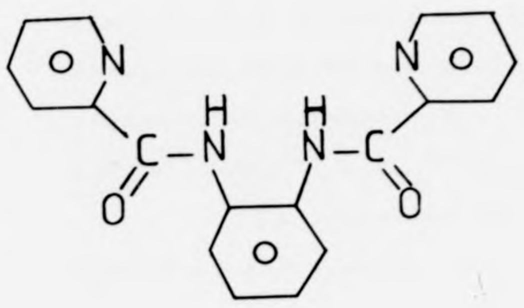
m = 2 or 3

L_7H_2 ref.14

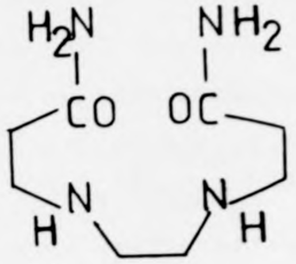


L_8H_2 ref.15

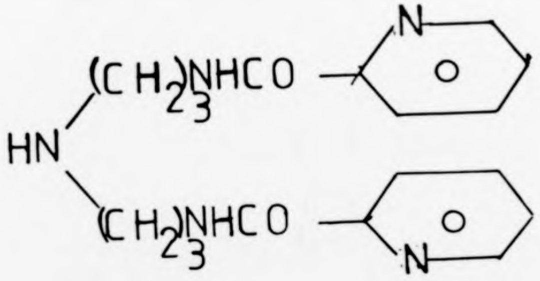
(3) continued:



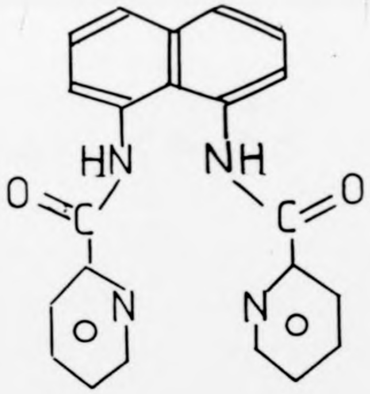
L_9H_2 ref.16



$L_{10}H_2$ ref.17



$L_{11}H_2$ ref.18

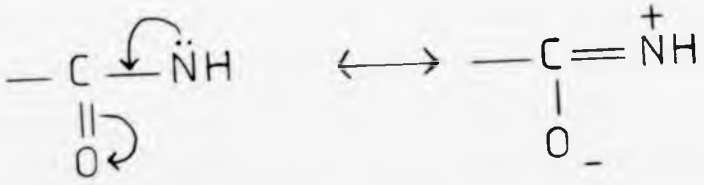


$L_{12}H_2$ ref.19

A large number of open chain ligands having amide groups as potential coordination sites have been synthesized, some typical examples are shown in (3). A number of studies have been made on the cationic and neutral complexes of these ligands for example L_1H_2,[11] L_2H_2,[12] (L_3H_2.L_4H_2.L_5H_2.L_6H_2),[13] L_7H_2,[14] L_8H_2,[15] L_9H_2,[16] $L_{10}H_2$,[17] $L_{11}H_2$,[18] $L_{12}H_2$.[19]

The syntheses of the ligand ethylenediaminetetra-acetamide and a number of its cationic metal complexes have been described. The deprotonated complex [CuL]$\cdot 2H_2O$ has also been characterised.[20]

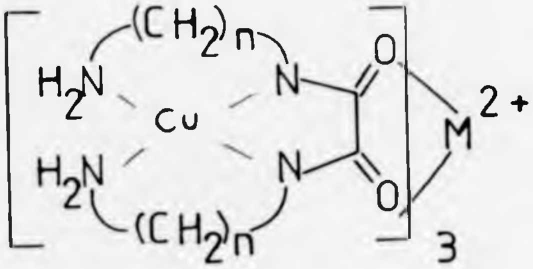
Coordination of the amide group via the deprotonated nitrogen atom is stabilised by a resonance energy contribution, see structure (4).



(4)

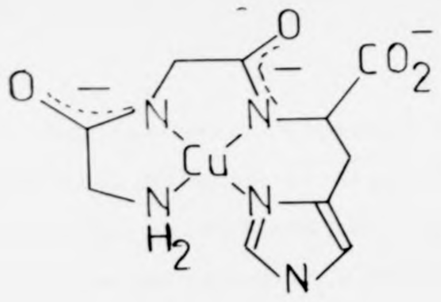
Donation via the protonated amide nitrogen leads to the loss of the resonance energy (ca. 40 KJ mol^{-1}) and this is a strong driving force for amide (or peptide) bond ionisation.

Transition metal complexes of open chain amide ligands having the deprotonated nitrogen atom bound to the metal ion also have the carbonyl oxygen atom of the amide group available for coordination for example the deprotonated Cu(11) complexes of ligands L_3H_2 and L_4H_2 in (3) form tetranuclear complexes[21] of the type shown in structure (5) where M = Co(11) and Ni(11).

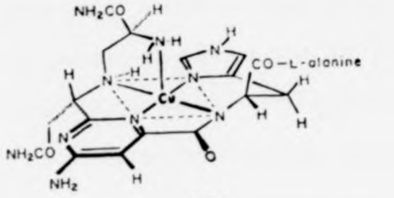


(5)

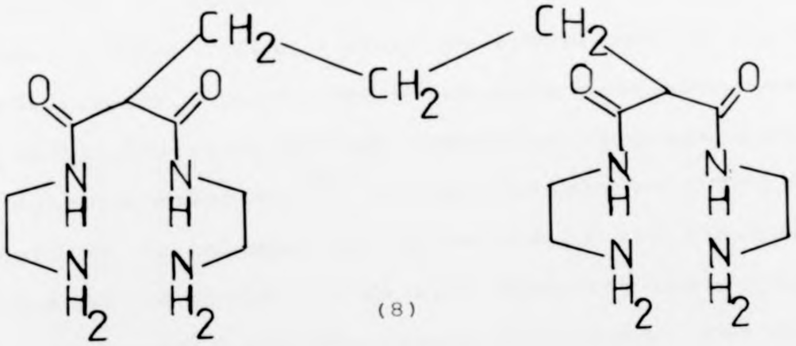
The interest in transition metal complexes of amides stemmed from their potential as models for metalloenzymes. It has been suggested that the zinc metalloenzyme carboxypeptidase catalyses the hydrolysis of peptide bonds by complexing with the amide oxygen so leading to Lewis acid catalysis. At one time binding of Cu(11) to a deprotonated peptide nitrogen was believed to occur in blue copper proteins such as plastocyanin and azurin.[22] However, X-ray crystallographic studies have shown that this is not the case.[23] Current studies suggest that there is a limited tendency for natural systems to incorporate deprotonated peptide-Cu(11) bonds. However, the biological use of deprotonated peptide-Cu(11) interactions is illustrated by serum albumin[25], Structure (6), and by the antibiotic bleomycin which has been isolated as a Cu(11)



(6)



(7)



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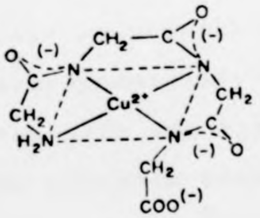


(9)

complex.[24] The bleomycin intermediate p-3A, Structure (7), shows copper (11) binding to five nitrogen donors including, in the equatorial plane both the deprotonated amide nitrogens and an imidazole nitrogen of a histidine residue.[26]

Attempts to mimic the biological oxygen carriers which have pairs of adjacent metal ions, for example (haemocyanin), led to the synthesis of the double cavity amide, Structure (8), prepared by bridging two diamide open chain ligands. Two copper (11) ions are incorporated into this ligand to give a neutral complex with formula Cu_2L.[27]

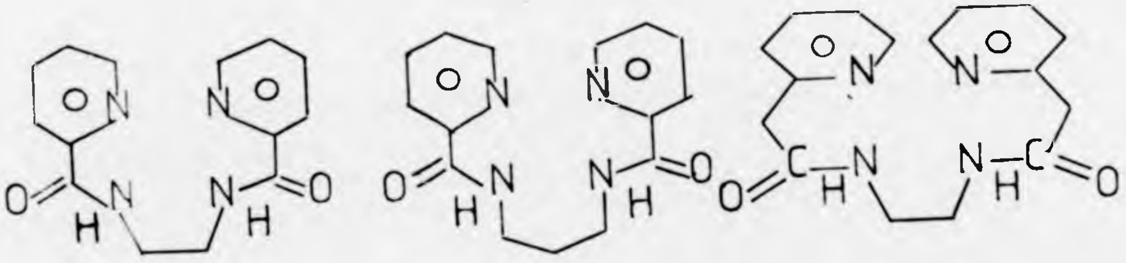
It has been found that complexation of transition metal ions to strongly donating, deprotonated amide nitrogens stabilises high oxidation states of the metal ion.

Bour and Steggerda[28] isolated crystalline Cu(111) complexes of biuret and oxamide providing some of the first evidence that Cu(111) could be stabilised by deprotonated amide groups. Electrode potentials have been measured for 40 Cu(11)/Cu(111) peptide complexes (including peptide amides) in aqueous solution.[29] The potentials were found to be very sensitive to changes in the nature of the ligands with the oxidation of Cu(11) to Cu(111) becoming easier as the number of deprotonated peptide groups increased. The triply deprotonated peptide complexes of copper, see Structure (9), have effective potentials at physiological pH such that O_2 oxidation to Cu(111) is thermodynamically possible. From a correlation between redox potentials and visible absorption maxima it was concluded that the relative gain in crystal field stabilisation energy for the change from d^9Cu(11) to d^8Cu(111) is an important factor in the overall thermodynamic stability of the Cu(111) peptide complexes.

Cyclic voltammetric studies[13] on the deprotonated Cu(11) and Ni(11) complexes of the ligands L_1H_2, L_3H_2, L_4H_2, L_5H_2 and L_6H_2 in (3) have revealed that the stabilisation of Cu(111) and Ni(111) is dependent on the number of atoms in the chelate backbone with the greatest stability found in the 5-5-5 fused ring structures (L_3H_2) rather than 5-6-5 (L_1H_2,L_6H_2) and 6-5-6 (L_4H_2,L_5H_2) fused rings. For the series of ligands the Cu(11) complex of ligand L_3H_2 has the lowest oxidation potential.

The present work is concerned with studies on the complexes of the picolinamide ligands shown in (10). The ligands have been prepared together with their neutral and cationic Cu(11) and Ni(11) complexes. Spectrophotometric and potentiometric titrations have been performed. While synthetic studies on ligands L_AH_2 and L_BH_2 are reported in the literature no electrochemical work on the picolinamides has been published.

In the present work cyclic voltammetric measurements have been made on the neutral Cu(11) and Ni(11) chelates (in acetonitrile) and the ease and reversibility of their oxidation processes monitored as a function of the ligand structure.



L_AH_2 L_BH_2 L_CH_2

(10)

Experimental

Ligands

N,N'-(dipicolyl)-1,2-diaminoethane (L_AH_2)

Ethyl picolinate (7.5g., 0.05 mol) was dissolved in ethanol (*ca*. 30 cm^3) and added to ethylenediamine (1.5g., 0.025 mol) dissolved in ethanol. The solution was refluxed for 2 hours and the solvent removed on a rotary evaporator to give a colourless solid which was recrystallised from chloroform. The product was dried *in vacuo*.

Calc. for $C_{14}H_{14}N_4O_2$: C,62.21; H,5.22; N,20.73;

Found: C,62.42; H,5.51; N,20.84%, m.p. 179-182°C.

The i.r. spectrum (KBr) has ν(NH) at 3330 cm^{-1} and the amide I band at 1655 cm^{-1}.

N,N'-(dipicolyl)-1,3-diaminopropane (L_BH_2)

Ethyl picolinate (7.5g., 0.05 mol) was dissolved in ethanol (*ca*. 30 cm^3) and added to 1,3-diaminopropane (1.85g., 0.025 mol). The solution was refluxed, then the solvent removed to give a colourless solid. The ligand was purified by dissolution in the minimum volume of warm methanol and precipitation by the dropwise addition of water. The product was filtered off and dried *in vacuo*.

Calc. for $C_{15}H_{16}N_4O_2$: C,63.37; H,5.67; N,19.71;

Found: C,63.09; H,5.41; N,19.60%, m.p. 94-95°C.

The i.r. spectrum (KBr) has ν(NH) at 3300 cm^{-1} and the amide I band at 1655 cm^{-1}.

L_CH_2 (N,N'-(di-2-picoylmethylene)-1,2-diaminoethane)

Ethyl 2-pyridyl acetate (5.0g., 0.03 mol) in ethanol (50 cm^3) was added to a solution of ethylenediamine (1.0g., 0.016 mol) in ethanol (50 cm^3). The mixture was refluxed for 4 hours. The volume was reduced to ca. 50 cm^3 on a rotary evaporator and on standing overnight in a refrigerator, white needle-like crystals of the product (0.35g) were obtained. The ligand was recrystallised from ethanol.

Calc. for $C_{16}H_{18}N_4O_2$: C,64.41; H,6.08; N,18.78;

Found: C,64.53; H,5.95; N,19.00%.

The mass spectrum has M^+ at 298 ($C_{16}H_{18}N_4O_2$ = 298).

The ligand has m.p. 165°-168°.

The i.r. spectrum (KBr) has ν(NH) at 3065 cm^{-1} and 3280 cm^{-1} and the amide I band at 1640 cm^{-1}.

Complexes

$[Cu(L_AH_2)](ClO_4)_2 \cdot H_2O$

The ligand L_AH_2 (0.5g., 1.84 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.69g., 1.86 mmol) were separately dissolved in methanol. Upon mixing the methanolic solutions the product precipitated as a pale blue solid. The complex was filtered off, washed with ethanol, diethyl ether and dried *in vacuo*.

Calc. for $C_{14}H_{14}N_4O_{10}$ $CuCl_2 \cdot H_2O$; C,30.56; H,2.93; N,10.17;

Found: C,30.4; H,2.5; N,9.8%.

$[CuL_A]2.5H_2O$

$[Cu(L_AH_2)](ClO_4)_2 \cdot H_2O$ (0.93g., 1.7 mmol) was suspended in water and sodium hydroxide (0.15g., 3.79 mmol) was added giving a purple solution. Concentration of the solution on a water bath followed by refrigeration allowed crystallisation of the product as a violet solid. The complex was filtered off, washed with diethyl ether and dried *in vacuo*.

Calc. for $C_{14}H_{12}N_4O_2$ Cu 2.5 H_2O; C,44.60; H,4.55; N,14.87;
Found: C,43.91; H,4.13; N,14.54%.

The visible spectrum of the complex $[CuL_A]2.5 \cdot H_2O$ measured in dilute aqueous sodium hydroxide has a band maximum, (λ_{max}) at 540 nm (ε = 240). In methanol the complex has λ_{max} at 544 nm (ε = 174).

$[Ni_2(L_AH_2)_3](ClO_4)_4 \cdot 6H_2O$

The ligand L_AH_2 (0.5g., 1.84 mmol) was dissolved in methanol (50 cm^3). A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (1.0g., 2.76 mmol) in methanol was added to give a pale blue solution. Heating on a water bath led to the rapid crystallisation of the complex. The solution was allowed to cool and the pale blue complex was filtered off, washed with diethyl ether and dried *in vacuo*.

Calc. for $C_{42}H_{42}N_{12}O_{24}$ $Ni_2Cl_4 \cdot 6H_2O$; C.35.17: H,3.80; N,11.72;
Found: C,35.01; H,2.95; N,11.61%.

$[NiL_A] \cdot H_2O$

The ligand L_AH_2 (0.5g., 1.84 mmol) was dissolved in methanol (30 cm^3) and $NiCl_2 \cdot 6H_2O$ (0.43g., 1.84 mmol) in methanol (30 cm^3) added. Sodium hydroxide (0.15g., 3.68 mmol) dissolved in water (*ca*. 5 cm^3) was added dropwise to give a yellow solution which was concentrated on a water bath to *ca*. 20 cm^3. Upon cooling yellow crystals of product precipitated. The complex was filtered off, washed with diethyl ether and dried *in vacuo*.

Calc. for $C_{14}H_{12}N_4O_2$ Ni·H_2O: C,48.74; H,4.09; N,16.24;
Found: C,47.51; H,3.91; N,15.65%.

In the visible electronic spectrum of $[NiL_A]\cdot H_2O$ (measured in dilute aqueous sodium hydroxide) the d-d band is obscured by a charge transfer band having λ_{max} at 377 nm (ε = 4,642). A solid state spectrum shows λ_{max} at 400 nm.

$[Cu(L_BH_2)](ClO_4)_2$

The ligand L_BH_2 (0.5g., 1.75 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.65g., 1.75 mmol) were dissolved in methanol (100 cm^3). Fine light blue crystals precipitated after heating on a water bath for several minutes. The solution was refrigerated for one hour, the complex filtered off, washed with diethyl ether and dried *in vacuo*.

Calc. for $C_{15}H_{16}N_4O_{10}Cl_2Cu$; Cu,32.95; H,2.95; N,10.25;
Found: C,32.07; H,2.55; N,9.96%.

$[CuL_B]\cdot 3H_2O$

$Cu(ClO_4)_2\cdot 6H_2O$ (0.65g., 1.75 mmol) dissolved in the minimum volume of methanol was added to a solution of the ligand L_BH_2 (0.5g., 1.75 mmol) dissolved in the minimum volume of methanol. A pale blue solid immediately precipitated but dropwise addition of sodium hydroxide (0.14g., 3.52 mmol) in water dissolved the precipitate giving a blue-violet solution which was heated at 60°C for 30 minutes. Upon cooling, dark blue crystals of the product precipitated from solution. The complex was filtered off, washed with water, diethyl ether and dried *in vacuo*.

Calc. for $C_{15}H_{14}N_4O_2Cu\cdot3H_2O$; C,45.05; H,5.04; N,14.01;

Found: C,44.83; H,4.76; N,13.78%.

Thermogravimetric analysis of the complex shows a 13.3% weight loss in the range 67-147°C equivalent to a loss of three water molecules per molecule of complex. The visible electronic spectrum of $[CuL_B]\cdot3H_2O$ in dilute aqueous sodium hydroxide has λ_{max} at 565 nm (ε = 93). In methanol the complex has λ_{max} at 574 nm (ε = 109).

$[Ni_2(L_BH_2)_3](ClO_4)_4$

The ligand L_BH_2 (0.5g., 1.75 mmol) and $Ni(ClO_4)_2\cdot6H_2O$ (0.96g., 2.62 mmol) were dissolved in methanol (100 cm^3) to give a pale blue solution. Concentration on a water bath allowed precipitation of the product as a pale blue solid. The solution was cooled and the complex filtered off, washed with diethyl ether and dried *in vacuo*.

Calc. for $C_{45}H_{48}N_{12}O_{22}Ni_2Cl_4$; C,39.50; H,3.54; N,12.29;

Found: C,40.24; H,3.68; N,12.27%.

$[NiL_B]\cdot2H_2O$

The ligand L_BH_2 (0.3g., 1.05 mmol) was dissolved in methanol (30 cm^3) and $NiClO_4\cdot6H_2O$ (0.38g., 1.05 mmol) in methanol (30 cm^3) added. Sodium hydroxide (0.09g., 2.25 mmol) dissolved in water (*ca*. 5 cm^3) was added dropwise and the resultant yellow solution was heated on a water bath. Upon refrigeration orange crystals of product precipitated. The complex was filtered off, washed with diethyl ether and dried *in vacuo*.

Calc. for $C_{15}H_{14}N_4O_2Ni$ $2H_2O$; C,47.78; H,4.81; N,14.86;
Found: C,47.70; H,4.24; N,14.89%.

The visible electronic spectrum of $[NiL_B]\cdot 2H_2O$ in dilute aqueous sodium hydroxide has λ_{max} at 372 nm (ε = 2,149) and λ_{sh} at 470 nm (ε = 87).

$[Cu(L_CH_2)](ClO_4)_2\cdot H_2O$

$Cu(ClO_4)_2\cdot 6H_2O$ (0.61g., 1.64 mmol) was dissolved in the minimum volume of water and added dropwise to a solution of the ligand L_CH_2 (0.5g., 1.67 mmol) in water. The pale, blue-green complex which rapidly precipitated was filtered off, washed with ethanol and dried *in vacuo*.

Calc. for $C_{16}H_{18}N_4O_{10}CuCl_2\cdot H_2O$; C,33.20; H,3.48; N,9.68;
Found: C,33.67; H,3.33; N,9.74%.

Thermogravimetric analysis of the complex shows a percentage weight loss in the range 87°-137° consistent with one water molecule per molecule of complex.

$[CuL_C]\cdot 3.5\ H_2O$

$[Cu(L_CH_2)](ClO_4)_2\cdot H_2O$ (0.5g., 0.86 mmol) from above was dissolved in a solution of sodium hydroxide (0.1g., 2.50 mmol). The violet solution was loaded onto a column of CM Sephadex-C25 cation exchange resin and eluted with water.

The eluted solution was concentrated on a water bath and the product crystallised out upon cooling. The violet crystals were filtered off, washed with ethanol and dried <u>in</u> <u>vacuo</u>.
Calc. for $C_{16}H_{16}N_4O_2Cu \cdot 3.5\ H_2O$; C,45.44; H,5.48; N,13.24;
Found: C,45.07; H,5.68; N,13.29%.
Thermogravimetric analysis of the complex shows a 16.5% weight loss in the range 67°-137° consistent with 4 water molecules per molecule of complex. A visible electronic spectrum of $[CuL_C]$ 3.5 H_2O measured in methanol has a band maximum λ_{max} at 536 nm (ε = 106).

$[Ni(L_CH_2)](ClO_4)_2$

$Ni(ClO_4)_2 \cdot 6H_2O$ (0.61g., 1.67 mmol) was dissolved in the minimum volume of water and added dropwise to a solution of the ligand L_CH_2 (0.5g., 1.67 mmol) in water. The pale, green solid which rapidly precipitated was filtered off, washed with ethanol and dried <u>in</u> <u>vacuo</u>.
Calc. for $C_{16}H_{18}N_4O_{10}NiCl_2$; C,34.57; H,3.26; N,10.08;
Found: C,35.63; H,3.64; N,10.04%.

$[NiL_C]$

Attempts to isolate this complex in the solid state were unsuccessful. Intense yellow solutions were produced by mixing $Ni(ClO_4)_2$ with LH_2 in dilute sodium hydroxide solution. Upon standing nickel hydroxide precipitated leaving the supernatant colourless.

Results and Discussion

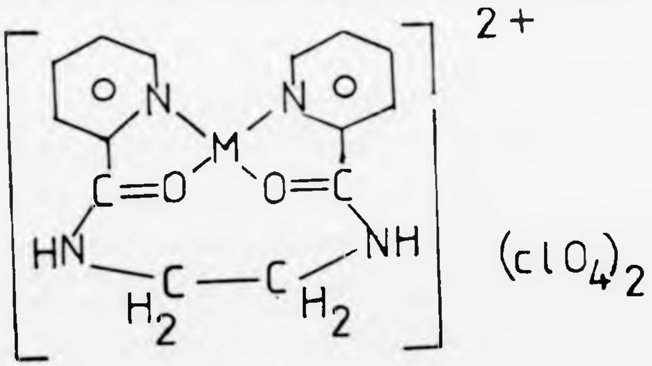
The ligands N,N'-(dipicolyl)-1,2-diaminoethane (L_AH_2) and N,N'-(dipicolyl)-1,3-diaminopropane (L_BH_2) were prepared by the reaction of ethyl picolinate (2 moles) with the appropriate diamine (1 mole) in ethanol. The ligand (L_CH_2) was prepared by the reaction of ethyl-2-pyridyl acetate with ethylenediamine in ethanol. Reaction of L_AH_2, L_BH_2 and L_CH_2 with copper (11) in neutral solution gives the cationic complexes $[Cu(L_AH_2)](ClO_4)_2.H_2O$, $[Cu(L_BH_2)](ClO_4)_2$ and $[Cu(L_CH_2)](ClO_4)_2.H_2O$ respectively. Reaction of the ligands with nickel (11) gives the dimeric complexes $[Ni_2(L_AH_2)_3](ClO_4)_4.6H_2O$, $[Ni_2(L_BH_2)_3](ClO_4)_4$ and the monomeric complex $[Ni(L_CH_2)](ClO_4)_2$. Under basic conditions neutral species are formed and the following complexes have been isolated:
$[CuL_A]2.5H_2O$, $[NiL_A].H_2O$, $[CuL_B].3H_2O$, $[NiL_B]2H_2O$, $[CuL_C]3.5H_2O$. In some cases the isolation of analytically pure complexes from analytically pure samples of L_AH_2, L_BH_2 and L_CH_2 has proved difficult, this may be due to the presence of polymeric complex impurities. The tendency for L_AH_2 and L_BH_2 to form dimeric nickel (11) complexes is noted. Vagg et al.[14] reported that several attempts to prepare $[Cu(L_AH_2)](ClO_4)_2$ gave products having microanalyses indicative of non-stoichiometric polymeric products, however the nitrate salt $[Cu(L_AH_2)](NO_3)_2$ was isolated in pure form. A change in counter ion may perhaps lead to easier isolation of these complexes.

I.r. spectra

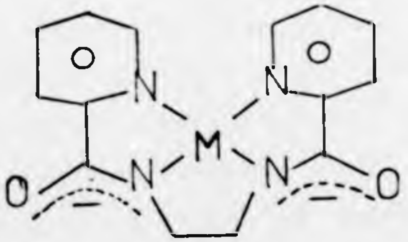
The nature of the bonding between transition metal ions and diamide open chain ligands in the cationic complexes of general formulae $[MLH_2](ClO_4)_2$ and $[M_2(LH_2)_3](ClO_4)_4$ is indicated by i.r. spectra.

Amide ligands display three characteristic i.r. bands, these are: Amide I (νCO + νCN), Amide II (νC-N + δNH) and Amide III (δNH + νCN). Upon coordination of the ligands to form cationic complexes where the amide is bonded to the metal ion through the carbonyl oxygen atom of the amide group the Amide I band shifts to lower frequency and the Amide II and Amide III bands shift to higher frequency. A comparison of i.r. spectra of free ligands and cationic complexes prepared in the present work show that the Amide I bands of the free ligands shift to lower frequency upon complexation, for example in the ligand L_AH_2 the Amide I band appears at 1655 cm^{-1} while in the complex $[Cu(L_AH_2)](ClO_4)_2.H_2O$ this band appears as two absorptions at 1625 and 1600 cm^{-1} which are not fully resolved. In the absence of deuterium exchange experiments, accurate band assignments are not possible but the trends in frequency shift for Amide I, Amide II and Amide III bands upon complexation suggest that the carbonyl groups of the amides are probably acting as donors and a possible structure for the protonated complexes of general formula $[M(LH_2)](ClO_4)_2$ is shown in (11). The complexes all show typical i.r. bands due to ionic perchlorate at 1100 cm^{-1} (broad) and 624 cm^{-1}. In the solid state it is possible that the perchlorate anions are weakly bonded in the two axial sites.

The neutral, deprotonated complexes of the type $[ML]^{\circ}$ obtained by reacting the ligand LH_2 with M^{2+} in basic media show quite different i.r. spectra from the cationic complexes of the form $[M(LH_2)](ClO_4)_2$. In the deprotonated complexes absorption bands associated with the N-H bond are absent. The Amide II and Amide III bands (combinations of νCN and δNH) are replaced by a strong absorption ca. 1400 cm^{-1} which is assigned to a C-N stretching mode. The Amide I band shifts to lower frequency, for example, the Amide I band of the ligand L_CH_2 appears at 1640 cm^{-1} and in the complex $[CuL_C]3.5H_2O$ it shifts to 1570 cm^{-1}. The bands due to ionic perchlorate in the cationic complexes are absent in the neutral species. The data are consistent with the complexes having N_4 donor sets involving two deprotonated amide nitrogens. The deprotonated complexes are believed to have the structures shown in (12).



(11)



(12)

An X-ray crystallographic study of $[CuL_B].3H_2O$ by Stephens and Vagg[30] has shown the Cu(11) environment to be square pyramidal with the tetradentate N_4 ligand encompassing the base and a water molecule occupying the apex.

Potentiometric titrations

This technique is generally useful for assessing the purity of ligands and was performed for the Cu(11) and Ni(11) complexes of L_CH_2.

A potentiometric titration was carried out by mixing equimolar amounts of $Cu(ClO_4)_2.6H_2O$ with L_CH_2 in 0.1 mol dm^{-3} (KNO_3) at 25°C and titrating against 0.05 mol dm^{-3} (NaOH). The complexation of Cu(11) is rapid and a sharp end point was obtained upon addition of two equivalents of base. On the basis that one mole of the ligand L_CH_2 reacts with two moles of base the experimental molecular weight of ligand is found to be 292. The calculated molecular weight is 298.

A potentiometric titration was carried out by mixing equimolar amounts of $Ni(ClO_4)_2.6H_2O$ with L_CH_2 in water at 25°C and titrating against 0.1 mol dm^{-3} (NaOH). The solution is diacidic and consumes two moles of base per mole of ligand.

Spectrophotometric titrations

The complexes $[CuL_A]2.5H_2O$, $[CuL_B].3H_2O$, $[CuL_C]3.5H_2O$, $[NiL_A]H_2O$, $[NiL_B]2H_2O$ and $[NiL_C]$ in water, were titrated against hydrochloric acid, under nitrogen, with the changes in visible spectra monitored against changes in solution pH.

$[CuL_A]2.5\ H_2O$

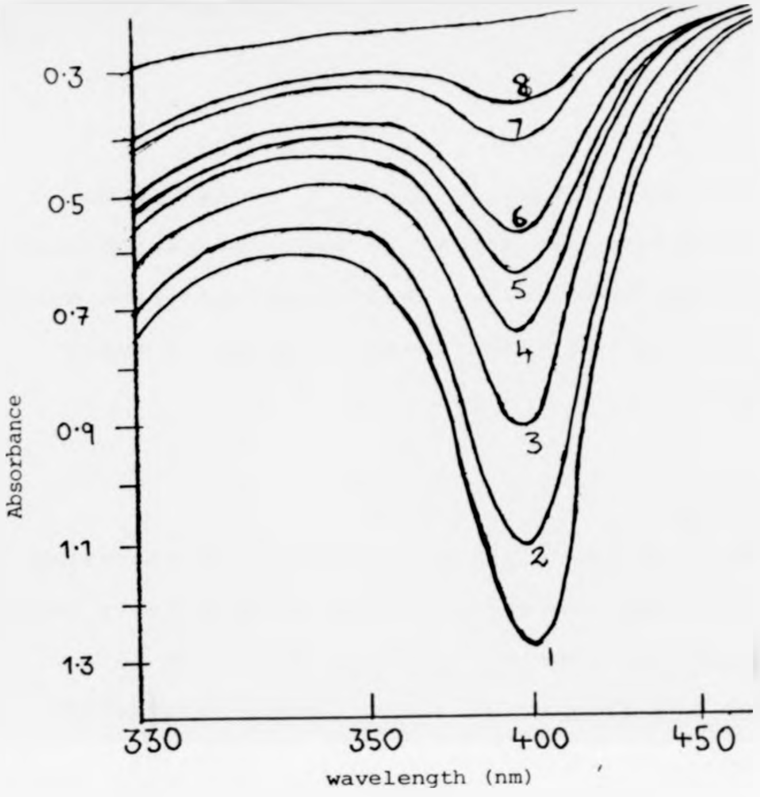
The deprotonated complex has λ_{max} at 540 nm but the titration was carried out at 335 nm where marked changes in the charge transfer band occur. Amide deprotonation occurs in the pH range 4-6 and the deprotonated complex is fully formed at pH 6.5.

$[CuL_B].3H_2O$

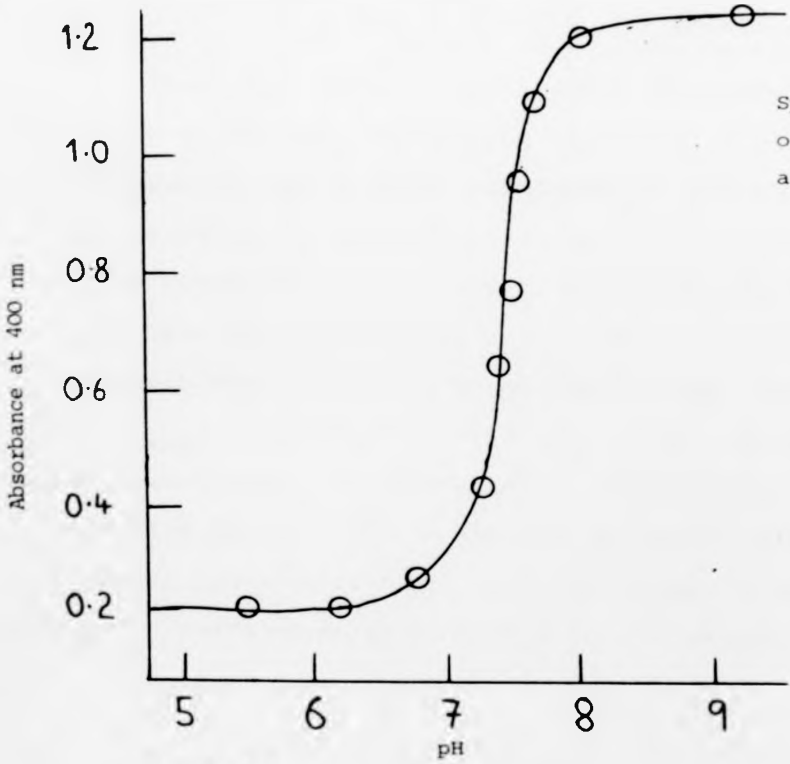
The titration shows amide deprotonation occurring in the pH range 4-6 with the deprotonated complex fully formed at pH 6.5. Although the complex has λ_{max} at 570 nm the absorbance changes are greater at 370 nm and were measured at this wavelength.

$[CuL_C]\cdot 3.5H_2O$

An equimolar aqueous solution of L_CH_2 and $Cu(ClO_4)_2.6H_2O$ was titrated spectrophotometrically against sodium hydroxide and hydrochloric acid in the pH range 2.5-12 using a series of visible spectra recorded at different pH values. Amide deprotonation occurs in the pH range 4-8.5. At pH 5.0 the solution shows a broad absorption band with λ_{max} *ca*. 700 nm. Upon addition of base the band moves to shorter wavelength (pH7, λ_{max} 585 nm; pH 10.2, λ_{max} 560 nm) and undergoes appreciable intensification. The deprotonated complex is fully formed at and above pH9. These data are consistent with a change in donor atom from amide oxygen to nitrogen as a result of amide ligand deprotonation. The final



Scan	pH
1	10.88
2	7.80
3	7.61
4	7.48
5	7.41
6	7.37
7	7.25
8	7.08



Spectrophotometric titration of a 1:1 mixture of Ni(II) and L_AH_2 at 400 nm

Figure 3.1

spectrum at pH 10 has λ_{max} 560 nm as expected for a $Cu(II)N_4$ chromophore.

$[NiL_A]\cdot H_2O$

A spectrophotometric titration of $[NiL_A]H_2O$ against hydrochloric acid shows that amide deprotonation takes place in the pH range 6-8 with the deprotonated complex fully formed at pH 8.5. During the titration the absorbance changes were monitored at λ_{max} = 400 nm. A typical curve for the titration is shown in Figure 3.1.

$[NiL_B]\cdot 2H_2O$

Amide ligand deprotonation occurs in the pH range 6.5-8.5 with the complex fully formed at pH 9.0. The absorbance change was monitored at 480 nm.

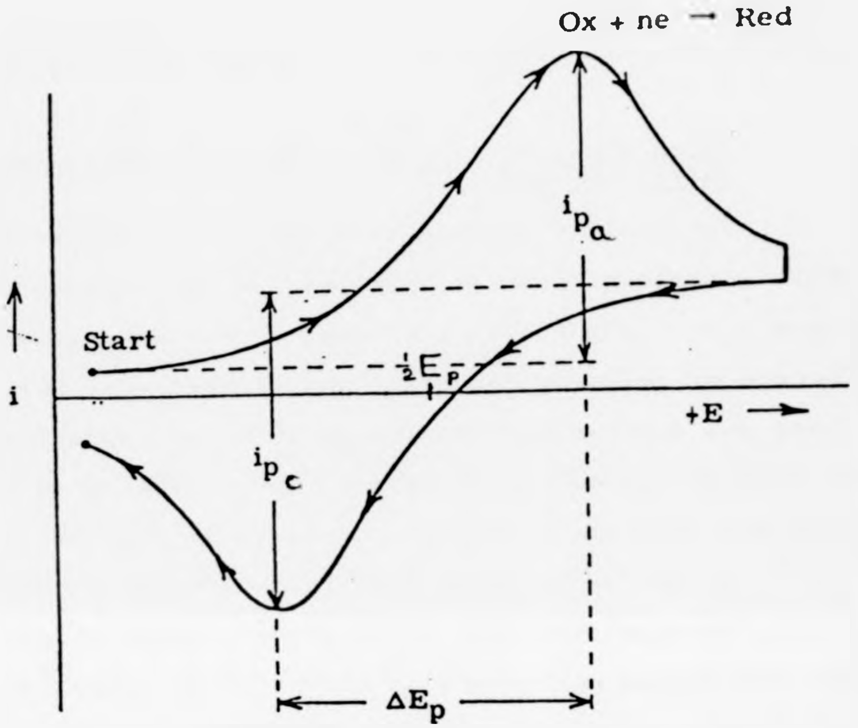
$[NiL_C]$

An equimolar aqueous solution of LH_2 and $Ni(ClO_4)_2\cdot 6H_2O$ was titrated spectrophotometrically against sodium hydroxide and hydrochloric acid in the pH range 5-12 with a series of spectra recorded at different pH values. Amide deprotonation takes place in the pH range 7.5-11.5. Below pH7 the solution shows no absorption in the visible region of the spectrum. As the pH is increased a broad absorption develops <u>ca</u>. 465 nm. Further addition of base gives appreciable band intensification. The deprotonated complex is fully formed at and above pH 12. These data are consistent with a change in donor atom from amide oxygen to nitrogen. The final spectrum λ_{max} 465 nm is consistent with that expected for a planar Ni(11)N_4 chromophore.

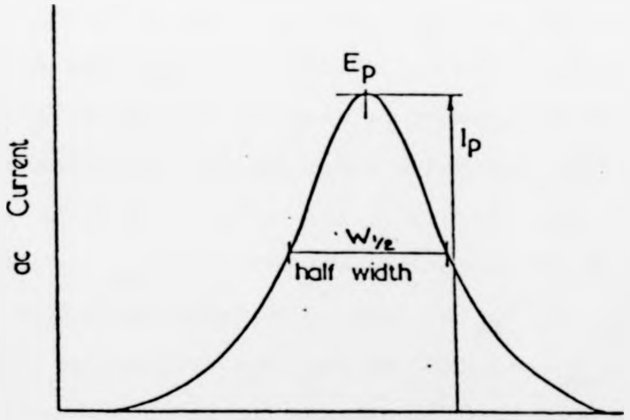
Solid state nujol mull spectra of protonated amide complexes

Solid state spectra were collected for the Cu(11) and Ni(11) protonated amide complexes of the ligands L_AH_2, L_BH_2 and L_CH_2. Insolubility of these chelates precludes the collection of solution spectra. The samples were prepared by grinding the appropriate complex in Nujol and spreading a thick film of the mull onto filter paper. The films were scanned for absorbance changes in the range 300-800 nm.

It has been established that octahedral complexes with NiO_6 chromophores have 3 reflectance bands at ca. 9000, 14,000 and 25,000 cm^{-1} assigned to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively and octahedral NiN_6 chromophores have 3 reflectance bands at ca. 11,000, 18,500 and 30,000 cm^{-1} assigned to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively. In the present work the complexes $[Ni_2(L_AH_2)_3](ClO_4)_4 \cdot 6H_2O$ and $[Ni_2(L_BH_2)_3]$-$(ClO_4)_4$ are pale blue solids. Solid state spectra of both chelates show broad d-d bands ca. 600 nm assigned to the transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ with steep charge transfer bands commencing ca. 400 nm. Applying the rule of average environments an octahedral NiO_3N_3 chromophore would have λ_{max} ca. 615 nm for the transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and an octahedral NiO_4N_2 chromophore would have λ_{max} ca. 645 nm for the transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$. Therefore the observed spectra of the Ni(11) complexes of L_AH_2 and L_BH_2 agree with those predicted for an octahedral NiO_3N_3 chromophore.



Cyclic Voltammagram



AC Voltammagram

Figure 3.2

The reflectance spectra for the Cu(11) complexes show for $[CuL_AH_2](ClO_4)_2 \cdot H_2O$ λ_{max} *ca.* 625 nm, $[CuL_BH_2](ClO_4)_2 \cdot H_2O$ λ_{max} *ca.* 612 nm and $[CuL_CH_2](ClO_4)_2$ λ_{max} *ca.* 626 nm. The similarity in λ_{max} for the three complexes suggests that they all have the same set of donor atoms. Detailed interpretation of solid state spectra of copper (11) complexes is usually complicated due to the relatively low symmetry of these species.

Redox Studies

As mentioned in the Introduction deprotonated amides for example, tripeptides, when bonded to metal ions are found to stabilise high oxidation states on the metal ions. Thus redox studies were performed on the deprotonated complexes prepared in the present work to determine their redox potentials. The solutions were prepared for $[CuL_A] \cdot 2.5H_2O$, $[NiL_A] \cdot H_2O$, $[CuL_B] \cdot 3H_2O$, $[NiL_B] \cdot 2H_2O$ and $[CuL_C] \cdot 3.5H_2O$ by dissolving the appropriate complex in a support electrolyte of 0.1 mol dm^{-3} tetra *n*-butyl ammonium perchlorate in acetonitrile to make the concentration of complex in solution *ca.* 1 x 10^{-3} mol dm^{-3}. $[NiL_C]$ was not isolated in the solid state and was prepared *in situ* by dissolving equimolar amounts of L_CH_2 and $Ni(ClO_4)_2 \cdot 6H_2O$ in the support electrolyte to give a concentration of complex *ca.* 1 x 10^{-3} mol dm^{-3}. For all studies a platinum indicator electrode was used and all potentials are expressed versus a saturated calomel electrode (SCE). The cyclic voltammagram and the AC voltammagram shown in Figure 3.2 illustrate the experimentally determined parameters discussed in the text.

$[CuL_A]\cdot 2.5H_2O$

The complex $[CuL_A]\cdot 2.5H_2O$ shows a fully reversible one-electron oxidation by cyclic voltammetry at a platinum electrode at $\frac{1}{2}E_p$ = + 0.91 volts where $\frac{1}{2}E_p$ is the mid-point between $E_p(a)$ (the potential at which $I_p(a)$, the forward peak current, is at a maximum) and $E_p(c)$ (the potential at which $I_p(c)$ the return peak current is at a maximum). The peak height ratio $I_p(a)/I_p(c)$ is close to unity and the peak to peak separation ΔE_p = 60 mV. A plot of $I_p(a)$ versus the square root of scan rate ($v^{\frac{1}{2}}$) is linear, passing through the origin, indicating diffusion control. AC measurements on platinum give E_p = + 0.92 volts with the wave width at half peak height ($w_{\frac{1}{2}}$) equal to 100 mv, close to that expected for a fully reversible one-electron transfer (90 mv). By stirred CV $E_{\frac{1}{2}}$ = + 0.91 volts. The cyclic voltammetric data for the complex are given in Table 3.1.

TABLE 3.1

Cyclic voltammetric data[a] for $[CuL_A]\cdot 2.5H_2O$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	19.5	17.0	1.14	+0.91	70
100	29.0	26.0	1.11	+0.91	60
200	38.0	35.0	1.08	+0.90	70
500	56.0	51.0	1.09	+0.91	80

a. Support electrolyte is 0.1 mol dm^{-3} tetra n-butyl ammonium perchlorate in acetonitrile. All potentials are measured at a platinum indicator electrode with respect to an SCE. The solution is 1 x 10^{-3} mol dm^{-3} in $[CuL_A]\cdot 2.5H_2O$

Redox chemistry of $[NiL_A]H_2O$ in 0.1 mol dm^{-3} tetra-n-butyl ammonium perchlorate in acetonitrile

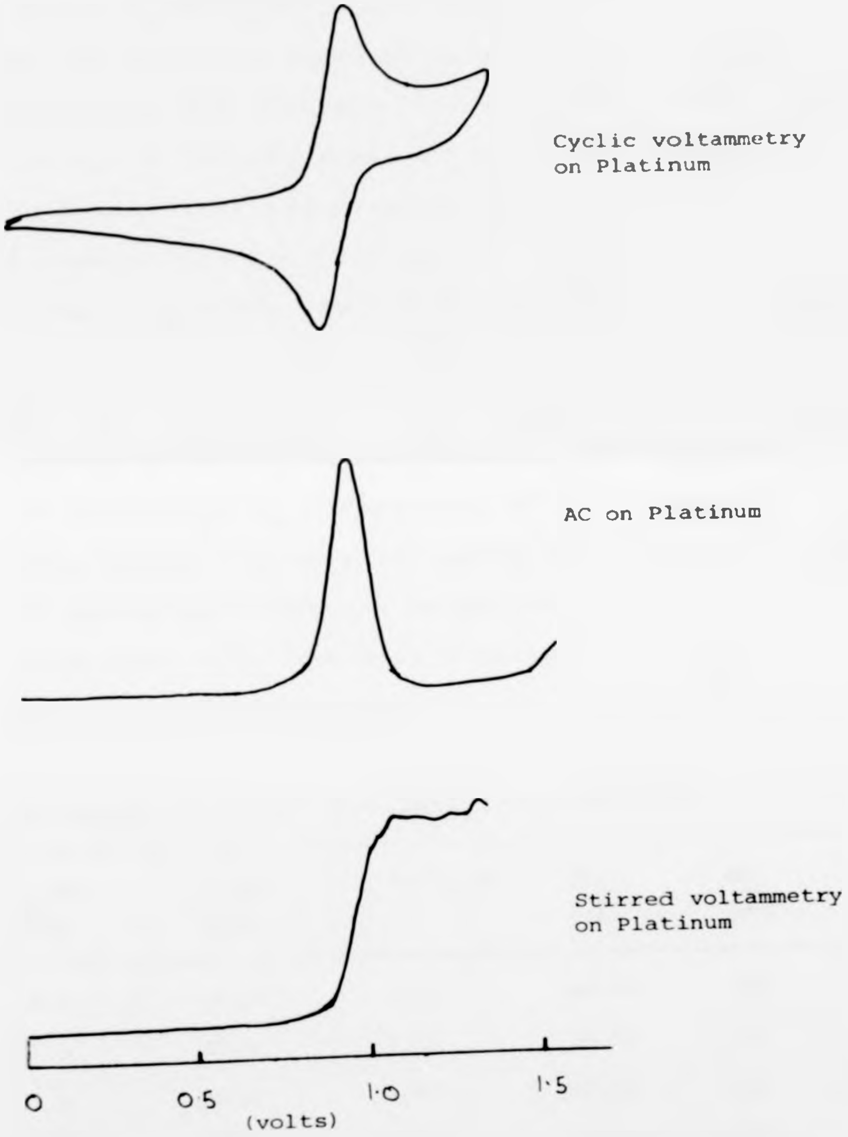


Figure 3.3

$[NiL_A]\cdot H_2O$

$[NiL_A]\cdot H_2O$ shows a quasi reversible one-electron oxidation at + 0.93 volts by CV at a platinum electrode with the ratio $I_p(a)/I_p(c)$ close to unity and ΔE_p = 100 mv. Thus while the oxidation product is stable on the timescale of the experiment and available for reduction on the return half of the cycle the ΔE_p value of 100 mv at a scan rate of 100 mv/s suggests that the electron transfer itself is sluggish. Diffusion control for this process is indicated by a linear plot of $I_p(a)$ versus $\nu^{\frac{1}{2}}$. By the AC technique, at a frequency of 205 Hz at a platinum wire electrode, the oxidation is present at E_p = + 0.95 volts. The peak current I_p shows a linear dependence on the square root of frequency ($w^{\frac{1}{2}}$) in the range 60Hz-305Hz with I_p independent of $w^{\frac{1}{2}}$ at higher frequencies, this fulfils the AC criteria for quasi-reversibility. The stirred CV technique shows the oxidation present at $E_{\frac{1}{2}}$ = + 0.94 volts, see Figure 3.3. The cyclic voltammetric data for the complex are given in Table 3.2.

TABLE 3.2

Cyclic voltammetric data[a] for $[NiL_A]\cdot H_2O$ at 25°C

ν (mv/s)	$I_p(a)$ (µA)	$I_p(c)$ (µA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	23.0	21.5	1.07	+0.93	80
100	31.5	27.0	1.16	+0.93	100
200	43.0	40.0	1.07	+0.93	100
500	68.6	60.0	1.14	+0.93	120

a. Support electrolyte is 0.1 mol dm^{-3} tetra n-butyl ammonium perchlorate in acetonitrile. All potentials are measured at a platinum indicator electrode versus an SCE. The solution is 1×10^{-3} mol dm^{-3} in $[NiL_A]\cdot H_2O$.

Redox Studies on $[NiL_B]$ in 0.1 mol dm^{-3} tetra-n-butyl ammonium perchlorate in acetonitrile

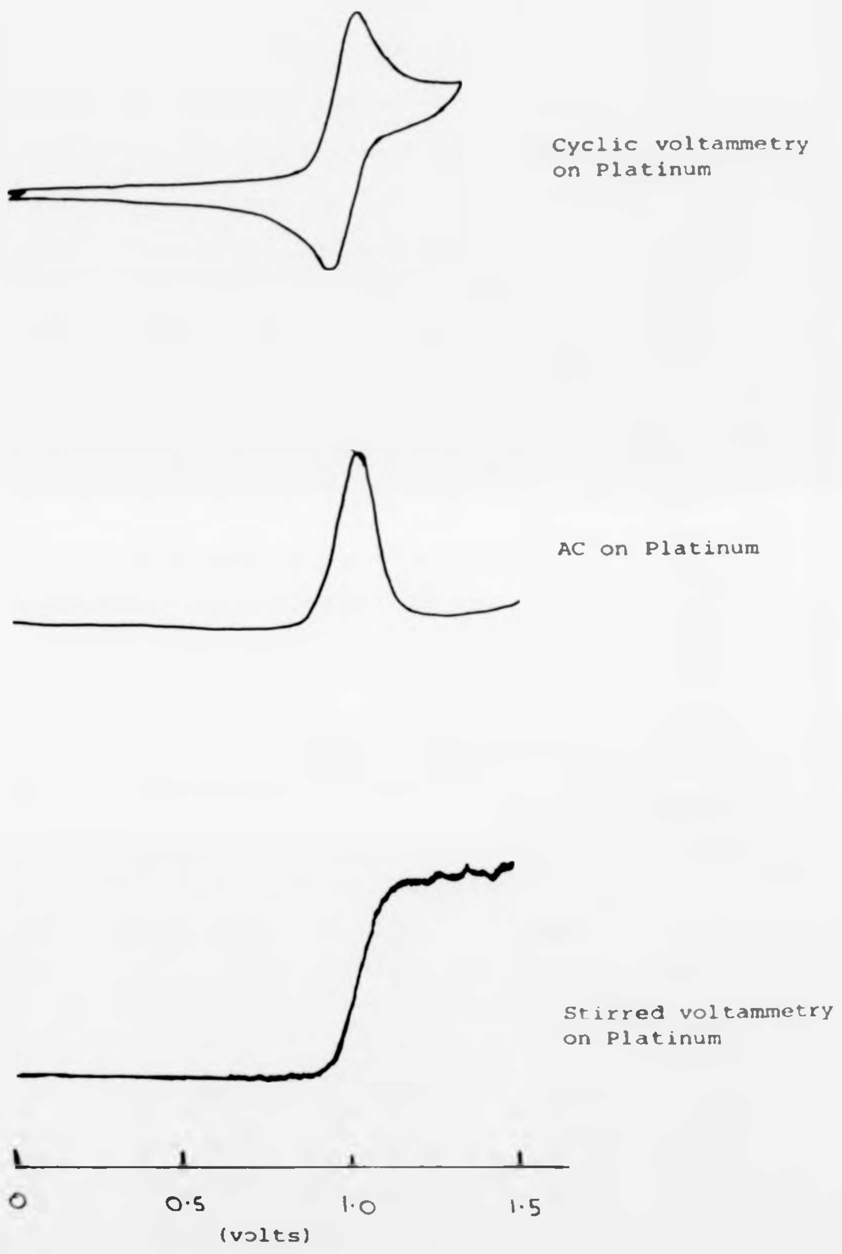


Figure 3.4

$[NiL_B].2H_2O$

The complex $[NiL_B]\cdot 2H_2O$ shows an irreversible one-electron oxidation at $\frac{1}{2}E_p$ = + 0.98 volts by cyclic voltammetry at a platinum wire electrode with the ratio $I_p(a)/I_p(c)$ equal to 1.66 at a scan rate of 100 mv/s suggesting that the product of oxidation is undergoing some decomposition following electron transfer. The peak to peak separation ΔE_p = 80 mv. The process is diffusion controlled as indicated by a linear plot of $I_p(a)$ versus $v^{\frac{1}{2}}$ passing through the origin. The oxidation is seen at E_p = + 1.01 volts by the AC technique on platinum with $W_{\frac{1}{2}}$ = 140 mv at 205Hz and I_p independent of $w^{\frac{1}{2}}$ confirming irreversibility. By stirred CV the oxidation wave appears at $E_{\frac{1}{2}}$ = + 1.02 volts, see Figure 3.4. The cyclic voltammetric data are given in Table 3.3.

TABLE 3.3

Cyclic voltammetric data[a] on $[NiL_B]\cdot 2H_2O$ at 25°C

v (mv/s)	$I_p(a)$ (µA)	$I_p(c)$ (µA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	37.5	26.5	1.41	+0.99	80
100	60.0	36.0	1.66	+0.98	80
200	75.0	54.0	1.39	+0.98	90
500	105	82.5	1.27	+0.98	110

a. Support electrolyte is 0.1 mol dm^{-3} tetra n-butyl ammonium perchlorate in acetonitrile. All potentials are measured at a platinum indicator electrode versus an SCE. The solution is 1 x 10^{-3} mol dm^{-3} in $[NiL_B]\cdot 2H_2O$ $[CuL_B]\cdot 3H_2O$

$[CuL_B]\cdot3H_2O$

The complex $[CuL_B]\cdot3H_2O$ shows an irreversible oxidation at $E_p(a) = +1.10$ volts by cyclic voltammetry at a platinum electrode. There is no current produced on the return half of the cycle. The process is diffusion controlled with a plot of $I_p(a)$ versus $v^{\frac{1}{2}}$ giving a straight line through the origin. By the AC technique at a platinum wire $E_p = +1.09$ volts with $w_{\frac{1}{2}} = 140$ mv at 205Hz. The independence of I_p on $w^{\frac{1}{2}}$ confirms irreversibility. By stirred CV at a platinum electrode $E_{\frac{1}{2}} = +1.13$ volts.

$[CuL_C]\cdot3.5H_2O$

The complex $[CuL_C]\cdot3.5H_2O$ by cyclic voltammetry at a platinum electrode shows an irreversible oxidation at $E_p(a)$ + 1.12 volts. There is no current produced on the return half of the cycle.

$[NiL_C]$

The complex $[NiL_C]$ shows an irreversible oxidation wave at $E_p(a) = +1.18$ volts. There is no peak current on the return half of the cycle.

The data are summarised in Table 3.4.

The redox orbitals involved in the one-electron oxidations of the deprotonated complexes studied in the present work are believed to be metal based. The strong in-plane ligand fields of the deprotonated amides are expected to stabilise the d^8 Cu(III) ions and chemical oxidation of $[CuL_A]\cdot2.5H_2O$ with hydrogen peroxide in water leads to a

TABLE 3.4

Cyclic voltammetric data[a] on deprotonated amide complexes

Complex	½E_p (v)	Degree of reversibility
$[CuL_A]\cdot 2.5H_2O$	+0.91	reversible
$[NiL_A]H_2O$	+0.93	quasi-reversible
$[CuL_B]\cdot 3H_2O$	+1.10	irreversible
$[NiL_B]\cdot 2H_2O$	+0.98	irreversible
$[CuL_C]\cdot 3.5H_2O$	+1.12	irreversible
$[NiL_C]$	+1.18	irreversible

a. Support electrolyte is 0.1 mol dm^{-3} tetra n-butyl ammonium perchlorate in acetonitrile. All potentials are measured at a platinum indicator electrode versus the SCE. The solutions are ca. 1 x 10^{-3} mol dm^{-3} in [ML].

yellow solution which lacks the d-d band at 540 nm due to the Cu(11) ion. Cyclic voltammetric studies coupled with e.s.r. measurements on the oxidation processes of a wide range of Cu(11) tri-peptides have established the redox orbital to be metal based, that is involving the Cu(11)/Cu(111) couple;[13] furthermore, a good correlation was found to exist between the absorption frequencies of the d-d bands of the Cu(11) complexes and their ease of oxidation to Cu(111) complexes. This correlation suggests that the relative gain in CFSE for the change from d^9 Cu(11) to d^8 Cu(111) is an important factor in the overall thermodynamic stability of the Cu(111) peptide complexes, see Table 3.5.

TABLE 3.5

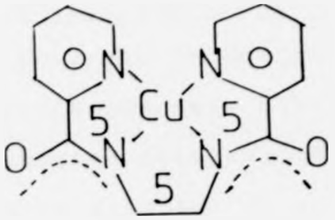
Correlations of $E_{\frac{1}{2}}$ and λ_{max} for tripeptides of copper (11)

Ligand[a]	λ_{max} (nm)	$E_{\frac{1}{2}}$[b] (v)
GGG	555	+0.92
GGA	551	+0.88
GAA	546	+0.85
AAA	543	+0.81
GGL	545	+0.87
GGV	543	+0.87

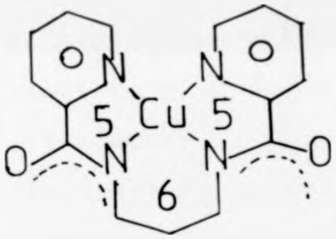
a. G = glycine, A = alanine, L = leucine, V = valine,

b. potentials measured by cyclic voltammetry at a carbon paste working electrode versus NHE. All data is taken from reference 29.

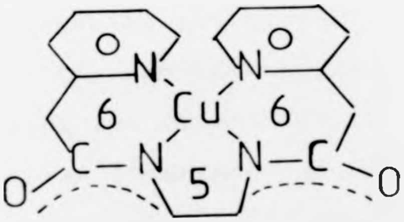
In the present work the only deprotonated amide complexes to show reversible oxidation processes are $[CuL_A]$ and $[NiL_A]$. This result is in keeping with the observation[13] that in metal based oxidations of open chain deprotonated amide complexes Cu(111) and Ni(111) are stabilised by 5-5-5 but not 5-6-5 or 6-5-6 fused ring structures (13).



[CuL$_A$] Reversible one-electron oxidation - 5,5,5 fused ring



[CuL$_B$] Irreversible one-electron oxidation - 5,6,5 fused ring



[CuL$_C$] Irreversible one-electron oxidation - 6,5,6 fused ring

Additional Reactions

Attempted preparations of L_3H_2, L_4H_2 and their Cu(11) and Ni(11) complexes

Interest in the transition metal complexes of deprotonated amide open chain ligands led, in the present work, to the attempted preparation of ligands L_3H_2 and L_4H_2 in (3) by the method of Ojima et al.[13,31] that is by the condensation of one equivalent of diethyl oxalate with two equivalents of ethylenediamine for L_3H_2 and by the condensation of one equivalent of diethyl oxalate with two equivalents of 1,3 diaminopropane for L_4H_2. The Japanese workers report the isolation of ligands L_3H_2 and L_4H_2 from these mixtures, but in the present work these starting materials (mixed at high dilution) resulted predominantly in high mass, polymeric materials, insoluble in water and alcohol. The white solid product from the L_3H_2 preparation had a m.p. above 320°C while the product from the L_4H_2 preparation started to decompose above 250°C. The difficulty in isolating pure samples of the ligands L_3H_2 and L_4H_2 by condensation of diethyl oxalate with ethylenediamine or 1,3-diaminopropane may be due to the formation of chain products.

The reaction product from the preparation of the ligand L_3H_2 was stirred in hot ethanol then filtered. The filtrate was evaporated to dryness to give a white solid having a m.p. of 172-175°C, however microanalysis of the sample did not correspond to the formulation for L_3H_2. Reaction of the solid with nickel hydroxide in basic solution gave a yellow solution having λ_{max} = 412 nm. A spectrophotometric titration of the solution in water against hydrochloric acid showed the deprotonated complex to be fully formed at and above pH 10.5. Upon standing, a yellow solid crystallised out of the basic solution but it did not analyse as $[NiL_3]$. Cyclic voltammetry of the yellow solid in 0.1 mol dm^{-3} $(NaClO_4)$ in water at pH 10.5 showed an irreversible oxidation on platinum at $\frac{1}{2}E_p$ = + 0.54 volts versus the SCE. Reacting the ligand with copper hydroxide in basic medium gave a violet solution having λ_{max} = 530 nm. A spectrophotometric titration of the solution in water against hydrochloric acid showed the deprotonated complex to be fully formed at and above pH 11. A solid complex was not isolated from this reaction. Cyclic voltammetry of the violet solution in 0.1 mol dm^{-3} $(NaClO_4)$ in water at pH 11 showed an irreversible oxidation at high potential in contrast to the quasi-reversible oxidation at $\frac{1}{2}E_p$ = + 0.72 volts versus the NHE reported in the literature.[13]

The crude reaction product from the preparation of the ligand L_4H_2 was stirred in hot ethanol then filtered. The filtrate was evaporated to dryness giving a solid having a m.p. of 175-178°C. A pH titration of an equimolar mixture of $Cu(ClO_4)_2$ and the ligand in 0.1 mol dm^{-3} $(NaClO_4)_2$ at 25°C against NaOH showed that if one mole of complex consumes two moles of sodium hydroxide then the ligand is 94.4% pure, this result is confirmed by microanalysis where the found element percentages are ca. 94% of the calculated element percentages. Reaction of the ligand with nickel hydroxide in basic solution gave a yellow solution having λ_{max} = 455 nm. A spectrophotometric titration of the yellow solution against hydrochloric acid in water showed the deprotonated complex to be fully formed at or above pH 10.5. Upon standing, the basic solution precipitated yellow crystals which could be formulated as $[NiL_4]$.

Calc. for $O_2C_8H_{16}N_4Ni$; C,37.10; H,6.22; N,21.63;

Found: C,37.05; H,6.12; N,22.17%.

Cyclic voltammetric studies on the complex in 0.1 mol dm^{-3} $(NaClO_4)_2$ in water at pH 10.5 showed a quasi-reversible oxidation on platinum at + 0.57 volts versus the SCE, see Table 3.6. A linear plot of $I_p(a)$ versus $v^{\frac{1}{2}}$ confirmed diffusion control for the process.

TABLE 3.6

Cyclic voltammetric data[a] on $[NiL_4]$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	29.5	31.0	0.95	+0.57	160
100	44.0	50.0	0.88	+0.57	130
200	55.0	52.5	1.04	+0.57	170
500	75.0	62.5	1.20	+0.56	200

a. Support electrolyte is 0.1 mol dm^{-3} $(NaClO_4)$ in water. All potentials are measured at a platinum indicator electrode versus an SCE. pH of solution is 10.5.

The ligand was reacted with copper hydroxide in basic medium giving a solution having λ_{max} at 540 nm. A

spectrophotometric titration of the solution against hydrochloric acid showed the deprotonated complex to be fully formed at or above pH 11.5. Upon standing a pink solid precipitated from the basic solution which could be formulated as [CuL_4].
Calc. for $O_2C_8H_{16}N_4Cu$; C,36.42; H,6.11; N,21.24;
Found: C,38.21; H,6.18; N,22.54%.

Cyclic voltammetry was performed on [CuL_4] in a support electrolyte of 0.1 mol dm^{-3} ($NaClO_4$) in water at pH 11.5. The complex showed a quasi-reversible one-electron oxidation on platinum at $\frac{1}{2}E_p$ = + 0.73 volts versus the SCE, see Table 3.7. The process is diffusion controlled as confirmed by a linear plot of $I_p(a)$ versus $v^{\frac{1}{2}}$.

TABLE 3.7

Cyclic voltammetric data[a] on [CuL_4] at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	23.5	9.5	2.47	+0.74	60
100	42.0	20	2.10	+0.73	60
200	58.0	42	1.38	+0.73	70
500	80.0	65	1.23	+0.73	95

a. Support electrolyte is 0.1 mol dm^{-3} ($NaClO_4$) in water. All potentials are measured at a platinum indicator electrode versus an SCE. pH of solution is 11.5.

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SECTION IV

Transition Metal Complexes of Deprotonated Amide Macrocycles

Introduction

Some aspects of transition metal-amide bonding have been discussed for linear amide ligands in Section III of this thesis. It has been found that cyclization of such ligands dramatically enhances the stability of their transition metal complexes. In general, macrocycles form much more stable and selective complexes with transition metal ions than do open chain analogues having the same donor arrangement.[1] Interest in synthetic nitrogen donor macrocycles arises from their potential as (a) models for biomolecules[2], for example, haemoglobin and myoglobin, (b) industrial catalysts, (c) specific cation carriers across membranes,[3] (d) sequestering agents for specific metal ions.[4] Deprotonated macrocyclic diamides provide a strong planar ligand field which makes them good models for naturally-occurring porphyrins which can be used to stabilise d^8 Cu(111). Some macrocyclic amides found in the literature are shown in (1). Ligands L_A-L_F[5,6,7] are prepared by condensing diethyl oxalate or diethyl malonate with the appropriate tetramines while L_G is the condensation product of diethyl malonate with tetraethylenepentamine.[8] The alkyl substituted macrocycles L_I are prepared by aminolytic condensation of substituted diethyl malonates[6,9] with 1,9-diamino-3,7-diazanonane. These hydrophobic substituents increase the solubility of the ligands in non-aqueous media.

Macrocyclic amide ligands vary in (a) the cavity size, (b) the number of nitrogen donor atoms, and (c) the relative positions of the dione groups in the ring and these differences are reflected in their complexation with transition metal ions.

Copper (11) complexes with L_A-L_F to form neutral amide-ionised species of the form $[Cu(L-2H)]^{\circ}$ in aqueous solution[4,5,7] with the 14-membered ring L_B forming the most stable Cu(11) complex[10] of the series in (2). The 12-membered ring L_M which contains two glycyl units gives the amide-ionised species $[Cu(L-2H)]^{\circ}$ [11] however the stability is much smaller than for the corresponding Cu(11) complexes of the larger macrocycles L_A, L_B and L_C. Another type of transition metal ion-amide bonding in macrocycles is found for the ligands L_Q and L_R[12] in (1). These ligands both have dangling amide side chains and in basic media (pH ca. 10) coordinate to Cu(11) via the four tetraza nitrogen atoms of the ring and the deprotonated amide nitrogen of the side chain giving five coordinate square pyramidal species.

Ring strain in macrocyclic complexes is reflected in the position of the d-d absorption band in the electronic spectra. Increasing ring strain moves the band to higher wavelength thus while CuL_B has λ_{max} at 506 nm the small strained complex CuL_D has λ_{max} at 596 nm.

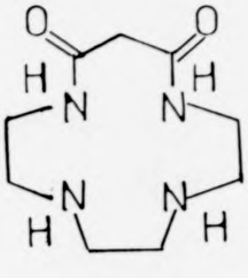
Studies on the macrocyclic effect and cation-ring size selectivity for the dioxo-tetra-amines have been made by measuring the rates of complexation between the ligands L_A, L_B and L_C and copper (11). In acetate buffer ($4.8 < pH < 5.7$) L_A and L_B form copper (11) complexes while L_C does not. The rate of complexation is ten times greater for L_A than for L_B.[4] The effect of ring size on the stability of the complexes is reflected in the kinetics of displacement of L_A, L_B and L_C from their deprotonated copper (11) complexes $[Cu(L-2H)]$.[10] The 14-membered complex CuL_B is the most stable of the series and is the most inert to substitution reactions.

In the complexes discussed so far the Cu(ll) ion is coordinated via two deprotonated amide nitrogens and two amine nitrogens. However for the ligand L_M the monoionised complex $[Cu(L-H)]^+$ has been observed and for the pyridyl containing 14-membered ligand L_K the complex $[CuL_K]Cl_2$ has been isolated in the solid state.[13] Addition of two equivalents of base to $[CuL_K]Cl_2$ in solution results in the amide ionised, neutral complex $[Cu(L_K-2H)]^{\circ}$, confirmed by the absorption maximum at 512 nm.[1]

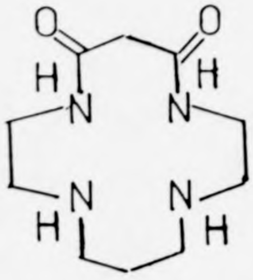
Complexation of the macrocyclic amides with Ni(ll) has established the presence of $[Ni(L-2H)]^{\circ}$ in solution for $L = L_A, L_B, L_C$,[11] L_E, L_F[5] and L_G[8] and allowed the isolation of solid $[Ni(L-2H)]^{\circ}$ for $L = L_B$[7] and L_E[5]. Complexation of Ni(ll) with the ligand L_D has not been detected presumably due to the small hole size. The Ni(ll) complex derived from L_M has been shown to undergo an octahedral ⇌ planar equilibrium.[11] Such equilibria are well established for a variety of Ni(ll) complexes of macrocyclic tetraaza ligands[16] and a similar situation occurs with the Ni(ll) complex of L_E.[5]

The possible use of macrocycles as sequestering agents for specific metal ions led to a study of the interaction of L_A, L_B, and L_C, with heavy metal ions Pb^{2+}, Cd^{2+} and Zn^{2+}, however no complexation was observed.[4]

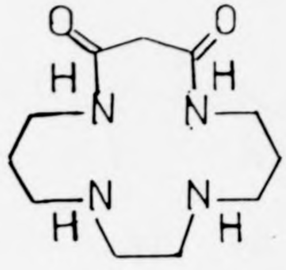
The strong σ-donating amide groups of the macrocyclic ligands help to stabilise high oxidation states on complexed transition metal ions, as redox studies have indicated. Cyclic voltammetric data collected for these systems are summarised in Table 4.1. Electron spin resonance experiments have



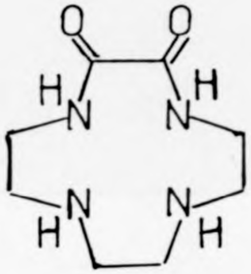
L_A ref.6



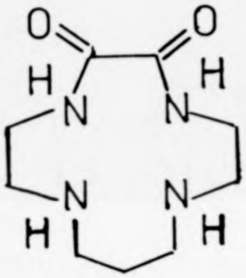
L_B ref.6,7



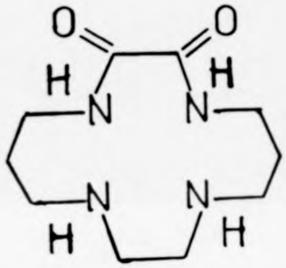
L_C ref.6



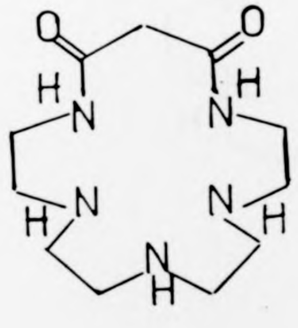
L_D ref.5



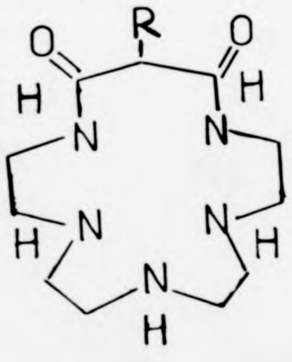
L_E ref.5



L_F ref.5

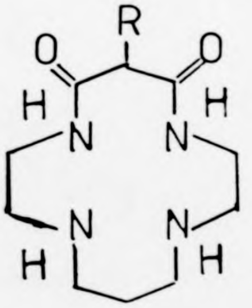


L_G ref.8



$R = CH_2C_6H_5$

L_H ref.8



$R = CH_2C_6H_5$

CH_2CH_2OH

$CH_2CH_2CH_3CH_3$

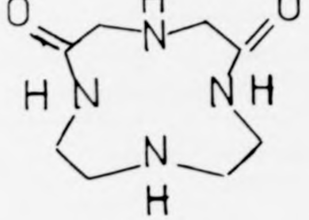
$CH_2CH_2CH_2CN$

$CH_2CH = CH_2$

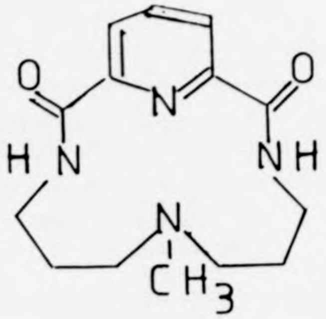
L_I ref.6,9

(1)

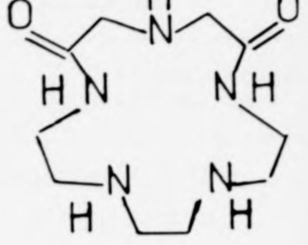
(1) continued:



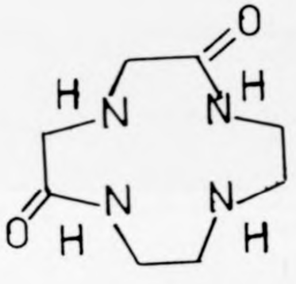
L_J ref.14



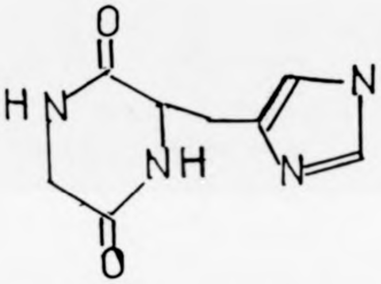
L_K ref.13



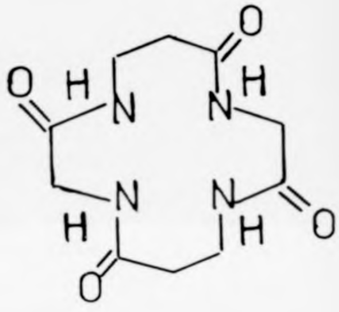
L_L ref.14



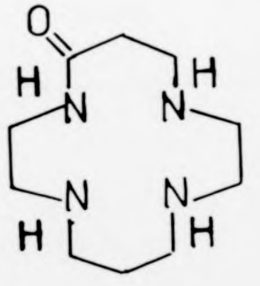
L_M ref.11



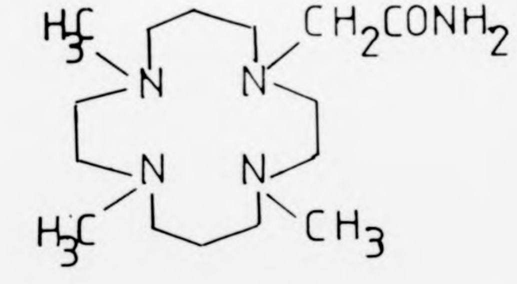
L_N ref.22



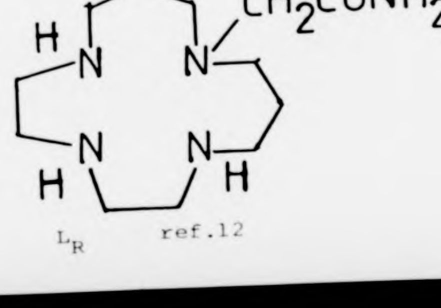
L_O ref.23



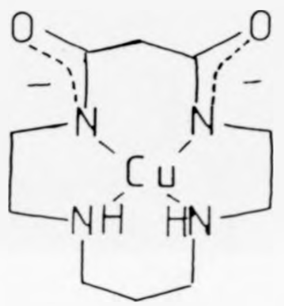
L_P ref.15



L_Q ref.12



L_R ref.12

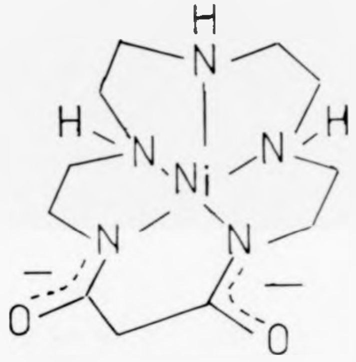


(2)

TABLE 4.1

Cyclic voltammetric data on macrocyclic amide complexes

Complex	$\tfrac{1}{2}E_p$ (volts)	Indicator Electrode	Reference Electrode	Support Electrolyte	Degree of Reversibility	Literature Reference
CuL_B	+0.65	Carbon paste	SCE	1M KCl in water	Reversible	(17)
NiL_B	+0.51	Platinum	SCE	3M KCl in water	Quasi-reversible	(17)
CuL_G	+0.68	Glassy carbon	SCE	0.5M Na_2SO_4 in water	Quasi-reversible	(8)
NiL_G	+0.24	Glassy carbon	SCE	0.5M Na_2SO_4 in water	Quasi-reversible	(8)
CuL_H	+0.74	Glassy carbon	SCE	0.5M Na_2SO_4 in water	Quasi-reversible	(8)
NiL_H	+0.24	Glassy carbon	SCE	0.5M Na_2SO_4 in water	Quasi-reversible	(8)
CuL_M	+0.42	Glassy carbon	SCE	0.5M Na_2SO_4 in water	Quasi-reversible	(11)
NiL_M	+0.62	Glassy carbon	SCE	0.5M Na_2SO_4 in water	Quasi-reversible	(11)



(3)

confirmed that the one-electron oxidation processes are metal based.[8,17] Electrochemical studies have revealed that the ring size of the macrocycle affects the redox potential of the M(II)/M(III) couple in the complexes, also the diamide macrocyclic complexes undergo metal-based one-electron oxidations more readily than the analogous complexes of tetraaza macrocycles. A comparison between redox potentials of tetraaza and N_4 diamide macrocyclic complexes shows that the increase in stabilisation of Ni(III) by the cyclic amide ligands is very small in comparison to the increase in stabilisation of Cu(III) upon moving from tetraaza to diamide macrocycles, this is believed to be a ligand field effect. The Ni(II) complexes of ligands L_G and L_H, that is the pentadentate N_5 macrocyclic diamide, undergo particularly facile oxidation[8] and it is believed that this is due to the special steric and electronic effects imposed by the basal two imide ligands in the rigid square pyramidal structure (3). The redox potentials for the Ni(II)/Ni(III) couples in [Ni(L_G-2H)] and [Ni(L_H-2H)] are much smaller than the corresponding Cu(II)/Cu(III) potentials reflecting coordinating environments much more favourable for the d^8 Ni(II) → d^7 Ni(III) transition than for the d^9 Cu(II) → d^8 Cu(III) transition.

The observation of low oxidation potentials for transition metal ions complexed to macrocyclic diamides and their similarity to biological O_2 carriers prompted study of their interaction with molecular oxygen. It was found that the 1:1 complex formed between Co(II) and doubly deprotonated L_B when reacted with excess imidazole or pyridine, yielded a five coordinate square pyramidal complex which reversibly binds O_2 at -70°C.[20] Studies of the Ni(11) complexes of L_G and L_H, the pentadentate N_5 donor diamide ligands have established that the air oxidation products are the 1:1 Ni(L-2H)-O_2 adducts. The nickel bound O_2 is found to be reactive and bubbling air through a mixture of [Ni(L_H-2H)] and benzene in borate buffer yields phenol.[8]

In the present work in order to expand the data on the macrocyclic diamides the preparation of L_A, L_B and L_C has been undertaken together with their transition metal complexes. The properties of the complexes in solution have been investigated by pH titration, spectrophotometric titration and cyclic voltammetry.

Experimental

1,4,7,10-Tetra-azacyclotridecane-11,13-dione (L_A)

The ligand 1,4,7,10-tetra-azacyclotridecane-11,13-dione was prepared essentially as described by Tabushi *et al*.[6] Diethyl malonate (8.0g., 0.05 mol) was dissolved in ethanol (975 cm^3) and heated to reflux. Triethylenetetramine (2,2,2-tet) (7.3g., 0.05 mol) dissolved in ethanol (25 cm^3) was added dropwise to the refluxing solution and the mixture refluxed for 3-5 days. At the end of this time the solution volume was reduced on a rotary evaporator until a white solid precipitated. The solid product was filtered off and washed with diethyl ether. The ligand is freely soluble in ethanol and was recrystallised from hot ethanol and dried *in vacuo*. Calc. for $C_9H_{18}N_4O_2$; C,50.45; H,6.36; N,16.83;

Found: C,50.72; H,6.40; N,16.70%.
The ligand has m.p. 173-176°C (lit.189°C).[15] The mass spectrum has M^+ at 214 ($C_9H_{18}N_4O_2$ = 214). The i.r. spectrum (KBr) has ν(NH) at 3180, 3250 and 3300 cm^{-1} and amide bands at 1570 and 1660 cm^{-1}. A second crop of white crystalline solid was obtained from the mother liquors upon standing. This solid was filtered off, washed with diethylether and dried *in vacuo*. The analysis is inconsistent with $C_9H_{18}N_4O_2$. The solid has m.p. (205°-208°) and is only sparingly soluble in hot ethanol suggesting that the material is polymeric.

1,4,8,11-Tetra-azacyclotetradecane-11,13-dione (L_B)

The ligand 1,4,8,11-tetra-azacyclotetradecane-11,13-dione was prepared as previously described[7], that is 1,9-diamino-3,7-diazanonane (2,3,2-tet) (7.3g., 0.045 mol) was dissolved in ethanol (1000 cm^3) and the solution cooled to *ca*. 0° in an ice bath, then with constant stirring diethyl malonate (8.0g., 0.05 mol) was added. The solution was stirred at room temperature for 7 days, during which time it became pale pink. The volume was reduced to *ca*. 25 cm^3 on a rotary evaporator and on standing overnight at 0°C, white needle shaped crystals of the product were obtained. The product was filtered off, washed with diethyl ether, recrystallised from ethanol and dried *in vacuo*.
Calc. for $C_{10}H_{20}N_4O_2$; C,52.61; H,8.83; N,24.54;
Found: C,51.90; H,8.86; N,24.07%.
The ligand has m.p. 164°-166°C (lit.164-166°C).[7]
The characteristic i.r. spectral bands are identical to those described in the literature.

1,4,8,12-Tetra-azacyclopentadecane-12,14-dione (L_C)

Diethyl malonate (8.7g., 0.05 mol) was dissolved in ethanol (975 cm^3) and heated to reflux. 1,10-Diamino-4,7-diazadecane (3,2,3-tet) (8.7g., 0.05 mol) dissolved in ethanol (25 cm^3) was added dropwise to the refluxing solution. The reaction mixture was refluxed for 5 days, then the volume reduced to ca. 75 cm^3. Upon standing at room temperature for several days a white powder crystallised out which was separated from the viscous supernatant by use of a centrifuge. The crude solid was stirred in ethanol and thus separated into an ethanol soluble fraction (the ligand, L_C) and an ethanol insoluble fraction believed to be a polymeric material. The ethanol solution was evaporated to dryness to give the product.

Calc. for $C_{11}H_{22}N_4O_2 0.5H_2O$; C,52.57; H,9.22; N,22.29;

Found: C,53.99; H,9.69; N,22.25%

The ligand has m.p. (182-187°C).

The mass spectrum has M^+ at 242 ($C_{11}H_{22}N_4O_2$ = 242).

The i.r. spectrum (KBr) has ν(NH) at 2800, 2900, 3180 and 3220 cm^{-1} and amide bands at 1555 and 1625 cm^{-1}.

The ethanol insoluble fraction from the preparation has a microanalysis inconsistent with the formula $C_{11}H_{22}N_4O_2$. The solid melts above 220°C and the mass spectrum has M^+ at 384. These experimental results suggest the presence of a polymeric material.

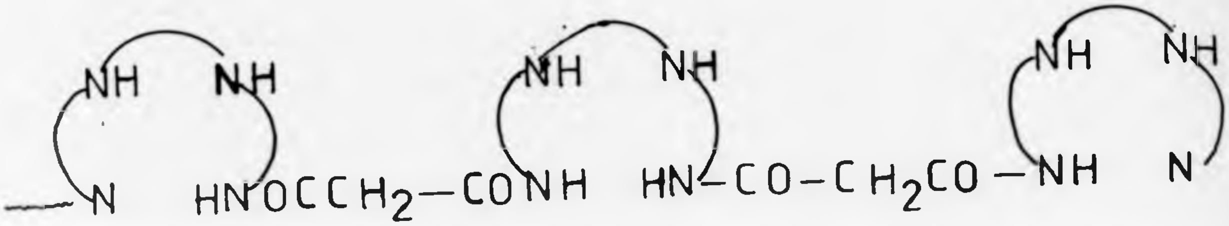
Infra-red spectra were determined as KBr discs using a Perkin-Elmer 402 spectrophotometer. All pH measurements were made with a Radiometer pHM64 pH meter, which was standardised using potassium hydrogen phthalate buffer (pH 4.01 at 25°C) and borate buffer (pH 9.18 at 25°C). Electrochemistry was carried out using a PAR 170 electrochemistry system. The mass spectrometer used was a JEOL D100.

Results and Discussion

The macrocyclic diamides prepared have 13-(L_A), 14-(L_B) and 15-(L_C) membered rings with variable cavity size. The ligands are readily prepared by the reaction of the appropriate tetramine with diethyl malonate in ethanol. Preparations of L_A and L_C indicated the presence of polymeric species in the product mixtures while the ligand L_B is readily obtained with no sign of polymeric impurity. Attempts were made to purify L_A, L_B and L_C by precisely following the TLC procedures documented in the literature[14] for isolating these ligands. However, these TLC systems were found to be completely ineffective and in fact when a pure sample of ligand L_B was applied to a TLC plate and placed in a tank of the recommended solvent mixture the ligand L_B was found to be so polar that it remained stationary throughout the passage of the solvent along the plate.

Complexation of L_A with Cu(11) and Ni(11) was studied by pH titration, spectrophotometric titration and cyclic voltammetry. The formation of [Pd(L_A-2H)] was confirmed by pH titration. The complexes [Cu(L_B-2H)], [Ni(L_B-2H)] and [Pd(L_B-2H)] were prepared in solution and redox studies performed on the neutral Ni(11) and Cu(11) complexes. Potentiometric pH titration of L_C with Cu(11) suggests that the ligand

L_C is only 59% pure, perhaps due to the presence of polymeric species. Thus complexation studies on this ligand are limited. Condensation of diethyl malonate with 3,2,3-tet as well as producing the cyclic ligand L_C could give linear chains of the type shown in structure (4) and this is suggested as a possible structure for the polymeric impurity.



(4)

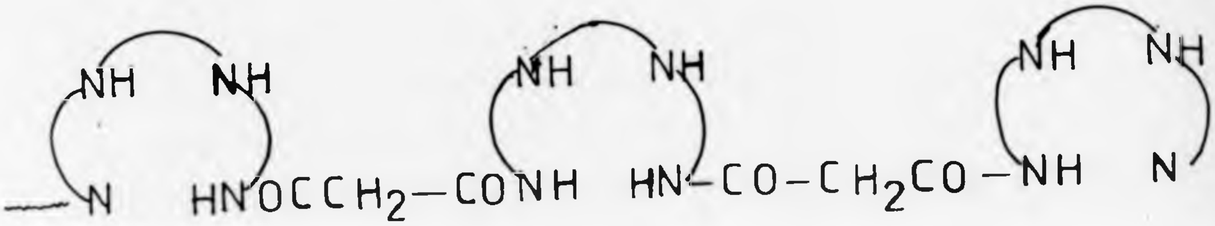
Transition Metal Complexes of L_A, L_B and L_C

Complexation of 1,4,7,10-tetra-azacyclotridecane-11,13-dione (L_A) with Cu(11), Ni(11), Pd(11) and Co(111)

Equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ and L_A were mixed in water, and sodium hydroxide added to ensure amide deprotonation. Upon standing, violet crystals precipitated and were filtered off and dried. The preparation was repeated several times and the products recrystallised, however the analytical data were inconsistent with the formulation $[Cu(L_A-2H)]$ but did support an empirical formula of $C_9H_{25}N_4$.

$Ni(ClO_4)_2 \cdot 6H_2O$ was reacted with L_A in basic solution. The yellow crystalline product which precipitated upon standing

L_C is only 59% pure, perhaps due to the presence of polymeric species. Thus complexation studies on this ligand are limited. Condensation of diethyl malonate with 3,2,3-tet as well as producing the cyclic ligand L_C could give linear chains of the type shown in structure (4) and this is suggested as a possible structure for the polymeric impurity.



(4)

Transition Metal Complexes of L_A, L_B and L_C

Complexation of 1,4,7,10-tetra-azacyclotridecane-11,13-dione (L_A) with Cu(11), Ni(11), Pd(11) and Co(111)

Equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ and L_A were mixed in water, and sodium hydroxide added to ensure amide deprotonation. Upon standing, violet crystals precipitated and were filtered off and dried. The preparation was repeated several times and the products recrystallised, however the analytical data were inconsistent with the formulation $[Cu(L_A-2H)]$ but did support an empirical formula of $C_9H_{25}N_4$.

$Ni(ClO_4)_2 \cdot 6H_2O$ was reacted with L_A in basic solution. The yellow crystalline product which precipitated upon standing failed to analyse as $[Ni(L_A-2H)]$ but had an empirical formula of $C_9H_{21}N_4$.

Equimolar quantities of K_2PdCl_4 and L_A were mixed in basic medium and refluxed for 3 hours to give $[Pd(L_A-2H)]$ in solution. The yellow crystals which precipitated upon standing at 0°C were filtered off, washed with ethanol and dried. The complex did not analyse as PdL_A but had an empirical formula $C_9H_{17}N_4$.

The preparation of $[Co(L_A-2H)(NH_3)_2]Cl$ was attempted by reacting chloropentamminecobalt (111) chloride with L_A. Reaction was indicated by the evolution of NH_3 and the solution becoming cherry red (λ_{max} = 485 nm in water), however the red solid which was isolated from solution gave poor analytical data.

In general, when analytically pure L_A is reacted with M^{2+} in basic media highly crystalline, coloured products are obtained (yellow for $M^{2+} = Ni^{2+}$, Pd^{2+} and violet for $M^{2+} = Cu^{2+}$). Microanalysis suggests that complexation does not proceed with the stoichiometry of 1:1 for $M^{2+} : (L_A-2H)$.

Complexation of 1,4,8,11-tetra-azacyclotetradecane-11,13-dione (L_B) with Cu(11), Ni(11), Pd(11) and Hg(11)

Copper (11) and nickel (11) complexes of L_B were readily prepared by the literature method.[7]

Equimolar quantities of K_2PdCl_4 and L_B were refluxed in methanol with sodium hydroxide. The brown crystals which crystallised out upon cooling were filtered off, washed with water and dried. The analytical data are not consistent with the formulation $[Pd(L_B-2H)]$.

The Hg(11) ion was found to be unsuitable for complexation with L_B. Equimolar quantities of Hg_2O and L_B were refluxed in methanol with sodium hydroxide, but there was no indication of complexation. Unreacted mercuric oxide was filtered off and the volume of filtrate reduced allowing crystallisation of a white solid which analysed as the free ligand L_B.

Complexation of 1,4,8,12-tetra-azacyclotetradecane-12,14-dione (L_C) with Cu(11) and Ni(11)

Mixing of equimolar quantities of $Cu(ClO_4)_2 \cdot 6H_2O$ and the ligand L_C in basic aqueous solution gave a violet solution, however no solid complex could be isolated from the mixture.

Equimolar quantities of $Ni(ClO_4)_2 \cdot 6H_2O$ and L_C were mixed in aqueous solution. Addition of sodium hydroxide gave a yellow solution indicating the presence of a planar Ni(11)N_4 chromophore. Upon standing, the solution became brown suggesting perhaps aerial oxidation to a Ni(111) species. No solid product was isolated.

A second method was devised for generating Cu(11) and Ni(11) complexes of L_A, L_B and L_C in aqueous solution, using an ion exchange technique. The macrocyclic diamides were prepared as described previously by refluxing the appropriate tetramine with diethyl malonate in ethanol for 3-5 days. At the end of this time, all ethanol and unreacted diethyl malonate was removed by distillation on a rotary evaporator, leaving a viscous gum containing the product ligand and unreacted tetramine. This gummy material was dissolved in the

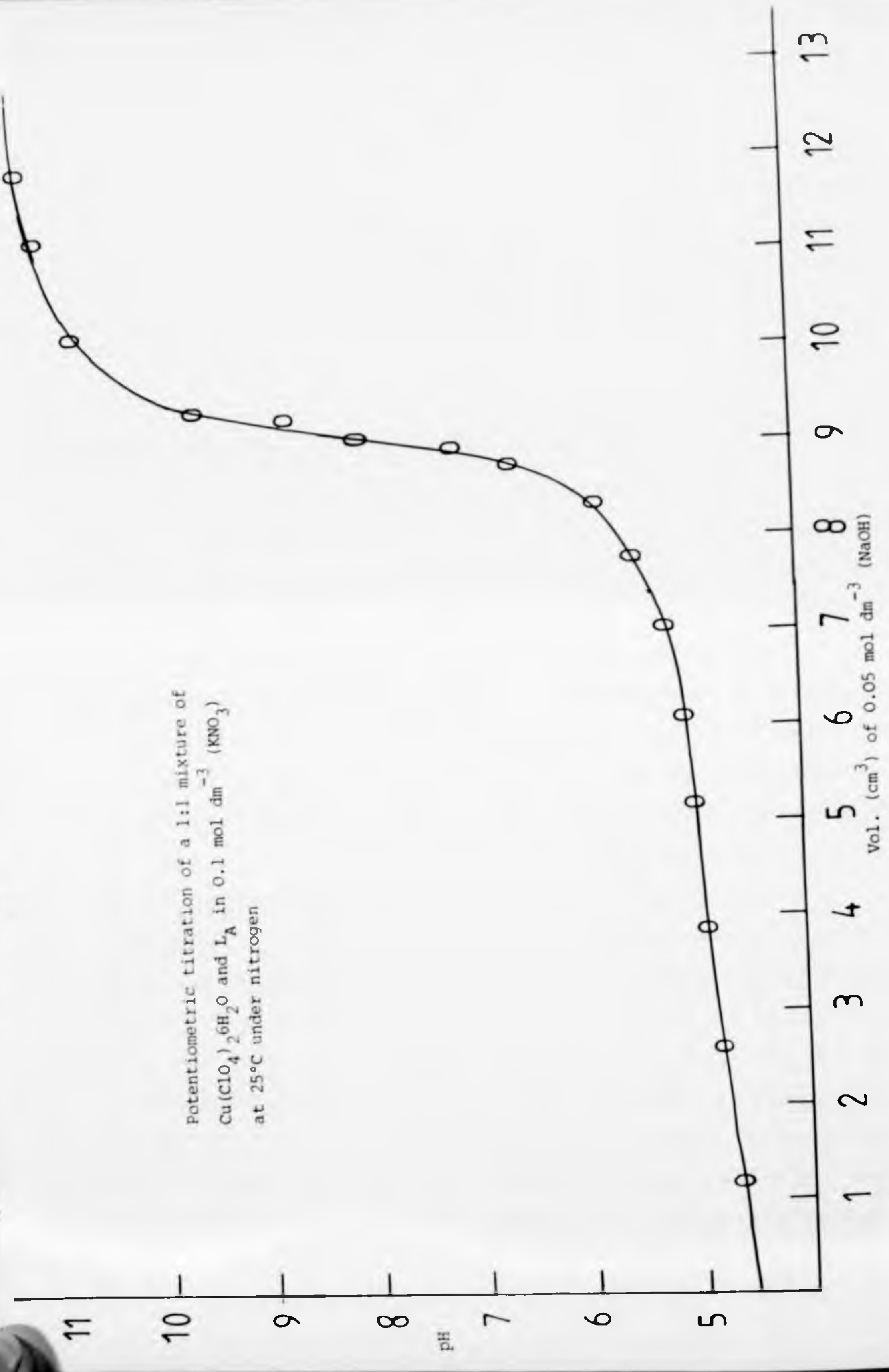


Figure 4.1 Potentiometric titration of a 1:1 mixture of $Cu(ClO_4)_2 6H_2O$ and L_A in 0.1 mol dm^{-3} (KNO_3) at 25°C under nitrogen

minimum of water and an aqueous solution containing either $Ni(ClO_4)_2$ or $Cu(ClO_4)_2$ added to it. The mixture was basified by addition of sodium hydroxide to ensure deprotonation of the ligand. The solution was loaded onto a column of CM Sephadex-C25 cation exchange resin and eluted with water. The neutral species $[M(L_A-2H)]$, $[M(L_B-2H)]$ or $[M(L_C-2H)]$ pass down the column while the charged species $[M(tetramine)]^+$ is retained on the resin. Thus an aqueous solution of ML_A, ML_B or ML_C can be obtained, free of reactant impurities. $[M(tetramine)]^+$ can be removed from the column by eluting with 0.05 mol dm^{-3} pyridinium acetate.[18]

Potentiometric and spectrophotometric titrations of ML_A

(M = Cu(II), Ni(II) and Pd(II))

A potentiometric titration was carried out by mixing equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ with L_A in 0.1 mol dm^{-3} (KNO_3) at 25°C and titrating against dilute sodium hydroxide. The incorporation of Cu(II) is rapid. The solution is diacidic and consumes two moles of base per mole of Cu(II) (or ligand). The titration curve is shown in Figure 4.1. An experimental molecular weight for the ligand can be calculated from the titration result. On the basis that one mole of ligand reacts with two moles of base the experimental molecular weight of ligand is found to be 204 amu. The calculated weight is 214 amu thus the ligand is shown to be 96% pure. A potentiometric titration was carried out by mixing equimolar amounts of $Ni(ClO_4)_2 \cdot 6H_2O$ with L_A in 0.1 mol dm^{-3} (KNO_3) at 25°C, and titrating against dilute sodium hydroxide. Due to the slow

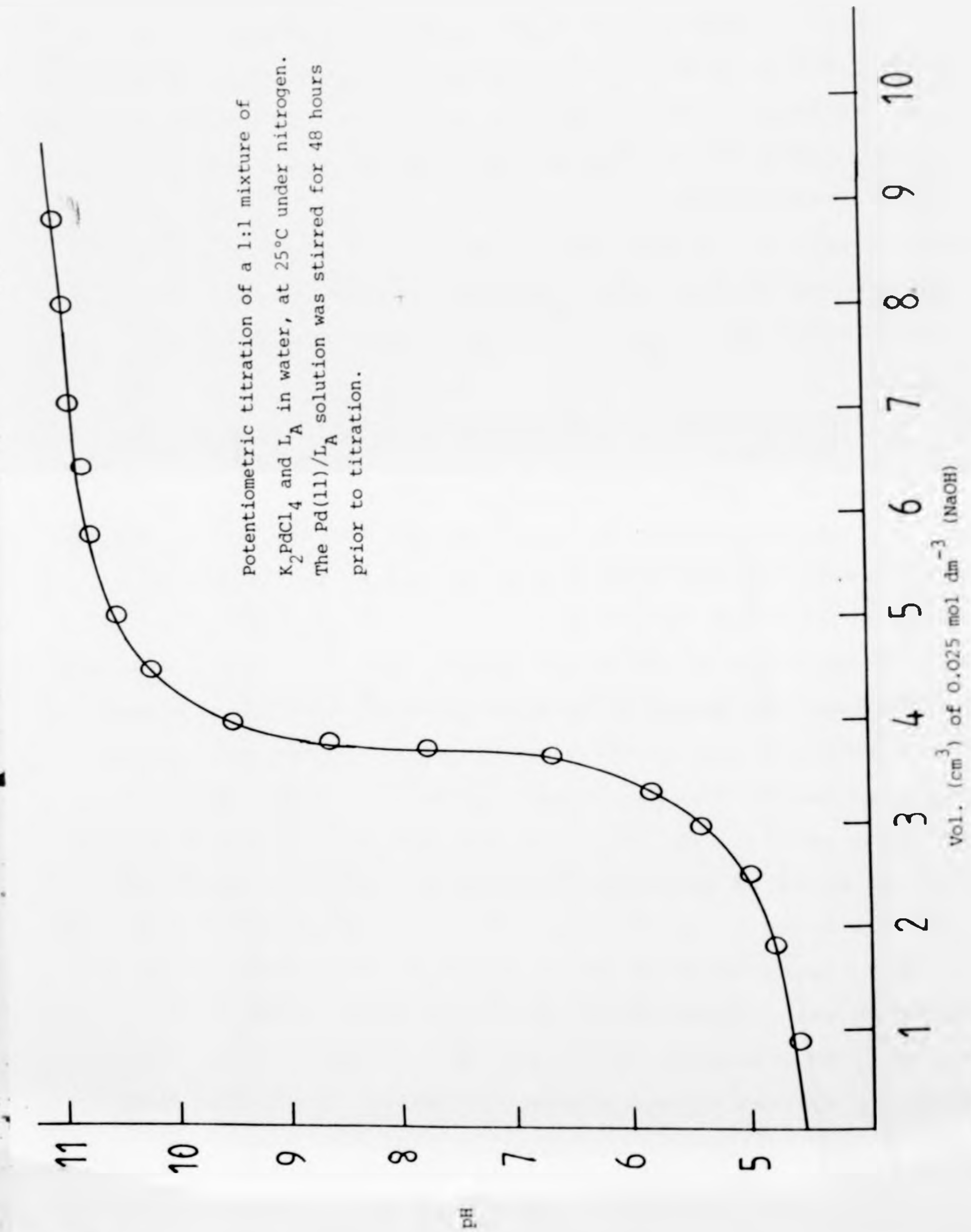


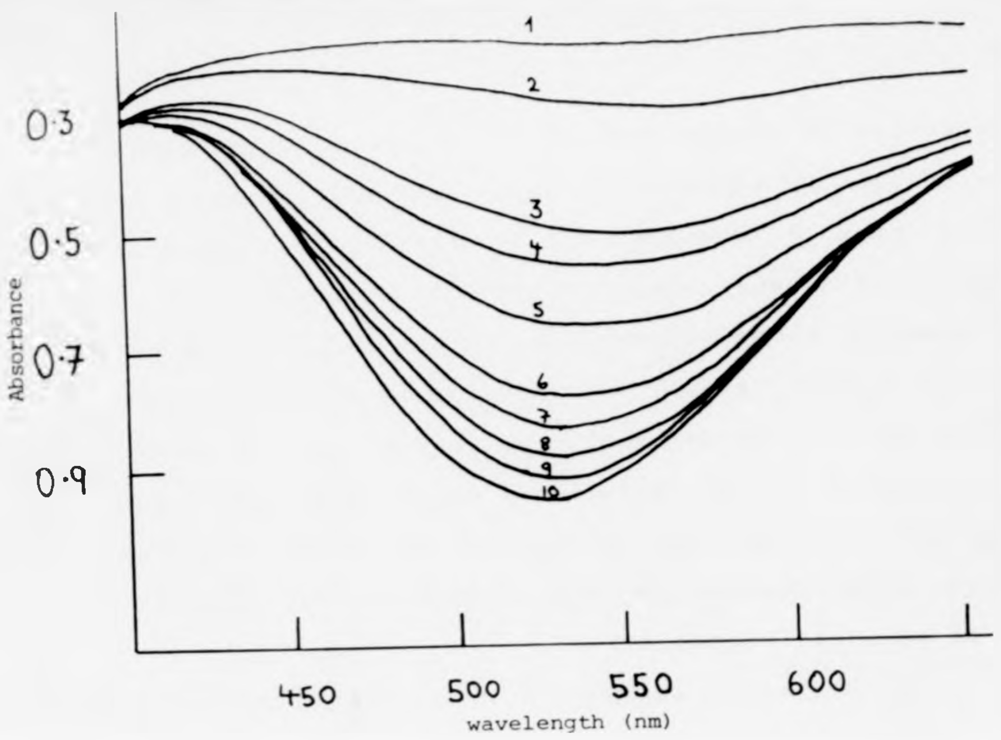
Figure 4.2

Potentiometric titration of a 1:1 mixture of K_2PdCl_4 and L_A in water, at 25°C under nitrogen. The Pd(11)/L_A solution was stirred for 48 hours prior to titration.

incorporation of nickel (11) it was necessary to allow the system to come to equilibrium after each base addition and the titration took ca. one hour for completion. Two moles of sodium hydroxide were consumed per mole of ligand. A potentiometric titration was carried out on an equimolar mixture of K_2PdCl_4 and L_A in 0.1 mol dm^{-3} (KNO_3) at 25°C, titrating against dilute sodium hydroxide. Due to slow complexation of Pd(11) the mixture was stirred for 72 hours at 40°C before commencing titration. Two moles of sodium hydroxide were consumed per mole of ligand. The titration curve is shown in Figure 4.2.

An equimolar aqueous solution of L_A and copper (11) was titrated spectrophotometrically in the pH range 2-13. The spectrum of the solution at pH 4.3 shows a broad absorption with λ_{max} ca. 560 nm. On addition of base this absorption moves to shorter wavelength (pH 4.75, λ_{max} 545 nm; pH 5.21, λ_{max} 530 nm) and undergoes appreciable intensification. The complex is fully formed at and above pH6 with a band maximum at 525 nm (Figure 4.3).

An equimolar aqueous solution of L_A and nickel (11) was titrated spectrophotometrically in the pH range 2-11. The spectrum of the solution below pH 5.70 shows negligible absorption in the visible region. On addition of base an absorption band develops, with λ_{max} = 412 nm. Further addition of base gives intensification of this band with no shift in λ_{max}. At and above pH 7.5 the complex is fully formed.



Scan	pH
1	4.04
2	4.36
3	4.66
4	4.75
5	4.89
6	5.09
7	5.21
8	5.38
9	5.60
10	6.11

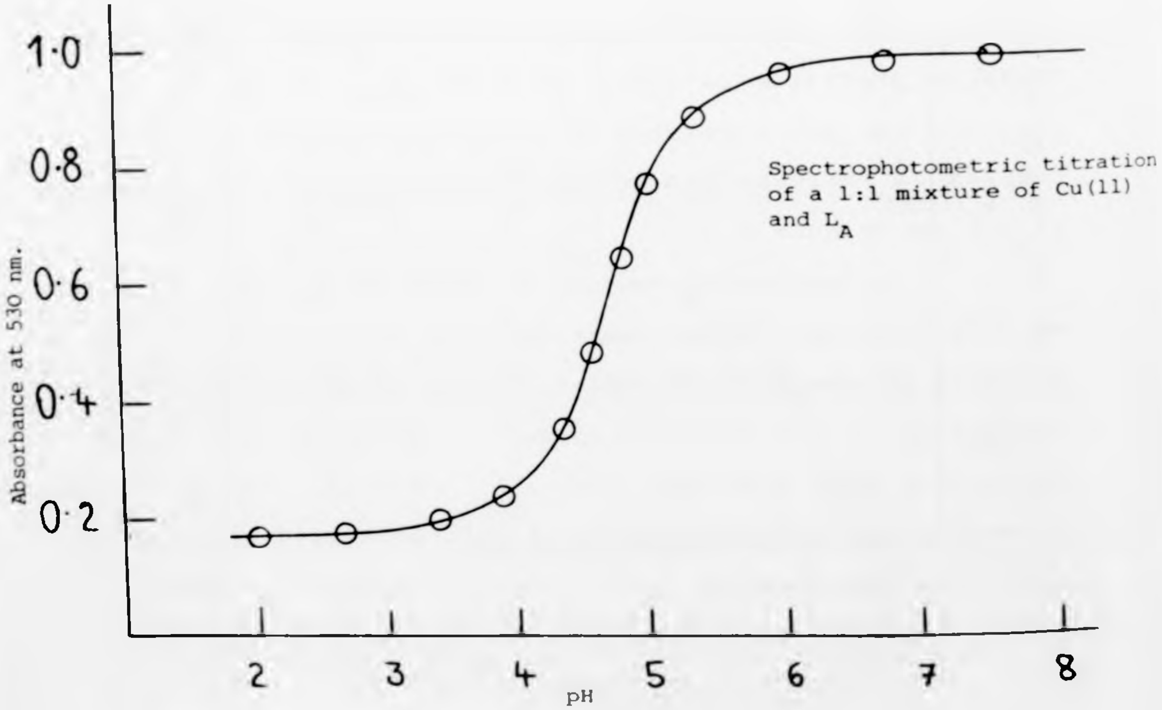


Figure 4.3

Potentiometric and spectrophotometric titrations of ML_B

(M = Cu(11), Ni(11) and Pd(11))

A potentiometric titration was carried out by mixing equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ and L_B in 0.1 mol dm^{-3} (KNO_3) at 25°C and titrating against dilute sodium hydroxide. The solution is diacidic and consumes two moles of base per mole of ligand (L_B). The titration curve corresponds to that found in the literature.[7] The experimental molecular weight of L_B derived from the titration curve is 224 amu. The calculated theoretical molecular weight is 228 amu. The ligand is thus 98.2% pure.

A potentiometric titration was carried out on an equimolar mixture of K_2PdCl_4 and L_B in 0.1 mol dm^{-3} (KNO_3) at 25°C, titrating against dilute sodium hydroxide. Due to slow complexation of Pd(11) with the ligand the mixture was stirred for 48 hours at 40°C prior to titration. Two moles of sodium hydroxide were consumed per mole of ligand.

An equimolar aqueous solution of L_B and $Cu(ClO_4)_2 \cdot 6H_2O$ was titrated spectrophotometrically in the pH range 2-12. The spectrum of the solution at pH 4.5 has an absorption band at λ_{max} = 506 nm. On addition of base the absorption band undergoes appreciable intensification with no shift in the band maximum. The complex is fully formed above pH6.

An equimolar aqueous solution of L_B and $Ni(ClO_4)_2 \cdot 6H_2O$ was titrated spectrophotometrically in the pH range 2-12. The spectrum of the solution shows no appreciable absorption in the visible region at or below pH3. On addition of base an absorption band develops with λ_{max} = 460 nm. Further addition of base gives intensification of the band with no shift in λ_{max}. The complex is fully formed at and above pH 7.5.

Potentiometric and spectrophotometric titrations of ML_C

($M = Cu(II)$)

A potentiometric titration was carried out by mixing equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ with L_C in 0.1 mol dm^{-3} (KNO_3) at 25°C and titrating against 0.05 mol dm^{-3} (NaOH). On the basis that two moles of base will be consumed per mole of ligand the end point in the titration curve shows that base consumption is only 59% of that expected, it seems unlikely that this is due to slow complexation of Cu(11) but more likely that the ligand is only 59% pure. While the analytical results were reasonable it may be that the ligand contains some polymeric material of the type shown in structure (4).

Redox studies

As mentioned in the Introduction, the planar, strong field, deprotonated macrocyclic diamides stabilise complexed Cu(111) ions and redox studies coupled with e.s.r. measurements by Fabbrizzi *et al.*[17] have shown that the redox orbital in the oxidation of $[Cu(L_B-2H)]^{\circ}$ to $[Cu(L_B-2H)]^{1+}$ is metal based. The redox chemistry of the metal complexes of L_A, L_B and L_C has been pursued in the present work.

$[Cu(L_A-2H)]$ was prepared *in situ* by dissolving equimolar amounts of $Cu(ClO_4)_2$ and L_A in 0.1 mol dm^{-3} $NaClO_4$ in water and raising the pH to *ca*.8 by addition of sodium hydroxide. The final solution was ca. 1 x 10^{-3} mol dm^{-3} in $[Cu(L_A-2H)]$. Cyclic voltammetry at a platinum wire electrode showed an irreversible one-electron oxidation at $\frac{1}{2}E_p$ = + 0.61 volts versus a saturated calomel reference electrode (SCE) where $\frac{1}{2}E_p$ is the mid-point between $E_p(a)$ (the potential at which $I_p(a)$ the forward peak current is at a maximum) and $E_p(c)$ (the potential at which $I_p(c)$ the return peak current is at a maximum). A plot of peak height $I_p(a)$ versus the square root of scan rate $v^{\frac{1}{2}}$ is linear, passing through the origin indicating a diffusion controlled process. The peak height ratio $I_p(a)/I_p(c)$ = 1.43 at a scan rate of 100 mv/s and the peak to peak separation ΔE_p = 160 mv at a scan rate of 100 mv/s increasing to 250 mv at a scan rate = 500 mv/s. At a carbon paste indicator electrode the irreversible oxidation wave is seen at + 0.65 volts versus an SCE, see Tables 4.2 and 4.3.

TABLE 4.2

Cyclic voltammetry of $[Cu(L_A-2H)]^a$ at 25°C

v (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	43	27	1.59	+0.61	140
100	56	39	1.43	+0.61	160
200	82	56	1.46	+0.60	190
500	120	64	1.87	+0.64	250

a. Support electrolyte is aqueous 0.1 mol dm^{-3} $(NaClO_4)$ with all potentials expressed versus the SCE. Potentials are measured at a platinum wire electrode. The solution is 1 x 10^{-3} mol dm^{-3} in $([Cu(L_A-2H)]^a)$.

TABLE 4.3

Cyclic voltammetry of $[Cu(L_A-2H)]^a$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	205	70	2.92	+0.65	340
100	330	150	2.20	+0.66	470
200	540	160	3.37	+0.64	550
500	1100	220	5.00	+0.65	750

a. Support electrolyte is aqueous 0.1 mol dm^{-3} ($NaClO_4$) with all potentials expressed versus the SCE. Potentials are measured at a carbon paste indicator electrode. The solution is 1 x 10^{-3} mol dm^{-3} in ($[Cu(L_A-2H)]^\circ$).

Cyclic voltammetry at platinum of a solution of $[Cu(L_A-2H)]^\circ$ prepared <u>in situ</u> in a support electrolyte of 0.3 mol dm^{-3} tetra-n-butyl ammonium perchlorate in dimethylsulphoxide shows a quasi-reversible one-electron oxidation at $\frac{1}{2}E_p$ = + 0.32 volts versus an SCE. A plot of $E_p(a)$ versus $v^{\frac{1}{2}}$ gives a straight line through the origin confirming diffusion control. The ratio of peak currents $I_p(a)/I_p(c)$ equals unity indicating that the product of the oxidation process is stable on the time scale of the experiment and available for reduction on the return half of the cycle. However, the observation that the peak to peak separation ΔE_p = 130 mv at a scan rate of 100 mv/s indicates a sluggish electron transfer, see Table 4.4.

Redox Studies of [CuL_A-2H] in 0.3 mol dm^{-3} tetra-n-butyl ammonium perchlorate in dimethyl sulphoxide

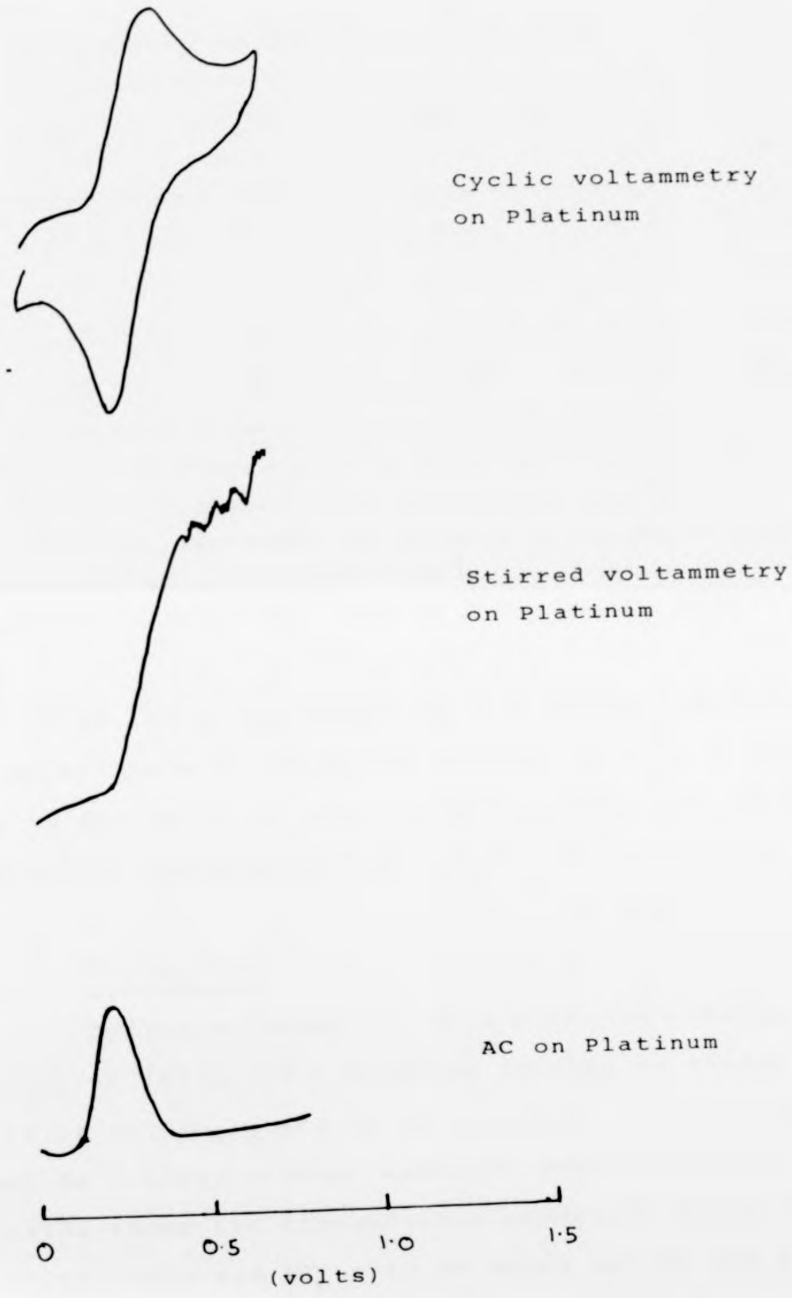


Figure 4.4

TABLE 4.4

Cyclic voltammetry[a] of $[Cu(L_A-2H)]^\circ$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	12.5	12.5	1.0	+0.33	110
100	17	17	1.0	+0.32	130
200	22	24	0.91	+0.32	160
500	26	30	0.86	+0.35	180

a. Support electrolyte is 0.3 mol dm^{-3} tetra-n-butyl ammonium perchlorate in dimethylsulphoxide with all potentials expressed versus the SCE. Potentials are measured at a platinum indicator electrode. The solution is 1 x 10^{-3} mol dm^{-3} in $[Cu(L_A-2H)]$.

By the AC technique at a platinum indicator electrode the complex shows an oxidation process at E_p = + 0.24 volts versus an SCE while by stirred CV the oxidation is present at + 0.47 volts, see Figure 4.4.

$[Ni(L_A-2H)]$

Cyclic voltammetry, at a platinum indicator electrode of $[Ni(L_A-2H)]$ prepared in situ by mixing equimolar amounts of $Ni(ClO_4)_2$ and L_A in a support electrolyte of 0.3 mol dm^{-3} tetra n-butyl ammonium perchlorate in dimethylsulphoxide shows two irreversible oxidation waves at $\frac{1}{2}E_p$ = +0.65 volts and $\frac{1}{2}E_p$ = +0.79 volts versus the SCE.

$[Cu(L_B-2H)]$

Cyclic voltammetry on ca. 1 x 10^{-3} mol dm^{-3} solutions of $[Cu(L_B-2H)]$ was carried out using both platinum and carbon paste indicator electrodes. The complex $[Cu(L_B-2H)]$ in a support electrolyte of 0.3 mol dm^{-3} tetra n-butyl ammonium perchlorate in dimethylsulphoxide shows a fully reversible one-electron oxidation at $\frac{1}{2}E_p$ = + 0.48 volts at a platinum wire versus an SCE. A linear plot of $I_p(a)$ versus $v^{\frac{1}{2}}$ confirms diffusion control. The separation of the anodic and cathodic peaks ΔE_p is 60 mv and the peak height ratio $I_p(a)/I_p(c)$ is close to unity. In addition $E_p(a)$, $E_p(c)$ and $\frac{1}{2}E_p$ are independent of scan rate, see Table 4.5.

TABLE 4.5

Cyclic voltammetry[a] of $[Cu(L_B-2H)]°$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	6.0	5.0	1.20	+0.48	70
100	8.25	7.0	1.17	+0.48	60
200	12.5	10.25	1.21	+0.48	70
500	17.25	17.0	1.01	+0.48	70

a. Support electrolyte is 0.3 mol dm^{-3} tetra n-butyl ammonium perchlorate in dimethylsulphoxide with all potentials expressed versus the SCE. Potentials are measured at a platinum indicator electrode. The solution is 1 x 10^{-3} mol dm^{-3} in $[Cu(L_B-2H)]°$.

$[Cu(L_B-2H)]$ in a support electrolyte of 0.1 mol dm^{-3} sodium perchlorate in water shows a diffusion controlled, fully

Redox Studies of $[CuL_B-2H]$ in 0.1 mol dm^{-3} $(NaClO_4)$

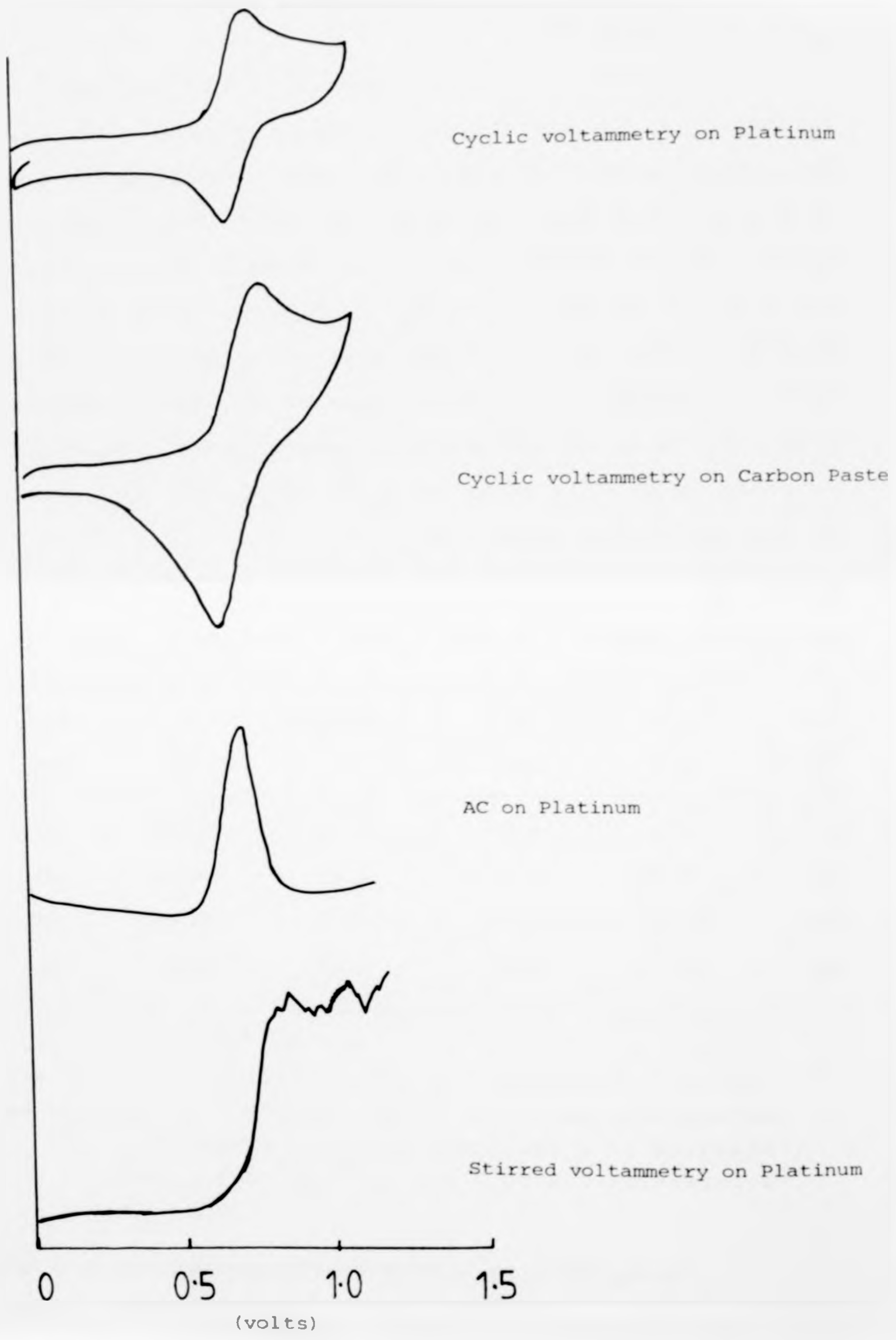


Figure 4.5

reversible one-electron oxidation on platinum at $\frac{1}{2}E_p$ = + 0.69 volts versus an SCE, ΔE_p is 60 mv and $I_p(a)/I_p(c)$ is close to unity, see Table 4.6.

TABLE 4.6

Cyclic voltammetry[a] of $[Cu(L_B-2H)]$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/(_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	23	19	1.21	+0.69	60
100	30	26	1.15	+0.69	70
200	46	39	1.17	+0.70	80
500	72.5	55	1.31	+0.69	95

a. Support electrolyte is 0.1 mol dm^{-3} $NaClO_4$ in water. All potentials are expressed versus the SCE. Potentials are measured at a platinum indicator electrode. The solution is 1 x 10^{-3} mol dm^{-3} in $[Cu(L_B-2H)]$.

By the AC technique at a platinum indicator electrode the oxidation is observed at + 0.69 volts versus the SCE. At a carbon paste electrode $\frac{1}{2}E_p$ = + 0.69 volts with the ratio $I_p(a)/I_p(c)$ equal to one, see Table 4.7, and Figure 4.5.

TABLE 4.7

Cyclic voltammetry[a] of $[Cu(L_B\text{-}2H)]$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\tfrac{1}{2}E_p$ (v)	ΔE_p (mv)
50	340	270	1.27	+0.69	110
100	540	480	1.12	+0.69	140
200	825	700	1.17	+0.69	150
500	1225	1175	1.04	+0.69	230

a. Support electrolyte is 0.1 mol dm^{-3} $NaClO_4$ in water. All potentials are expressed versus the SCE. Potentials are measured at a carbon paste indicator electrode. The solution is 1×10^{-3} mol dm^{-3} in $[Cu(L_A\text{-}2H)]$.

$[Ni(L_B\text{-}2H)]$

Cyclic voltammetry of $[Ni(L_B\text{-}2H)]$ in 0.3 mol dm^{-3} tetra n-butyl ammonium perchlorate dimethylsulphoxide at a platinum electrode shows a diffusion controlled irreversible oxidation at $\tfrac{1}{2}E_p = +\ 0.43$ volts versus an SCE. The peak current ratio $I_p(a)/I_p(c) = 1.2$ at a scan rate of 100 mv/s with $\Delta E_p = 220$ mv, see Table 4.8.

TABLE 4.8

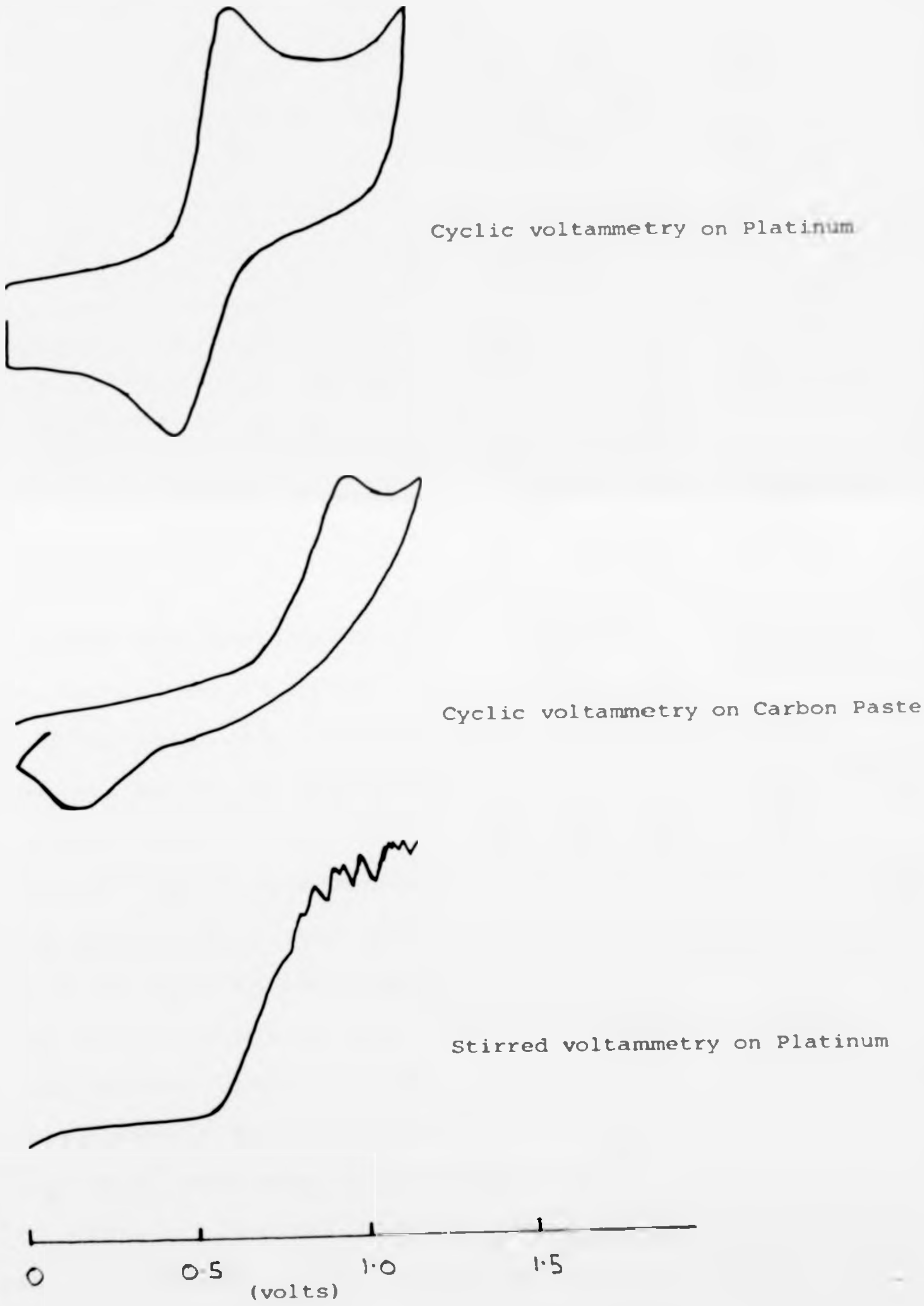
Cyclic voltammetry[a] of $[Ni(L_B-2H)]$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	20.5	16	1.28	+0.43	180
100	27.5	23	1.19	+0.42	220
200	37	30	1.23	+0.44	270
500	54	44	1.22	+0.43	340

a. Support electrolyte is 0.3 mol dm^{-3} tetra n-butyl ammonium perchlorate in dimethylsulphoxide. All potentials are expressed versus the SCE. Potentials were measured at a platinum indicator electrode. The solution is 1×10^{-3} mol dm^{-3} in $[Ni(L_B-2H)]$.

Using the AC technique, at a platinum wire electrode, the oxidation is seen at E_p = + 0.43 volts versus the SCE. Cyclic voltammetry of $[Ni(L_B-2H)]$ in a support electrolyte of 0.1 mol dm^{-3} sodium perchlorate in water shows an irreversible oxidation at a platinum indicator electrode at $\frac{1}{2}E_p$ = + 0.59 volts versus the SCE. The process is diffusion controlled as indicated by a linear plot of $I_p(a)$ versus $v^{\frac{1}{2}}$ with irreversibility indicated by ΔE_p = 160 mv and $I_p(a)/I_p(c)$ = 1.5 at a scan rate of 100 mv/s, see Table 4.9 and Figure 4.6.

Redox Studies of $[NiL_8\text{-}2H]$ in 0.1 mol dm^{-3} $(NaClO_4)$



<u>Figure 4.6</u>

TABLE 4.9

Cyclic voltammetry[a] of $[Ni(L_B-2H)]$ at 25°C

ν (mv/s)	$I_p(a)$ (μA)	$I_p(c)$ (μA)	$I_p(a)/I_p(c)$	$\frac{1}{2}E_p$ (v)	ΔE_p (mv)
50	30	19	1.57	+0.59	160
200	77	46	1.67	+0.58	210
500	112.5	70	1.60	+0.61	270

a. Support electrolyte is 0.1 mol dm^{-3} $NaClO_4$ in water. All potentials are expressed versus an SCE. Potentials are measured at a platinum indicator electrode. The solution is 1×10^{-3} mol dm^{-3} in $[Ni(L_B-2H)]$.

At a carbon paste electrode an irreversible oxidation takes place at $\frac{1}{2}E_p = +0.58$ volts versus the SCE.

The electrochemical data collected in the present work are summarised in Table 4.10. In the absence of e.s.r. results it is difficult to ascertain whether the redox processes are metal or ligand based, however by analogy with previous work where redox studies were coupled with e.s.r. measurements[17] metal based oxidations are indicated for the complexes discussed in the present work. From consideration of Table 4.10 several facts emerge: one-electron oxidations of $[Cu(L_A-2H)]$ and $[Cu(L_B-2H)]$ show a greater degree of reversibility than the oxidation processes for the corresponding Ni(II) complexes suggesting that $[Cu^{(III)}(L_A-2H)]^+$ and $[Cu^{III}(L_B-2H)]^+$ are more stable than $[Ni^{III}(L_A-2H)]^+$ and $[Ni^{III}(L_B-2H)]^+$. Perhaps the irreversibility in the oxidation processes for planar Ni(II) going to Ni(III) suggests that a

TABLE 4.10

Cyclic voltammetric data[a] on Cu(11) and Ni(11) complexes of L_A and L_B

Complex	$\frac{1}{2}E_p$ (volts)	Indicator Electrode	Reference Electrode	Support Electrolyte	Degree of Reversibility
CuL_A	+0.61	Platinum	SCE	0.1M $NaClO_4$ in water	Irreversible
CuL_A	+0.65	Carbon paste	SCE	0.1M $NaClO_4$ in water	Irreversible
CuL_A	+0.32	Platinum	SCE	0.3M Et_4NClO_4 in DMSO	Quasi-reversible
NiL_A	+0.65, +0.79	Platinum	SCE	0.3M Et_4NClO_4 in DMSO	Both waves irreversible
CuL_B	+0.48	Platinum	SCE	0.3M Et_4NClO_4 in DMSO	Reversible
CuL_B	+0.69	Platinum	SCE	0.1M $NaClO_4$ in water	Reversible
CuL_B	+0.69	Carbon paste	SCE	0.1M $NaClO_4$ in water	Reversible
NiL_B	+0.43	Platinum	SCE	0.3M Et_4NClO_4 in DMSO	Irreversible
NiL_B	+0.59	Platinum	SCE	0.1M $NaClO_4$ in water	Irreversible
NiL_B	+0.58	Carbon paste	SCE	0.1M $NaClO_4$ in water	Irreversible

a. All data collected in the present work structural rearrangement takes place following electron transfer to give a more favourable geometry for the Ni(lll) species. From CFSE considerations the change from planar Cu(ll) to planar Cu(lll) would be favoured over the change from planar Ni(ll) to planar Ni(lll). Comparing redox potentials for the oxidation processes of [Cu(L_A-2H)] and [Cu(L_B-2H)] in dimethylsulphoxide [Cu(L_A-2H)] has $\frac{1}{2}E_p$ = + 0.32 volts and oxidises more readily than [Cu(L_B-2H)] with $\frac{1}{2}E_p$ = + 0.48 volts, this perhaps reflects the strain of fitting a Cu(ll) ion into the small cavity of ligand L_A which is somewhat relieved upon oxidation to Cu(lll). In terms of ligand cavity size [Cu(L_B-2H)] is less strained than [Cu(L_A-2H)] and will benefit less from the decrease in size of the metal ion in going from Cu(ll) to Cu(lll). The greater strain in [Cu(L_A-2H)] relative to [Cu(L_B-2H)] is reflected in the position of the d-d bands in the aqueous electronic spectra with [Cu(L_A-2H)] having λ_{max} at 525 nm and [Cu(L_B-2H)] having λ_{max} at 506 nm. Finally it is noted that there is a solvent dependence on the redox potentials of [Cu(L_B-2H)] that is at a platinum electrode in 0.3 mol dm^{-3} tetra n-butyl ammonium perchlorate in dimethylsulphoxide $\frac{1}{2}E_p$ = + 0.48 volts while at a platinum electrode in 0.1 mol dm^{-3} sodium perchlorate in water $\frac{1}{2}E_p$ = + 0.69 volts.

Acid-catalysed Dissociation Kinetics of [Cu(L_B-2H)] and [Ni(L_B-2H)]

In this laboratory[19] the kinetics of acid-catalysed dissociation for [Cu(L_B-2H)] and [Ni(L_B-2H)] have been measured. These studies show that two moles of protons are consumed per mole of complex, with the experimental rate law showing a second order dependence on hydrogen ion concentration $[H^+]$. Least squares analysis of the data for $[Cu(L_B\text{-}2H)]$ gives $k_{obs}/[H^+]^2 = (1.15 \pm 0.03) \times 10^7\ M^{-2}\ s^{-1}$ at 25°C and $I = 0.1$ mol dm^{-3} and for $[Ni(L_B\text{-}2H)]$ $k_{obs}/[H^+]^2 = (1.22 \pm 0.03) \times 10^5\ M^{-2}\ s^{-1}$ at 25°C and $\mu = 0.1$ mol dm^{-3}.

Temperature dependence studies on the acid dissociation processes allowed evaluation of activation parameters, for $[Cu(L_B\text{-}2H)]$ $\Delta H^{\neq} = +\ 71.3$ KJ mol^{-1} and $\Delta S^{\neq}_{298} = 129\ JK^{-1}\ mol^{-1}$ while for $[Ni(L_B\text{-}2H)]$ $\Delta H^{\neq} = +\ 64.1$ KJ mol^{-1} and $\Delta S^{\neq}_{298} = 67\ JK^{-1}\ mol^{-1}$. Dissociation of the complex $[Cu(L_B\text{-}2H)]$ the 14-membered macrocyclic amide differs markedly from that of the 14-membered tetra-aza macrocycles. The latter normally show a first order dependence on $[H^+]$.[21] In addition the amide complex dissociates much more rapidly than the corresponding tetra-aza macrocycle.

The condensation reaction between diethyl malonate and tetraethylenepentamine (attempts to prepare L_G)

The preparation of the pentadentate N_5 donor ligand, L_G in (1), was attempted on several occasions by the condensation of diethyl malonate with tetraethylenepentamine in ethanol. Experimental conditions were varied, that is, reaction time, order of mixing reagents, concentration, temperature of reaction, but no solid product was obtained. The Sephadex ion exchange procedure, successful for obtaining Cu(11) and Ni(11) complexes of ligands L_A, L_B and L_C from crude ligand product mixtures, in which crystallization of ligand is sluggish has been described previously. This technique was used in attempts to obtain an aqueous solution of $[Cu(L_G-2H)]$. Diethyl malonate and tetraethylenepentamine were refluxed in ethanol for seven days. At the end of this time the ethanol and unreacted diethyl malonate were removed by distillation on a rotary evaporator, leaving a gummy material which was taken up in the minimum volume of water. An aqueous solution of $Cu(ClO_4)_2$ was added and the mixture raised to pH 9.5 by addition of sodium hydroxide. The resulting blue-violet solution was loaded onto a column of CM Sephadex-C25 cation exchange resin and eluted with water. Kimura et al.[8] report that the doubly deprotonated complex $[Cu(L_G-2H)]^\circ$ exists above pH9 therefore the water eluted fraction should be a solution of $[Cu(L_G-2H)]^\circ$. The water eluted solution was titrated spectrophotometrically in the pH range 1-12.7. The spectrum of the solution at pH 4.3 shows a broad absorption with λ_{max} = 610 nm. As the pH is increased the absorption band moves to shorter wavelength (pH 4.65, λ_{max} 600 nm; pH 6.75, λ_{max} 590 nm) and undergoes intensification. The complex is fully formed at pH8 with a band maximum at 580 nm. At higher pH in the range 8-12.7 while λ_{max} remains constant at 580 nm the absorbance intensity decreases slightly. Solid $[Cu(L_G-2H)]^\circ$ could not be isolated from the solution. The position of λ_{max} at 580 nm suggests a strained complex when compared with $[Cu(L_A-2H)]$, λ_{max} = 525 nm and $[Cu(L_B-2H)]$, λ_{max} = 506 nm. Some of the violet solution containing $[Cu(L_G-2H)]^\circ$ was taken up in 0.1 mol dm^{-3} $NaClO_4$ in water and cyclic voltammetry performed at a platinum electrode. An irreversible oxidation wave was seen at $\frac{1}{2}E_p$ = + 0.8 volts versus the SCE but this was not studied further.

In an attempt to prepare $[Ni(L_G-2H)]$ the crude ligand product mixture was dissolved in water, treated with $Ni(ClO_4)_2$ and sodium hydroxide then eluted with water on a Sephadex column. The yellow eluted solution was titrated spectrophotometrically in the pH range 3-12. The complex is fully formed at and above pH 8.5 with a band maximum ca. 440nm, on the edge of an intense charge transfer band.

The preparation of a pentadentate N_5 donor ligand by condensation of diethyl oxalate with tetraethylenepentamine in ethanol was attempted but no solid ligand was obtained from the reaction mixture. The ethanol and unreacted diethyl oxalate were distilled off and the gummy residue was dissolved in water, treated with $Cu(ClO_4)_2$ and sodium hydroxide then eluted with water on a Sephadex column. The blue-violet solution was titrated spectrophotometrically in the pH range 3-12.5. The spectrum of the solution at pH 4.22 shows a broad absorption with λ_{max} = 610 nm. As the pH is increased the absorption band moves to shorter wavelength (pH 6.75, λ_{max} 600 nm; pH 8.12, λ_{max} = 590 nm) and undergoes intensification. The complex is fully formed at pH 8.0 with a band maximum at 565 nm. Above pH8 in the range pH 8-13 while λ_{max} remains constant at 565 nm the absorbance intensity decreases.

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A Binuclear Copper(II) Complex of N,N',N'',N'''-Tetra(2-aminoethyl)-1,1,5,5-pentanetetraamide. A Double Cavity Amide Ligand

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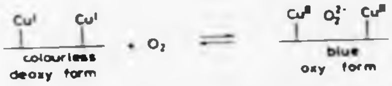
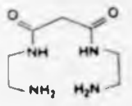
A number of dinucleating ligands have been used to bring two copper atoms into close proximity [1, 2]. Such complexes are of considerable interest as the biological function of many metalloproteins is believed to be associated with the occurrence of pairs of adjacent metal ions capable of mutual interaction via small bridging ligands. Thus in the O_2-carrying haemocyanins, the dioxygen uptake has been attributed [3] to the equilibrium (1), and a number of synthetic macrocyclic Cu(I) complexes having reversible O_2-binding activity with a $2Cu:O_2$ stoichiometry have been described [4, 5].

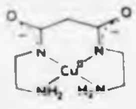


(1)

Hill and Raspin [6] first reported the preparation of the copper(II) complex of 1,9-diamino-3,7-diazanonane-4,6-dione (I) and established that deprotonation of both amide groups occurred on complexation with copper to give (II). Ligands of this type bear a structural resemblance to tripeptides which are well known to ionise two amide protons on coordination to metal ions such as copper(II). A large number of macrocyclic diamides have now been characterised [7].

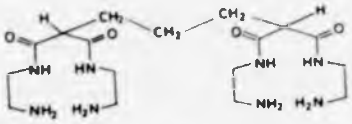


(I)



(II)

The present paper discusses the synthesis and physical properties of the double cavity amide ligand (III) and its copper complex.



(III)

Experimental

Tetraethyl 1,1,5,5-pentanetetracarboxylate was prepared by reaction of diethyl malonate with 1,3-dibromopropane in the presence of sodium ethoxide [8]. The product was fractionated through a Vigreux column, b.p. 198–202 °C at 2.5 mm, i.r. (liquid film) νCO 1735 cm^{-1} (br). ^1H n.m.r., CH_3 1.25 δ (12 H) triplet; OCH_2 4.15 δ (8 H) quartet; $CH_2\mathit{CH_2}CH_2$ 3.30 δ (2 H) triplet, CH_2 1.90 δ (4H) quartet. ^{13}C n.m.r. CH_3 14.11 δ; CH_2 25.14 δ, CH_2 28.41 δ, CH 51.86 δ, CH_2O 61.25 δ, CO_2R 169.14 δ ($CDCl_3$ solution). Calc. for $C_{17}H_{28}O_2$ m/e = 360.1785, found m/e = 360.1768.

The ligand, N,N',N'',N'''-tetra(2-aminoethyl)-1,1,5,5-pentanetetraamide was prepared as follows. Tetraethyl 1,1,5,5-pentanetetracarboxylate (20 g, 0.055 mol) was added dropwise with stirring to 1,2-diaminoethane (73 g, 1.21 mol) at 0 °C. After completion of the addition, the mixture was allowed to stand at room temperature for 7 days. The excess 1,2-diaminoethane was removed under vacuum to give a brown glassy material. Trituration with ethanol gave a colourless hygroscopic solid (4.9 g). The copper(II) complex was prepared as follows. The ligand (0.5 g) was dissolved in water (7 cm^3) and added to a solution of copper(II) sulphate pentahydrate (0.69 g) in water (7 cm^3). A blue precipitate formed at this stage, which dissolved on slow addition of sodium hydroxide (0.22 g) in water (100 cm^3) The solvent was removed on a rotary evaporator and the residue extracted with methanol. Removal of the methanol gave a purple solid. The crude complex was dissolved in the minimum volume of water, the solution cooled in ice and the complex reprecipitated by the addition of ice-cold ethanol. The complex was filtered and washed with ethanol then ether and dried *in vacuo*. *Anal.* Calc. for $C_{17}H_{32}N_8O_4Cu_2\cdot 6H_2O$: C, 31.4; H, 6.8; N, 17.2; H_2O, 16.7. Found: C, 31.2; H, 6.6; N, 16.9; H_2O 16.5. The water content was determined by thermogravimetric analysis. The i.r. spectrum (KBr disc) has a strong broad νOH band at *ca.* 3350 cm^{-1} and νNH at 3160 cm^{-1}. There is a strong amide band at 1580 cm^{-1} characteristic of deprotonated copper(II) complexes of this type [7].

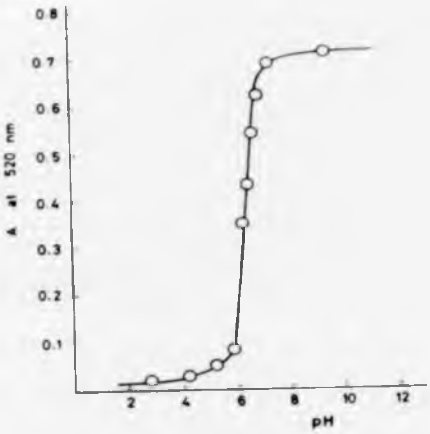


Fig. 1. Spectrophotometric titration of $Cu_2L\cdot 6H_2O$ with hydrochloric acid.

Nmr measurements (^1H and ^{13}C) were carried out using a Bruker WP80 instrument, with $CDCl_3$ as solvent and TMS as internal standard. Ir spectra were determined on a Perkin Elmer 457 instrument using KBr discs, and visible spectra on a Perkin Elmer 402 spectrophotometer. Magnetic susceptibilities were determined by the Gouy method using $Hg[Co(CNS)_4]$ as calibrant.

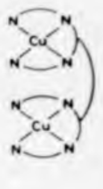
Results and Discussion

Reaction of an excess of 1,2-diaminoethane with 1,1,5,5-pentanetetracarboxylate gives an acceptable yield (*ca.* 25%) of the ligand(III). The tetraamide reacts with copper(II) in basic solution to give a purple complex in which four protons are lost from the ligand,

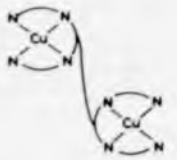
$$LH_4 + 2Cu(II) \rightleftharpoons Cu_2L + 4H^+$$

The binuclear copper(II) complex is neutral, and conductivity measurements confirmed that it was a non-electrolyte in aqueous solution. Spectrophotometric titration of the complex against hydrochloric acid (Fig. 1), indicates that ligand deprotonation begins at pH 5.5 and is complete at pH 8.0. The complex has a symmetrical d–d band at 525 nm (ϵ = 133) and a strong band at 205 nm (ϵ = 15,750). The d–d spectrum may be compared with that of the copper(II) complex of N,N′-di(2-aminoethyl)malondiamide-(II) where λ_{max} is 516 nm (ϵ = 63) [6]. The doubling of the band intensity is fully consistent with the incorporation of two copper(II) ions into the ligand. Molecular models indicate that as a result of the trimethylene bridge the complex is quite flexible and can adopt two extreme conformations which can be represented diagramatically as (IV) and (V).

The eclipsed conformation (IV) is expected to be less favoured than the staggered conformation (V).



(IV)



(V)

Magnetic susceptibility measurements confirm that the complex is paramagnetic with μ_{eff} = 3.52 B.M. at 18 °C (1.76 B.M. per copper(II)). There is no antiferromagnetic coupling of the type which might be expected with (IV). Attempts have been made to ring close the copper(II) complex by reaction with acetone to give two linked macrocycles. Such acetone condensation reactions have been used successfully on a number of occasions [9]. In the present case reddish-brown products are slowly formed on dissolving the complex in acetone, but it has not, as yet, been possible to characterise the products.

Acknowledgement

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Synthetic and Kinetic Studies on Copper(II), Nickel(II) and Cobalt(III) Complexes of 1,4,7,11,14-Penta-azacycloheptadecane([17]aneN$_5$)

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The preparation of the pentadentate macrocyclic ligand L (= II, 4,7,11,14-penta-azacycloheptadecane) is described. The complexes $[CuL](ClO_4)_2$, $[NiL(H_2O)](ClO_4)_2$, $[CoClL](ClO_4)_2$, $[CoL(CO_3)]ClO_4$, $[Co([15]aneN_5)CO_3]ClO_4$, $[CoL(DMF)](ClO_4)_3$, $[CoL(OOCH)](ClO_4)_2$ *and* $[CoL(OH_2)](ClO_4)_2$ *have been prepared and characterised. The copper(II) complex appears to be square pyramidal on the basis of its d–d spectrum and the nickel(II) complex is octahedral. The copper and nickel complexes dissociate in acidic solution and the reactions have been studied kinetically. For the copper(II) derivative, rate* $= k_H[\text{Complex}][H^+]^2$ *with* $k_H = 1.2 \times 10^3\ M^{-2}\ s^{-1}$ *at 25 °C and* $I = 0.1$ M $(NaClO_4)$ $(\Delta H^\ddagger = 29.8\ kJ\ mol^{-1}$ *and* $\Delta S_{298}^\ddagger = -86\ JK^{-1}\ mol^{-1})$. *Dissociation rates of the copper complexes increase in the order* $[15]aneN_5 < [16]aneN_5 < [17]aneN_5$. *For the dissociation of the nickel(II) complex, rate* $= k_H[\text{Complex}][H^+]$ *with* $k_H = 0.23\ M^{-1}\ s^{-1}$ *at 25 °C* $(\Delta H^\ddagger = 44.0\ kJ\ mol^{-1}, \Delta S_{298}^\ddagger = -109\ JK^{-1}\ mol^{-1})$. *Mechanisms for these reactions are considered. The nickel(II) complex is oxidised to nickel(III) in acetonitrile solvent in a pseudo-reversible process* $(E_{1/2} = +1.11$ *V with reference to S.C.E.).*

Mercury(II) catalysed aquation of $[CoClL]^{2+}$ *has been studied* $(k_{Hg} = 1.4 \times 10^{-2}\ M^{-1}\ s^{-1}$ *at 25 °C). Potentiometric titration of the aqua-complex gives pKa = 6.2 for the aqua ⇌ hydroxo equilibrium. The hydroxo complex* $[CoL(OH)]^{2+}$ *reacts rapidly with* CO_2 *to give the monodentate carbonato complex* $[CoL(CO_3)]^+$. *Decarboxylation of the carbonato complex occurs in acidic solution and the reaction has been studied kinetically,* $k = 0.43\ s^{-1}$ *at 25 °C* $(\Delta H^\ddagger = 48.4\ kJ\ mol^{-1}; \Delta S_{298}^\ddagger = -90\ JK^{-1}\ mol^{-1})$. *Similar studies on* $[Co([15]aneN_5)CO_3]^+$ *are also reported. The base hydrolysis of the monodentate formato complex* $[CoL(OOCH)]^{2+}$ *has also been investigated* $(k_{OH} = 3.0 \times 10^4\ M^{-1}\ s^{-1}$ *at 25 °C,* $\Delta H^\ddagger = 41.1\ kJ\ mol^{-1}; \Delta S_{298}^\ddagger = -20\ JK^{-1}\ mol^{-1})$.

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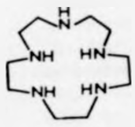
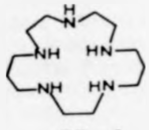
Introduction

The preparation of penta-aza macrocycles using the Richman and Atkin's procedure [1] is now relatively straightforward [2, 3]. In a previous paper we have described synthetic and kinetic studies on copper(II), nickel(II) and cobalt(III) complexes of 1, 4, 7, 10, 13-penta-azacyclopentadecane (*I* = [15]-aneN$_5$). The present paper discusses various aspects of the coordination chemistry of 1,4,7,11,14-penta-azacycloheptadecane (*II*) (one of the possible isomers of [17]aneN$_5$). The nickel(II) complex of (*II* = L) has previously been characterised and the electrochemistry of the $[NiL]^{2+}/[NiL]^{3+}$ redox system studied using acetonitrile as solvent [2, 5].


(I)


(II) = L

Experimental

N,O,O'-Tritosyldiethanolamine was prepared as previously described [4]; N,N',N'',N'''-Tetratosyl-1,10-diamino-4,7-diazadecane (the tetratosylate of 3, 2, 3-tet) was prepared by a procedure which has subsequently been described [2]. Condensation of the two tosylates in DMF using sodium hydride, and hydrolysis of the pentatosylate with sulphuric acid was carried out by previously described procedures [2, 4]. The ligand pentahydrochloride L·5HCl was prepared by literature procedures [2, 4].

$CuL(ClO_4)_2$

The ligand pentahydrochloride (0.5 g) was dissolved in water (20 cm^3) and copper(II) carbonate (0.2 g) added. The mixture was heated on a water bath for *ca.* 0.5 hr, and the solution cooled and filtered to remove unreacted copper(II) carbonate. The filtrate was concentrated to *ca.* 5 cm^3 and treated with $NaClO_4 \cdot 6H_2O$ (0.2 g). On cooling blue needle-like crystals of the copper complex crystallised as the perchlorate salt. ***Anal.*** Calcd. for $C_{12}H_{29}N_5Cl_2O_8Cu$: C, 28.5; H, 5.8; N, 13.9. Found: C, 28.6; H, 5.8; N, 14.0%. The complex has Λ_M = 243 ohm^{-1} cm^2 in water and Λ_M = 144 ohm^{-1} cm^2 in nitromethane.

$NiL(ClO_4)_2H_2O$

This complex was prepared essentially as described above using nickel(II) carbonate or the basic carbonate. Violet crystals of the perchlorate salt were obtained: ***Anal.*** Calcd. for $C_{12}H_{29}N_5Cl_2O_8NiH_2O$: C, 27.8; H, 6.0; N, 13.6. Found: C, 27.7; H, 6.1; N, 13.9%. The complex has Λ_M = 235 ohm^{-1} cm^2 in water and Λ_M = 145 ohm^{-1} cm^2 in nitromethane.

$[CoLCl](ClO_4)_2$

The ligand pentahydrochloride (0.5 g) was dissolved in water (20 cm^3) and treated with freshly prepared $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (0.2 g). The mixture was heated on a steam bath for *ca.* 1 hr then cooled and filtered. To the filtrate was added $NaClO_4 \cdot 6H_2O$ (0.2 g) and the solution concentrated to *ca.* 5 cm^3. On cooling the pink complex crystallised. The complex was filtered off and washed with 2-propanol then ether and air dried. ***Anal.*** Calcd. for $C_{12}H_{29}N_5Cl_3O_8Co$: C, 26.9; H, 5.5; N, 13.0. Found: C, 27.0; H, 5.4, N, 12.8%.

$[CoLCO_3]ClO_4$

The complex $[CoLCl](ClO_4)_2$ (0.2 g) was dissolved in water (25 cm^3) and treated with excess AgOH. The mixture was heated on a steam bath for *ca.* 15 min, then cooled and filtered. To the filtrate was added $LiCO_3$ (0.1 g) and the mixture heated for *ca.* 1 hr on a steam bath. The solution was cooled and filtered. The filtrate was reduced in volume to *ca.* 5 cm^3 (steam bath). Addition of $LiClO_4$ (0.05 g) and cooling gave the pink complex which was filtered off, washed with ethanol then ether and dried *in vacuo*. ***Anal.*** Calcd. for $C_{13}H_{29}N_5O_7ClCo$: C, 33.8; H, 6.3; N, 15.1. Found: C, 33.8; H, 6.0; N, 15.0%.

$[Co([15]aneN_5)CO_3]ClO_4$

The complex $[Co([15]aneN_5)H_2O](ClO_4)_3$ (0.2 g) prepared as previously described [3] was dissolved in water (20 cm^3) and treated with Li_2CO_3 (0.1 g). The mixture was heated on a steam bath for *ca.* 0.5 hr and then slowly taken to dryness. The residue was extracted with water (10 cm^3) and the aqueous extract treated with $LiClO_4$ (0.05 g). The solution was warmed for *ca.* 10 min to 60 °C, then cooled and filtered. The filtrate was reduced in volume to *ca.* 3 cm^3 (steam bath) and the carbonato complex precipitated by the addition of excess ethanol. The complex was filtered off and washed with ethanol then ether and dried *in vacuo*. ***Anal.*** Calcd. for $C_{11}H_{29}N_5ClO_7Co$: C, 30.5; H, 5.8; N, 16.15. Found: C, 30.8; H, 5.9; N, 16.1%.

$[CoL(H_2O)](ClO_4)_3$

The chloro-complex $[CoLCl](ClO_4)_2$ (0.54 g) was dissolved in water (20 cm^3) and the solution warmed to *ca.* 50 °C. Silver perchlorate (0.21 g) was added and the solution warmed for a further 15 min to complete precipitation of AgCl. After cooling, the precipitated AgCl was filtered off and the filtrate concentrated to *ca.* 3 cm^3. Cooling in ice followed by the addition of a few drops of 70% $HClO_4$ gave the red complex which was filtered off and washed with ethanol then ether and dried *in vacuo*. ***Anal.*** Calcd. for $C_{12}H_{29}N_5Cl_3O_{12}Co$: C, 23.3, H, 5.05, N. 11.3. Found: C, 23.05; H, 4.9; N, 11.2%.

$[CoL(DMF)](ClO_4)_3$

The chloro-complex $[CoLCl](ClO_4)_2$ (0.27 g) was dissolved in DMF (1 cm^3) and $AgClO_4$ (0.11 g) added. The mixture was heated for *ca.* 10 min at about 50 °C, then cooled and filtered to remove AgCl. To the filtrate was added ethanol (10 cm^3) followed by excess ether, which on standing gave an oil. Trituration of the oil with ethanol gave a pink solid which was filtered off, washed with ethanol, then ether and dried *in vacuo*. ***Anal.*** Calcd. for $C_{15}H_{34}N_6Cl_3O_{13}Co$: C, 26.7; H, 5.4; N, 12.5. Found: C, 26.5; H, 5.3; N, 12.6%. The DMF ligand is bonded *via* the oxygen donor with a $\nu C{=}O$ band at 1660 cm^{-1}. The ^1H NMR spectrum has two methyl signals at 2.74 and 2.98 (due to the non-equivalent methyl groups) and a formyl singlet at 7.96δ.

$[CoL(OOCH)](ClO_4)_2 \cdot H_2O$

The complex $[CoLCl](ClO_4)_2$ (0.27 g) was suspended in formic acid (2 cm^3) and mixed with $AgClO_4$ (0.11 g). The mixture was heated for *ca.* 10 min at 50 °C, then cooled and the precipitated AgCl filtered off. Addition of ethanol to the filtrate gave the pink complex which was filtered off, washed with ethanol, then ether and air dried. ***Anal.*** Calcd. for $C_{13}H_{30}N_5Cl_2O_{11}Co$: C, 26.7; H, 5.4; N, 12.4. Found: C, 27.2; H, 5.6; N, 12.5%.

Kinetics

The kinetics of the acid catalysed dissociation of $CuL(ClO_4)_2$ were monitored at 300 nm. Measurements were made using $HClO_4$ solutions adjusted to $I = 0.1$ *M* with sodium perchlorate. The kinetics of dissociation were followed on a Durrum D110 stopped-flow spectrophotometer. The signal was stored by a Datalab 901 transient recorder on line to a CBM 3016 computer. The acid dissociation of $NiL(ClO_4)_2 \cdot H_2O$ was monitored at 220 nm using a Gilford 2400S spectrophotometer interfaced with an Apple II computing system. Measurements were made with $HClO_4$ solutions adjusted to I = 0.1 *M* with $NaClO_4$. Activation parameters were calculated by least-squares analysis of Eyring plots.

Mercury(II) catalysed aquation of $[CoClL]^{2+}$ was studied spectrophotometrically using a total ionic strength of 0.49 *M*. Mercury(II) solutions were prepared using the nitrate salt.

Decarboxylation of the monodentate carboxylato complexes $[Co([15]aneN_5)CO_3]^+$ and $[Co([17]aneN_5)CO_3]^+$ was monitored by stopped flow measurements at 490 nm using HCl solutions (0.05 *M*). Base hydrolysis of [CoL(OOCH)] was monitored spectrophotometrically at 280 nm. Measurements were made using acetate and citrate buffers adjusted to I = 0.1 *M*. Hydroxide ion concentrations were determined from the pH using listed values of the ionic product of water and a molar activity coefficient of 0.77 estimated from the Davies equation.

General

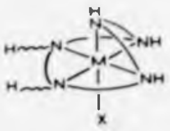
Infrared spectra were determined as KBr discs using a Perkin-Elmer 457 instrument. Conductivity measurements were made with a Portland Electronics Model P310 conductivity meter using 10^{-3} *M* solutions at 25 °C. All pH measurements were made with a Radiometer PHM64 Research pH meter, which was standardised using 0.05 *M* potassium hydrogen phthalate (pH 4.008) and phosphate buffer (0.025 *M*), pH 6.86 at 25 °C.

Electrochemistry was carried out with a PAR 170 electrochemistry system. Measurements were made using 1 × 10^{-3} *M* solution in acetonitrile with 0.1 *M* $Bu_4N^+ClO_4^-$ as the supporting electrolyte. Potentials are expressed *versus* S.C.E., using a platinum electrode.

Results and Discussion

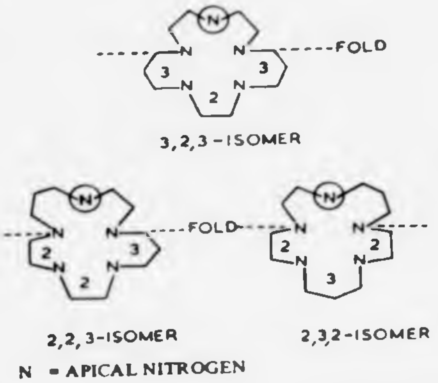
The ligand 1,4,7,11,14-penta-azacycloheptadecane is readily prepared by the reaction of the disodium salt of the tetratosylate of 1,10-diamino-4,7-diazadecane with the tritosylate of diethanolamine in N,N-dimethylformamide solution, followed by cleavage of the tosyl groups with concentrated sulphuric acid. The ligand is expected to act as a pentadentate, giving rise to complexes of type (*III*) with metal ions favouring six coordination. Complexes of this type contain two chiral nitrogen centres indicated by the slashed lines.

The unsymmetrical 1,4,7,11,14-penta-azacycloheptadecane presents further scope for isomerism



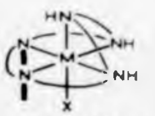
(III)

depending upon the nitrogen adopted as the apical donor (Scheme)



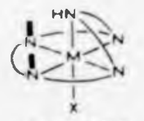
Scheme. Possible isomers of complexes of 1,4,7,11,14-penta-azacycloheptadecane.

As a result of the two chiral nitrogen centres, each of these gives rise to three diastereoisomeric species, the *meso*-syn (IV), the *meso*-anti (*V*) and the racemate (*VI*)



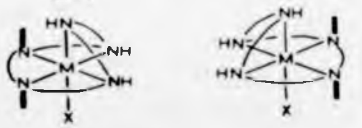
MESO-SYN

(IV)



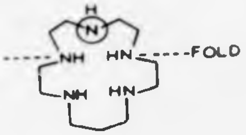
MESO-ANTI

(V)



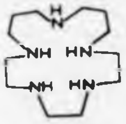
RACEMATE (VI)

Crystallographic work on $[Co([16]aneN_5)Cl](ClO_4)_2$ [6] has indicated that the single 6-membered chelate ring assumes a chair conformation while all five membered rings are gauche. The ligand has the 2,3,2-configuration (*VII*) and the chiral nitrogens have opposite chirality giving the *meso*-syn diastereoisomer.

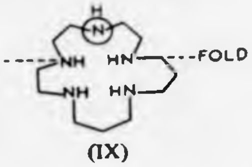


(VII)

Crystallographic work has also been carried out [7], on the cobalt(III) complex $[CoL_1Cl](ClO_4)_2$ where L_1 = 1,4,7,10,14-penta-azacycloheptadecane (*VIII*) which is the second possible isomer of $[17]aneN_5$. In this complex the configuration of the ligand is as



(VIII)



(IX)

in (*IX*), *i.e.* the 2,3,3-isomer with an N-*racemic* arrangement of the chiral nitrogen centres. The available evidence on the 16- and 17-membered ring systems indicates that the six-membered chelate ring occurs in the 'backbone' of the complex so that the 2,3,2-isomer of complexes of 1,4,7,11,14-penta-azacycloheptadecane may be favoured.

The copper(II) complex of $[17]aneN_5$, $[CuL](ClO_4)_2$ is readily isolated by the reaction of L·5HCl with copper(II) carbonate, followed by addition of sodium perchlorate. The complex gives a somewhat low conductivity in the non-coordinating solvent nitromethane with Λ_M = 144 ohm^{-1} cm^2 mol^{-1} at 25 °C possibly indicating ion association, but it is a 2:1 electrolyte in water (Λ_M = 243 ohm^{-1} cm^2 mol^{-1} at 25 °C). The visible spectrum in acetonitrile solvent has λ max 590 nm (ϵ = 180 M^{-1} cm^{-1}) Table I, which may be compared with λ max 585 nm (ϵ = 200 M^{-1} cm^{-1}) for the analogous complex of $[15]aneN_5$. Both complexes also display an additional weaker band, red shifted from the major d–d absorption band. For $[Cu[15]aneN_5](ClO_4)_2$ in water this band occurs at 825 nm ($\epsilon \sim 70$) while for $[CuL](ClO_4)_2$ in acetonitrile the band occurs at 840 nm ($\epsilon \sim 65$). This additional d–d absorption is indicative of axial interaction in a five coordinate system [8, 9]. A five coordinate square-pyramidal structure can be proposed on the basis of the observation of two bands in the visible and near infrared region [8–10]. The CuN_6 chromophores in complexes such as $[Cu(haco)]^{2+}$ (haco = 1,4,7,10,13,16-hexa-azacyclooctadecane) and $[Cu(dien)_2]^{2+}$ absorb at 615 and 640 nm, respectively [11]. The former complex lacks any band in the near infrared region, Fig. 1.

TABLE I. Electronic Spectra of the Complexes.

Complex	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
$CuL(ClO_4)_2$	582	180
	840	65 (acetonitrile)
$[NiL(H_2O)](ClO_4)_2$	820	5.6
	780	4.6
	540	4.6
	355	8
$[CoLCl]ClO_4$	550	132
	380	174
$[CoL(CO_3)]ClO_4$[a]	510	180
$[Co([15]aneN_5)CO_3]ClO_4$[a]	505	280
$[CoL(OH_2)](ClO_4)_3$	506	148
	360	142
$[CoL(DMF)](ClO_4)_3$	514	273
	362	153
$[CoL(OOCH)](ClO_4)_2H_2O$	530	106
	375	135

[a] Spectra determined using dilute $NaHCO_3$ solutions, all other spectra determined using aqueous solutions.

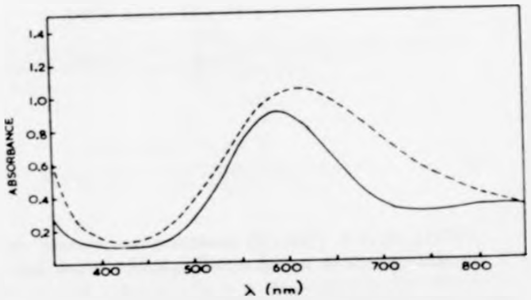


Fig. 1. Absorption spectra of $[Cu([17]aneN_5)](ClO_4)_2$ (——) in acetonitrile and $[Cu(haco)](ClO_4)_2$ in water (------).

The complex $CuL(ClO_4)_2$ is kinetically labile in dilute acid and the kinetics of dissociation were investigated using perchloric acid solutions, Table II. The reaction is first order in the complex and second order in $[H^+]$; rate = $k_H[CuL][H^+]^2$, with k_H = 1.2 × 10^3 M^{-2} s^{-1} at 25 °C and I = 0.1 *M* ($NaClO_4$). The temperature dependence of k_H, Table III, gives $\Delta H^{\ddagger}$ = 29.8 kJ mol^{-1} and $\Delta S_{298}^{\ddagger}$ = –86 JK^{-1} mol^{-1} with a correlation coefficient of 0.9835 for the Eyring plot.

TABLE II. The Acid Catalysed Dissociation of $CuL(ClO_4)_2$ at I = 0.1 *M* ($NaClO_4$).

10^2 [$HClO_4$] (*M*)	10^4[H^+]^2 (M^2)	k_{obs} (s^{-1})	$10^{-3}k_{obs}/[H^+]^2$ (M^{-2} s^{-1})
2.05	4.20	0.50	1.19
4.20	17.69	2.35	1.33
6.10	37.21	4.31	1.16
7.90	62.24	6.69	1.07
8.90	79.21	8.98	1.13
	$k_H = 1.2 \times 10^3$ M^{-2} s^{-1}		

TABLE III. Temperature Dependence of the Dissociation of $CuL(ClO_4)_2$ at I = 0.1 *M*.

Temp. (°C)	k_{obs}[a] (s^{-1})	10^{-3} k_H (M^{-2} s^{-1})
20	1.59	0.90
25	2.35	1.19
29.5	2.63	1.49
35	3.00	1.70

[a] [$HClO_4$] = 2.05×10^{-2} *M*. $\Delta H^{\ddagger} = 29.8 \pm 3.9$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -86 \pm 13$ J K^{-1} mol^{-1} (r = 0.9835).

The dissociation of the copper(II) complexes of [15]aneN_5, [16]aneN_5 and [17]aneN_5 all show a second order dependence on [H^+], Table IV. A plot of log k_H *versus* the ring size shows good linearity, Fig. 2. Dissociation of $[Cu([17]aneN_5)]^{2+}$ is some 2.4×10^3 times faster than that of $[Cu([15]aneN_5)]^{2+}$ at 25 °C [3].

The second order dependence on the hydrogen ion concentration indicates the participation of two protons in the transition state of the reaction. The kinetic behaviour of $[CuL]^{2+}$ in acidic solution can be described in terms of the eqns. (1) to (3). Monoprotonation of $[CuL]^{2+}$ to $[Cu(HL)]^{3+}$ is expected

$$[CuL]^{2+} + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} [Cu(HL)]^{3+} \quad (1)$$

$$[Cu(HL)]^{3+} + H^+ \overset{K_2}{\rightleftharpoons} [Cu(H_2L)]^{4+} \quad (2)$$

$$[Cu(H_2L)]^{4+} \xrightarrow{k} Cu^{2+}(aq) + H_2L^{2+} \quad (3)$$

to involve protonation at the apical nitrogen atom, as the axial copper–nitrogen bond is expected to be weaker as a result of Jahn-Teller distortion. Species of the type $[Cu(HL)]^{3+}$ have often been reported in potentiometric studies of copper(II) polyamine complexes [12]. The rate equation (4) can be readily derived from eqns. (1) to (3). Under the conditions of the present experiments ($K_1[H^+] + K_1K_2[H^+]^2$) $\ll 1$ and $k_H = kK_1K_2$. Protonation in the equatorial plane of the macrocycle is a prerequisite for dissociation to occur. Possible mechanisms have been previously outlined [3].

$$\text{Rate} = \frac{k_1K_1K_2[CuL^{2+}][H^+]^2}{(1 + K_1[H^+] + K_1K_2[H^+]^2)} \quad (4)$$

The nickel(II) complex $[NiL(H_2O)](ClO_4)_2$ was isolated as a violet solid. The complex is a 2:1 electrolyte in water (Λ_M = 235 ohm^{-1}cm^2 mol^{-1} at 25 °C) and gives a typical octahedral d–d spectrum, Table I. Fabbrizzi *et al.* [13] have reported that the nickel(II) complexes of [15]aneN_5, [16]aneN_5 and [17]aneN_5 (perchlorate salts) dissolve in acetonitrile as 2:1 electrolytes, and display electronic spectra typical for high spin distorted octahedral chromophores. The pentadentate macrocycle is probably folded to span five coordination sites with the sixth site occupied by a solvent molecule. The energy of the lowest energy absorption band decreases in the series $Ni([15]aneN_5) > Ni([16]aneN_5) > Ni([17]aneN_5)$ indicating a progressive

TABLE IV. Acid Dissociation Kinetics of Copper(II) Complexes of [15]aneN_5, [16]aneN_5 and [17]aneN_5 at 25 °C.

Ring Size	k_H (M^{-2} s^{-1})
15	0.049
16	4.85[a]
17	1.18×10^3

[a] R. W. Hay and R. Bembi, unpublished results.

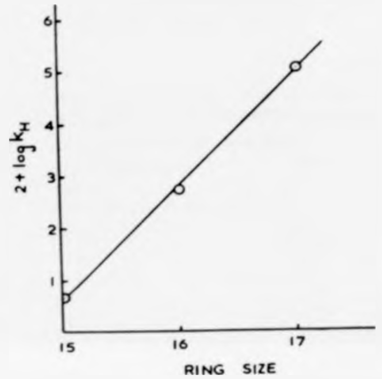


Fig. 2. Dissociation rates of copper(II) complexes of penta-aza macrocycles as a function of ring size.

TABLE V. Cyclic Voltammetry on $[Ni([15]aneN_5)](ClO_4)_2$ at 25 °C.[a]

ν (mV/s)	Ip(c) (μA)	Ip(a) (μA)	Ip(c)/Ip(a)	ΔEp (mV)	½Ep (V)
50	51	49	1.03	65	+1.03
100	67	59	1.13	80	+1.03
200	93.5	86.5	1.08	80	+1.03
500	135	128.5	1.05	90	+1.03

[a] 1×10^{-3} *M* $[Ni([15]aneN_5)](ClO_4)_2$ in acetonitrile with 0.1 *M* $Bu_4\dot{N}\ ClO_4^-$ as the supporting electrolyte. Cyclic voltammetry on Pt with SCE reference.

TABLE VI. Cyclic Voltammetry on $[Ni([17]aneN_5)]$ $ClO_4)_2$ at 25 °C.[a]

ν (mV/s)	Ip(c) μA	Ip(a) μA	Ip(c)/Ip(a)	ΔEp (mV)	½Ep (V)
50	36	40	0.90	70	+1.10
100	50	54	0.92	70	+1.10
200	87.5	80	1.09	70	+1.10
500	117.5	125	0.94	80	+1.10

[a] 1×10^{-3} *M* $[Ni(17]aneN_5)](ClO_4)_2$ in acetonitrile with 0.1 *M* $Bu_4\dot{N}ClO_4^-$ as the supporting electrolyte. Cyclic voltammetry on Pt with SCE reference.

TABLE VII. Summary of Electrochemical Data for the Ni(II)/Ni(III) Couples.

Complex	$E_{1/2}$[a] (V)	$E_{1/2}$(lit)[b] (V)
$[Ni([15]aneN_5)]^{2+}$	+1.03(+0.73)	+0.737
$[Ni([16]aneN_5)]^{2+}$	+1.04(+0.74)[c]	+0.772
$[Ni([17]aneN_5)]^{2+}$	+1.10(+0.80)	+0.817

[a] Present data *versus* SCE reference, the values in parenthesis have been converted to the Ag/0.1 *M* $AgNO_3$ reference. [b] Ag/0.1 *M* $AgNO_3$ reference, from ref. 2. [c] R. W. Hay and F. McLaren to be published.

TABLE VIII. The Acid Catalysed Dissociation of $NiL(ClO_4)_2H_2O$ at I = 0.1 *M* ($NaClO_4$) at 25 °C.

$10^3[HClO_4]$ (*M*)	10^3k_{obs} (s^{-1})	$k_{obs}/[H^+]$ ($M^{-1}\ s^{-1}$)
2.1	0.48	0.23
6.0	1.39	0.23
9.9	2.38	0.24
20.7	4.98	0.24
40.6	9.42	0.23

TABLE IX. The Temperature Dependence of the Dissociation of $NiL(ClO_4)_2 \cdot H_2O$ at I = 0.1 *M*.

Temp. (°C)	k_{obs}[a] (s^{-1})	k_H ($M^{-1}\ s^{-1}$)
25	1.39	0.23
29.5	1.78	0.297
33	2.39	0.395
39	3.15	0.525

[a] $HClO_4 = 6.0 \times 10^{-3}$ *M*. $\Delta H^{\ddagger} = 44.0 \pm 3.1$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -109 \pm 10$ J K^{-1} mol^{-1} (r = 0.9951).

weakening of the Ni–N bonds as the ring size increases.

The oxidation of $[Ni([15]aneN_5)](ClO_4)_2$ and $[Ni([17]aneN_5)](ClO_4)_2$ to the corresponding nickel(III) complexes was studied by cyclic voltammetry using acetonitrile as solvent. Cyclic voltammetry was carried out on Pt with an SCE reference. The data obtained with $[Ni[15]aneN_5]^{2+}$ are summarised in Table V. The Ni(II)/Ni(III) couple is essentially reversible with Ip(c)/ Ip(a) close to unity and ΔEp = 65 mV at ν = 50 mV s^{-1}. A plot of Ip(c) *versus* $\nu^{1/2}$ is linear passing through the origin indicating diffusion control. The value of $E_{1/2}$ = +1.03 V with reference to an SCE. AC measurements on Pt also gave $E_{1/2}$ = +1.03 V while stirred CV measurements gave $E_{1/2}$ = +1.08 V.

Similar measurements were carried out on $[Ni([17]aneN_5)]^{2+}$ giving the data shown in Table VI. The Ni(II)/Ni(III) redox couple is essentially reversible, thus plots of Ip(c) *versus* $\nu^{1/2}$ are linear passing through the origin indicating diffusion control and the ratio Ip(c)/Ip(a) is close to unity. The value ΔEp (*ca.* 70 mV) is somewhat higher than expected for a fully reversible one electron process (60 mV) presumably indicating sluggish electron transfer. The $E_{1/2}$ values obtained are in good general agreement with the results obtained by Bencini, Fabbrizzi and Poggi [2] which relate to a Ag/AgNO₃ (0.01 *M*) reference in acetonitrile solvent. Correction of $E_{1/2}$ to the Ag/AgNO₃ reference (–0.30 V) [14] gives the data shown in Table VII.

Dissociation of the nickel(II) complex of [17]-aneN₅ occurs quite readily in acidic solutions. In the range (2.1–40.6 × 10^{-3} *M* $HClO_4$, the reaction shows a first order dependence on $[H^+]$, with rate = k_H[complex $[H^+]$, Table VIII, with k_H = 0.23 M^{-1} s^{-1} at 25 °C and I = 0.1 *M* ($NaClO_4$). The tempera-

TABLE X. Mercury(II) Catalysed Aquation of $[CoLCl]^+$ at 25 °C and I = 0.49 *M* ($NaNO_3$).

$10^3[Hg^{2+}]$ (*M*)	10^3k_{obs} (s^{-1})	10^2k_{Hg} ($M^{-1}\ s^{-1}$)
9.0	0.62	6.9
18.0	1.26	7.0
29.0	2.15	7.4
41.0	3.12	7.6
48.3	3.54	7.3
	$k_{Hg} = 7.2 \pm 0.3\ M^{-1}\ s^{-1}$	

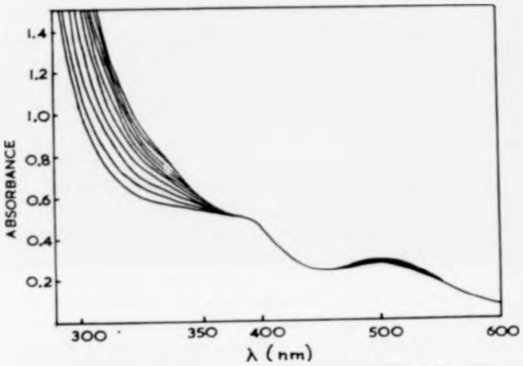


Fig. 3. Uptake of CO_2 by $[Co([17]aneN_5)OH]^{2+}$ in borax buffer at pH 9.66. The time interval between scans is 1 min.

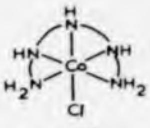
ture dependence of k_H gives $\Delta H^\ddagger = 44.0$ kJ mol^{-1} and $\Delta S_{298}^\ddagger = -109$ JK^{-1} mol^{-1} with a correlation coefficient of 0.9951, Table IX.

The dissociation of $Ni([17]aneN_5)^{2+}$ differs from that of $Ni([15]aneN_5)^{2+}$ as the dissociation of the latter complex displays a second order dependence on the concentration of the hydrogen ion. It appears that $Ni([17]aneN_5)^{2+}$ is fully protonated as $[NiLH]^{3+}$ throughout the acidity range employed, with only the four equatorial nitrogens coordinated.

Cobalt(III) Complexes

Reaction of the ligand pentahydrochloride with $[Co(CO_3)_3]^{3-}$, followed by addition of $NaClO_4$ gives the pink cobalt(III) complex $[CoLCl](ClO_4)_2$. The ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition occurs at 550 nm (ϵ = 132 M^{-1} cm^{-1}) and the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition at 380 nm (ϵ = 174 M^{-1} cm^{-1}), Table I.

The mercury(II) catalysed aquation of the complex was studied at 25 °C and I = 0.49 *M*, Table X. The rate expression is of the form, rate = k_{Hg}[complex]$[Hg^{II}]$ with $k_{Hg} = 7.2\ M^{-1}\ s^{-1}$. Mercury(II) catalysed aquation of the macrocyclic complex is considerably faster than that of the αα-$[Co(tetren)Cl]^{2+}$ (*X*) where $k_{Hg} = 1.42 \times 10^{-2}\ M^{-1}\ s^{-1}$ at 25 °C and I = 0.3 *M* [15].



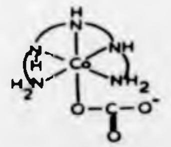
(X)

The aqua-complex $[CoL(OH_2)]^{3+}$ was readily prepared from the chloro-complex by silver(I) catalysed aquation. Potentiometric titration of the aqua-complex gives a pK_a of 6.2 for the aqua ⇌ hydroxo equilibrium at 25 °C and I = 0.1 *M*. The hydroxo-complex reacts rapidly with CO_2 to give the monodentate carbonato complex, Fig. 3. This reaction involves nucleophilic attack by the coordinated hydroxide ion on the CO_2 molecule [16]. The complex $[CoL(CO_3)]ClO_4$ was characterised by the reaction of Li_2CO_3 with the aqua complex. Decarboxylation of the monodentate carbonato complex occurs in acidic solution, and the acid-catalysed decarboxylation was studied kinetically by stopped flow techniques over a range of temperatures, Table XI. Dasgupta and Harris [16] have shown that the acid-catalysed decarboxylation of αβS-$[Co(tetren)CO_3]^+$ (*XI*) involves the equilibria,

$$[Co(tetren)(CO)_3]^+ + H^+ \rightleftharpoons [Co(tetren)(CO_3H)]^{2+},\ 1/K_c$$

$$[Co(tetren)CO_3H]^{2+} \xrightarrow[k]{r.d.} [Co(tetren)OH] + CO_2$$

The corresponding rate expression is $k_{obs} = k[H^+]/([H^+] + K_c)$ where pK_c has the value 6.4. Decarboxylation of $[Co([17]aneN_5)CO_3]^+$ and $[Co([15]aneN_5)CO_3]^+$ was studied using 0.05 *M* HCl so that the only process is the direct decarboxylation step of the protonated species. For the $[17]aneN_5$ derivative k = 0.43 s^{-1} at 25 °C ($\Delta H^\ddagger$ = 48.4 kJ mol^{-1}, $\Delta S_{298}^\ddagger = -90$ JK^{-1} mol^{-1}) and for the $[15]aneN_5$ complex k = 0.33 s^{-1} at 25 °C, Table XI, with $\Delta H^\ddagger$ =



(XI)

TABLE XI. Acid Catalysed Decarboxylation of $[CoLCO_3]^{+}$ in 0.05 *M* HCl.

	Temp. (°C)	10 k_{obs} (s^{-1})
L = [17]aneN_5[a]		
	25	0.43
	28	0.52
	32	0.65
	37	0.96
L = [15]aneN_5[b]		
	25	0.33
	28.5	0.44
	32	0.59
	37	0.85

[a] For L = [17]aneN_5, $\Delta H^{\ddagger} = 48.4 \pm 3.1$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -109 \pm 10$ JK^{-1} mol^{-1} (r = 0.9959). [b] For L = [15]aneN_5, $\Delta H^{\ddagger} = 58.3 \pm 1.0$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -58 \pm 3$ JK^{-1} mol^{-1} (r = 0.9997).

TABLE XIII. Base Hydrolysis of $[CoL(OOCH)]^{2+}$ in Acetate and Citrate Buffers at 25 °C and I = 0.1 *M*.

pH	$10^{10}[OH^-]$ (*M*)	$10^4 k_{obs}$ (s^{-1})	$10^{-4} k_{OH}$ (M^{-1} s^{-1})
4.84	9.02	0.25	2.8
5.31	26.63	0.71	2.7
5.47	38.49	1.16	3.0
5.85	92.34	3.19	3.4
6.15	184.29	6.21	3.3
			$k = 3.0 \times 10^4$ M^{-1} s^{-1}

TABLE XIV. Temperature Dependence of the Base Hydrolysis of $[CoL(OOCH)]^{2+}$ at I = 0.1 *M*.

Temp. (°C)	pH	$10^{10}[OH^-]$ (*M*)	$10^4 k_{obs}$ (s^{-1})	$10^{-4} k_{OH}$ (M^{-1} s^{-1})
25	5.85	92.3	3.19	3.45
29	5.88	144.7	6.75	4.66
33	5.90	203.8	10.14	4.97
36	5.90	253.5	17.47	6.89
$\Delta H^{\ddagger} = 41.1$ kJ mol^{-1}			$\Delta S_{298}^{\ddagger} = -20$ JK^{-1} mol^{-1}	

58.3 kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = -58$ JK^{-1} mol^{-1}. For the open chain tetren complex, k = 0.28 s^{-1} at 25 °C with $\Delta H^{\ddagger} = 65.3$ kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = -36$ JK^{-1} mol^{-1} [16]. The kinetic parameters for the acid-catalysed decarboxylation of monodentate carbonato complexes are summarised in Table XII. There is little variation in the values of the rate constants at 25 °C which fall within the range 0.3–1.1 s^{-1} for a wide range of 'inert' ligands ranging from the pentaammine, through the polyamine tetren to the pentadentate macrocycles. The activation parameters indicate that this result arises due to a close interplay of $\Delta H^{\ddagger}$ and $\Delta S_{298}^{\ddagger}$ which exert a compensatory effect. Reaction of $[CoClL]^{2+}$ with formic acid in the presence of $AgClO_4$ gives the pink formato complex $[CoL(OOCH)]^{2+}$ readily isolated as the perchlorate salt. A similar reaction can be used to prepare other derivatives such as $[CoL(DMF)]^{3+}$ in which the DMF ligand is coordinated *via* the carbonyl oxygen. The ^1H NMR spectrum reveals two methyl signals at 2.74 and 2.98, and a formyl singlet at 7.96δ. The methyl doublet arises due to restricted rotation about the N–CO bond due to delocalisation of the lone pair on nitrogen. The ^1H NMR data is very comparable with that of $[Co(NH_3)_5DMF]^{3+}$ where the $N(CH_3)_2$ doublet occurs at 2.88 and 3.03δ and the formyl singlet at 7.43δ [17]. The infrared spectrum has $\nu C{=}O$ at 1660 cm^{-1} similar to that of $[Co(NH_3)_5DMF]^{3+}$ at 1665 cm^{-1}. The first ligand field band occurs at 514 nm, very similar to that of $[CoL(OH_2)]^{3+}$ (506 nm) so providing additional evidence for the CoN_5O chromophore. The complex

TABLE XII. Kinetic Parameters for the Acid-catalysed Decarboxylation of Monodentate Carbonato Complexes.

Complex	$k_{25 °C}$ (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})
$[Co(NH_3)_5CO_3]^{+}$ [a]	1.10	66.1	22
αβS-$[Co(tetren)CO_3]^{+}$ [b]	0.28	65.3	−36
$[Co([15]aneN_5)CO_3]^{+}$	0.33	58.3	−58
$[Co([17]aneN_5)CO_3]^{+}$	0.43	48.4	−109

[a] Data for $[Co(NH_3)_5CO_3]^{+}$ from E. Chaffee, T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, *95*, 4169 (1973) (See footnote 19). [b] Data for αβS-$[Co(tetren)CO_3]^{+}$ from ref. 17.

TABLE XV. Values of k_{OH} for the Base Hydrolysis of Formato Derivatives of Pentamine cobalt(III) Complexes.

Complex	k_{OH} (25 °C) (M^{-1} s^{-1})	Rel. Rate
$[Co(NH_3)_5OOCH]^{2+}$	5.8×10^{-4} [a]	1
αα-$[Co(tetren)OOCH]^{2+}$	153[b]	2.6×10^5
$[Co([17]aneN_5)OOCH]^{2+}$	3×10^4	5.2×10^7

[a] R. B. Jordan, Ph.D. Thesis, University of Chicago 1964, quoted by D. A. Buckingham, J. MacB. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc., 96*, 1726 (1974). [b] F. McLaren and R. W. Hay, unpublished results. The αα-nomenclature is that of Snow *et al., J. Chem. Soc. Chem. Comm.*, 891 (1969).

[CoL(OOCH)] undergoes rapid base hydrolysis in the pH range 4.8–6.2, with $k_{OH} = 3.0 \times 10^4$ M^{-1} s^{-1} at 25 °C, Table XIII. The temperature dependence of k_{OH}, Table XIV gives $\Delta H^{\ddagger} = 41.1$ kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = -20$ JK^{-1} mol^{-1}. Current values of k_{OH} for the hydrolysis of formato derivatives of pentaminecobalt(III) complexes are summarised in Table XV. The complex $[Co([17]aneN_5)OOCH]^{2+}$ undergoes base hydrolysis some 5.2×10^7 times faster than $[Co(NH_3)_5OOCH]^{2+}$ at 25 °C.

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Kinetics of the Acid Dissociation of the Copper(II) and Nickel(II) Complexes of 5,7-Dioxo-1,4,8,11-tetraazacyclotetradecane

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Received August 24, 1983

The acid dissociation kinetics of open-chain polyamine complexes have been extensively studied,[1-9] and the topic has been reviewed.[10] Currently there is considerable interest in the kinetics and mechanism of the acid dissociation of macrocyclic polyamine complexes.[11-20] For 14-membered tetraaza

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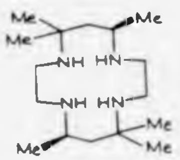
Table I. Acid Dissociation of [CuL] at 25 °C and μ = 0.1 M

pH	$10^5[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^{-7}k_{obsd}/[H^+]^2$, $M^{-2}\ s^{-1}$
4.73	2.41	6.68	1.15
4.81	2.01	4.49	1.11
4.87	1.75	3.68	1.21
4.94	1.49	2.59	1.17
5.00	1.30	1.95	1.16
5.05	1.15	1.43	1.07
5.25	0.72	0.60	1.12

ligands these reactions are quite slow,[12,20] and thus the dissociation of the blue copper(II) complex of *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**1**) occurs at a measurable rate at 25 °C in 1–5 M HNO_3.[19]



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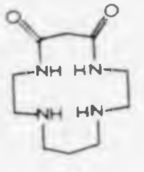

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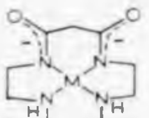
In a previous paper[21] we have described the preparation of the macrocyclic diamide ligand 5,7-dioxo-1,4,8,11,-tetraazacyclotetradecane (**2** = LH_2) and its copper(II) and nickel(II) complexes [ML] (**3**), formed by deprotonation of two amide



3

groups. The dissociation of the copper(II) and nickel(II) complexes in acidic solution is quite rapid, and we now discuss the acid dissociation kinetics in detail.

Experimental Section

The ligand 5,7-dioxo-1,4,8,11-tetraazacyclotetradecane (LH_2) and its copper(II) and nickel(II) complexes were prepared as previously described.[21]

The dissociation kinetics were monitored using a pH stat. The equipment and general experimental procedure employed have been outlined.[22] The concentration of the metal complex used in the kinetic study was 5×10^{-4} M, and the titrating acid ($HClO_4$) was 2.5×10^{-2} M. Two moles of acid was consumed per mole of complex in the reaction. The ionic strength was 0.1 M, maintained by using $NaClO_4$. Values of the hydrogen ion concentration were obtained from the pH by using a molar activity coefficient γ_1 of 0.772 at 25 °C estimated by using the Davies equation.[23] Values of k_{obsd}, the observed first-order rate constant, at constant pH were evaluated from the titration data by using a desk-top computer. At the other temperatures employed the appropriate values of γ are 0.774 (20 °C), 0.770 (30 °C), and 0.768 (35 °C).

Results and Discussion

Dissociation of [CuL] was conveniently monitored by pH stat in the pH range 4.73–5.25 at 25 °C and μ = 0.1 M. Two moles of protons was consumed per mole of complex, corresponding to the reaction stoichiometry

$$ML + 2H^+ \rightarrow M^{2+}(aq) + LH_2$$

Values of k_{obsd} at various pH values for dissociation of the copper(II) complex are summarized in Table I. Plots of k_{obsd} vs. $[H^+]$ are curved (Figure 1), but plots of k_{obsd} vs. $[H^+]^2$ are linear, confirming a second-order dependence on the hydrogen ion concentration. Least-squares analysis of the data gives $k_{obsd}/[H^+]^2 = (1.15 \pm 0.03) \times 10^7\ M^{-2}\ s^{-1}$ at 25 °C and I = 0.1 M. There is no indication of any solvolytic pathway, and dissociation occurs exclusively by an acid dissociation process similar results are obtained with the nickel(II) complex (Table II), where $k_{obsd}/[H^+]^2 = (1.23 \pm 0.03) \times 10^5\ M^{-2}\ s^{-1}$ at 25 °C and μ = 0.1 M. Dissociation of the copper(II) complex is about 100-fold faster than that of the nickel(II) complex. Slower dissociation of the planar d^8 complex is expected.

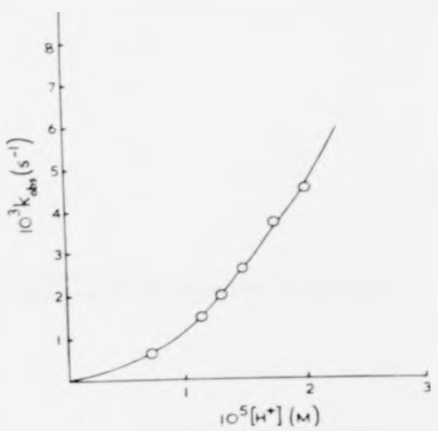


Figure 1. Dissociation of [CuL] over the pH range 4.73–5.25 at μ = 0.1 M and 25 °C.

Table II. Acid Dissociation of [NiL] at 25 °C and μ = 0.1 M ($NaClO_4$)

pH	$10^5[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^{-5}k_{obsd}/[H^+]^2$, $M^{-2}\ s^{-1}$
3.69	26.44	8.52	1.22
3.80	20.53	5.40	1.28
3.90	16.31	3.33	1.25
3.96	14.20	2.43	1.20
4.04	11.81	1.67	1.20
4.09	10.52	1.36	1.23
4.12	9.83	1.18	1.22
4.25	7.28	0.65	1.23
4.40	5.16	0.33	1.24

Table III. Acid Dissociation of [CuL] at 20, 30, and 35 °C and μ = 0.1 M

T, °C	pH	$10^5[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^{-7}k_{obsd}/[H^+]^2$, $M^{-2}\ s^{-1}$
20	4.77	2.19	3.31	0.69
	4.87	1.74	2.19	0.72
	4.92	1.55	1.58	0.66
	5.00	1.29	1.14	0.68
	5.05	1.15	0.98	0.74
30	4.95	1.46	4.16	1.95
	4.97	1.39	3.41	1.76
	5.03	1.21	2.79	1.90
	5.08	1.08	2.27	1.95
	5.18	0.86	1.29	1.74
35	4.96	1.43	6.31	3.08
	5.02	1.24	4.62	3.00
	5.13	0.97	3.02	3.21
	5.17	0.88	2.47	3.19

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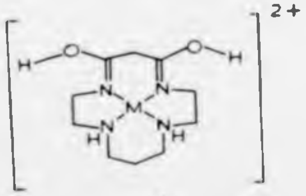
Table IV. Acid Dissociation of [NiL] at 20, 30, and 35 °C and μ = 0.1 M

T, °C	pH	$10^5[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^{5}k_{obsd}/[H^+]^2$, $M^{-2}\ s^{-1}$
20	3.74	23.51	4.34	0.79
	3.86	17.84	2.48	0.78
	3.94	14.84	1.72	0.78
	4.12	9.80	0.75	0.78
	4.20	8.15	0.53	0.79
30	3.93	1.53	4.51	1.93
	4.00	1.30	3.33	1.97
	4.07	1.11	2.47	2.00
	4.10	1.03	2.08	1.96
	4.18	0.86	1.49	2.01
35	4.05	1.16	3.97	2.95
	4.10	1.03	3.24	3.05
	4.15	0.92	2.48	2.93
	4.20	0.82	1.99	2.96

The kinetic data establish that two protons are involved in the transition state of the reaction. Dissociation of the copper(II) complex of the 14-membered macrocyclic amide complex differs quite markedly from that of 14-membered tetraaza macrocycles. The latter normally show a first-order dependence on $[H^+]$ and often display an acid-independent solvolytic pathway.[19] In addition, the amide complex dissociates much more rapidly in acidic solution. These observations suggest that protonation may first occur on the amide oxygen atoms to give the iminol tautomer (**4**), followed by intramolecular proton transfer to the nitrogen donors. Protonation in strong acid of $[Co(NH_3)_4(glyNH)]^{2+}$ [24] and $[Co(glyglyO)_2]^-$ [25] has been shown to occur at the amide oxygen, rather than the amide nitrogen. X-ray studies[25] of the protonated $[Co(glyglyO)_2]^-$ cation indicate that the double-bond character of the carbon–nitrogen bond is increased while that of the carbon–oxygen bond is decreased in accord with the equilibrium



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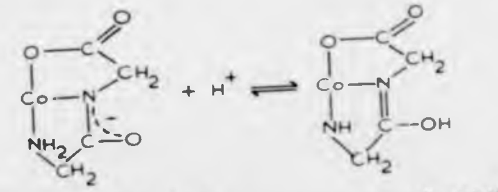


The temperature dependence of the acid-catalyzed dissociation of the copper(II) and nickel(II) complexes was studied at the additional temperatures of 20, 30, and 35 °C, and the data obtained are summarized in Tables III and IV. Rate constants and activation parameters are collected in Table V. For the dissociation of the copper complex $\Delta H^{\ddagger} = 71.7 \pm 1.5$ kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = 131 \pm 5$ J K^{-1} mol^{-1}, while for the nickel complex $\Delta H^{\ddagger} = 64.5 \pm 0.5$ kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = 69 \pm 2$ J K^{-1} mol^{-1}.

Table V. Activation Parameters and Rate Constants for the Acid-Catalyzed Dissociation of [CuL] and [NiL]

compd	T, °C	k_H, $M^{-2}\ s^{-1}$
[CuL][a]	20	$(0.68 \pm 0.03) \times 10^7$
	25	$(1.15 \pm 0.03) \times 10^7$
	30	$(1.92 \pm 0.16) \times 10^7$
	35	$(2.97 \pm 0.13) \times 10^7$
$\Delta H^{\ddagger} = 71.7 \pm 1.5$ kJ mol^{-1}; $\Delta S^{\ddagger}_{298} = 131 \pm 5$ J K^{-1} mol^{-1}		
[NiL][b]	20	$(0.78 \pm 0.01) \times 10^5$
	25	$(1.23 \pm 0.01) \times 10^5$
	30	$(1.91 \pm 0.03) \times 10^5$
	35	$(2.98 \pm 0.13) \times 10^5$
$\Delta H^{\ddagger} = 64.5 \pm 0.5$ kJ mol^{-1}; $\Delta S^{\ddagger}_{298} = 69 \pm 2$ J K^{-1} mol^{-1}		

A possible kinetic scheme for the acid dissociation could involve the steps

$$ML + 2H^+ \overset{K}{\rightleftharpoons} MLH_2^{2+} \qquad (1)$$

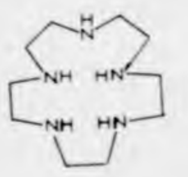
$$MLH_2^{2+} \xrightarrow{k} M^{2+}(aq) + LH_2 \qquad (2)$$

involving a rapid preequilibrium protonation step (eq 1) and a slow rate-determining dissociation (eq 2). It can be readily shown that

$$\text{rate} = \frac{kK[ML][H^+]^2}{1 + K[H^+]^2}$$

$$k_{obsd} = \frac{kK[H^+]^2}{1 + K[H^+]^2}$$

Under the conditions of the present experiments $K[H^+]^2 << 1$ and $k_{obsd} = kK[H^+]^2$ with $k_H = kK = k_{obsd}/[H^+]^2$. The activation parameters thus relate to combined rate and equilibrium constants. One interesting feature of the acid-catalyzed dissociation of macrocyclic complexes is that multiprotonation of the complex is often required for the dissociation of the ligand to occur. Thus, we have previously shown[14] that dissociation of the pentaaza macrocycle [15]-ane-N_5 (**5**) from copper(II) and nickel(II) involves a second-order dependence on $[H^+]$, while dissociation of [18]-ane-N_6 (**6**) involves a third-order dependence on $[H^+]$. Breaking of the second or third metal–nitrogen bond may well be the rate-determining step in some of these reactions.



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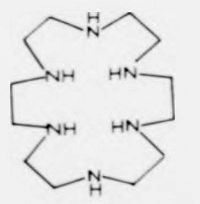

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Registry No. 3 (M = Cu), 72547-88-7; 3 (M = Ni), 74994-10-8.

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