"THE BIS(DIETHYLENETRAMINE)COBALT(III) COMPLEX SYSTEM: STEREOCHEMICAL AND KINETIC STUDIES"

Frank Richard Keene

B.Sc. (Hons.) University of Adelaide

Thesis submitted for the degree of
Doctor of Philosophy

Department of Physical and Inorganic Chemistry
University of Adelaide

February, 1972

The work described in this thesis was carried out by the candidate himself in the Department of Physical and Inorganic Chemistry, University of Adelaide, under the supervision of Dr. G.H. Searle.

During the course of the work it was realised that the same problem was being investigated by Prof. K. Yamasaki at the University of Nagoya. Some data has been exchanged with Prof. Yamasaki but the work described in this thesis is the candidate's own, except where due acknowledgement is made.

The thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and to the best of my knowledge and belief contains no material previously published or written by another person, except when due reference is made in the text.

F.R. Keene

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Dr. G.H. Searle, for his very willingly given help, encouragement and guidance throughout the course of this work, and also to Dr. M.R. Snow for his supervision of the crystal structure work described in Chapter 9 of this thesis.

I wish to thank Prof. D.R. Stranks, Dr. M. Dwyer and Messrs. R.J. Geue and K.R. Butler (all of this Department), Dr. K.R. Turnbull (AMDEL) and Drs. D.A. Buckingham and A.M. Sargeson (A.N.U.) for helpful discussions. My appreciation is also extended to Drs. Buckingham and Sargeson for the use of facilities at A.N.U., and for the measurement of some ORD and 100 MHz PMR spectra.

I am grateful to Profs. K. Yamasaki (University of Nagoya), S.F. Mason (King's College, London), J.I. Legg (Washington State University), and Dr. H.H. Schmidtke (University of Frankfurt) for the exchange of correspondence. Prof. Mason is thanked also for the measurement of the CD spectra.

I acknowledge the financial assistance of a Commonwealth Postgraduate Award. The research was financed solely from the Departmental research budget, and I thank Prof. D.O. Jordan for making the facilities available.

I am indebted to Union Carbide Australia Ltd. for the gift of dien.

Finally, I wish to sincerely thank Mrs. D.L. Hewish for her very efficient typing of this thesis, and my wife Cheryl for her patience and encouragement during this work and also for her help with the diagrams.

SUMMARY

The bis(diethylenetriamine)cobalt(III) complex system, $[Co\ dien_2]^{3+}$, has been separated into its three possible geometric forms (designated s-cis (symmetrical), u-cis (unsymmetrical) and trans), and the latter two isomers have been further separated into their optical forms. Unequivocal assignment of the geometric configurations was made from the different racemisation behaviours of the corresponding optical isomers, and these assignments were confirmed by PMR spectral data. On the basis of these three known geometric structures, IR criteria have been proposed for such assignments in similar complexes.

The separation of the geometric isomers was achieved by fractional crystallisation and chromatographic methods, which involved an extensive study of the applicability of the various available chromatographic techniques to this system.

Variable temperature studies of the synthesis of the complex under equilibrium conditions allowed assessment of the enthalpy and entropy differences between the isomers. Furthermore, by variation of experimental environmental parameters (concentration, ion-association, solvation, temperature, and pH) the energetic contributions associated with the changes in isomer proportions produced by these parameters could be assessed.

Many of the previous studies of isomerisation mechanisms have involved complexes containing bidentate ligands, and the mechanisms proposed have not always been unequivocal. Because the tridentate ligand confers some

restrictions to the ways in which isomerisation of the [Co dien_2]$^{3+}$ complexes may occur, the observed isomerisations have been able to provide evidence for intramolecular "twist" mechanisms being involved in these processes.

The absolute configuration of the active u-cis species has been assigned from optical rotatory studies. The optical activity of the trans isomer cannot be rationalised on the basis of the conventionally considered chirality sources and has consequently been ascribed to a previously unrealised source of chirality. Therefore the absolute configuration of this ion cannot be assigned from the optical data since no appropriate reference structures are available. An absolute X-ray crystal structure analysis to determine the absolute configuration of this ion was unsuccessful however because of disorder within the unit cell.

The racemisation of the active trans isomer occurs through hydrogen exchange at the coordinated secondary amino group which allows configurational inversion about this sec-N atom, accompanied by conformational interchange in the two adjoined chelate rings. The detailed mechanism of inversion about such nitrogen centres is of considerable current interest, and the kinetic studies of the exchange and racemisation processes in this isomer are reported.

A study of the analogous [Co(4-$\text{Medien})_2$]$^{3+}$ complex system should allow comparison with the above work, and extension of some of the ideas. The complex has been prepared and the three geometric isomers separated but studies of the optical activity and isomerisation aspects have not been completed.

CONTENTS

CONTENTS

Page

CONTENTS Page

CONTENTS Page

CHAPTER 6 EQUILIBRIUM ISOMER PROPORTIONS AND THEIR DEPENDENCE ON ENVIRONMENTAL PARAMETERS 91

CONTENTS Page

CONTENTS Page

7.4 (contd.)

CONTENTS

CONTENTS

Page

10.1.2 (contd.)

PUBLICATIONS

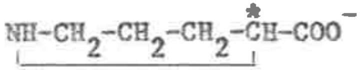
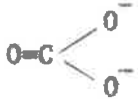
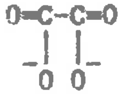
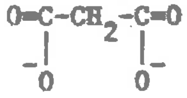
Parts of this work have been published, or accepted for publication, in the following articles:

1. "Geometric and Optical Isomers of the Bis(diethylenetriamine)cobalt(III) Ion", F.R. Keene, G.H. Searle, Y. Yoshikawa, A. Imai, and K. Yamasaki, Chem. Commun., 784 (1970).
2. "The Circular Dichroism and the Chirality of the Unsymmetric-*cis*- and the (+)-*trans*-Bis(diethylenetriamine)cobalt(III) Ion", F.R. Keene, G.H. Searle, and S.F. Mason, Chem. Commun., 839 (1970).
3. "The Isomers of the Bis(diethylenetriamine)cobalt(III) Ion, and a New Source of Optical Activity", F.R. Keene and G.H. Searle, Inorg. Chem., **11**, 148 (1972).
4. "Racemisation and Hydrogen Exchange in the *trans*-Bis(diethylenetriamine)cobalt(III) Ion", G.H. Searle and F.R. Keene, Inorg. Chem., in the press.

Parts of Chapters 3, 5 and 8 of this thesis were presented to the Third Conference of the Coordination and Metal Organic Chemistry Division of the Royal Australian Chemical Institute, Canberra, 1970. The paper was entitled "Isomers of the Bis(diethylenetriamine)cobalt(III) Ion" by F.R. Keene and G.H. Searle, (Proceedings, p. 22).

ABBREVIATIONS USED FOR MULTIDENTATE LIGANDS

Bidentate Ligands.

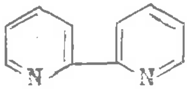
en	=	ethylenediamine	$NH_2-(CH_2)_2-NH_2$
pn	=	propylenediamine	$NH_2-\overset{*}{C}H(CH_3)-CH_2-NH_2$
N-Meen	=	N-methylethylenediamine	$CH_3-NH-(CH_2)_2-NH_2$
N,N'-Me_2en	=	N,N'-dimethylethylenediamine	$CH_3-NH-(CH_2)_2-NH-CH_3$
tn	=	trimethylenediamine	$NH_2-(CH_2)_3-NH_2$
gly	=	glycinato anion	$NH_2-CH_2-COO^-$
sarc	=	sarcosinato anion	$CH_3-NH-CH_2-COO^-$
N-Me-N-Etgly	=	N-methyl-N-ethylglycinato anion	$(CH_3)(C_2H_5)NH-CH_2-COO^-$
N-Me-S-ala	=	N-methyl-S-alaninato anion	$CH_3-NH-\overset{*}{C}H(CH_3)-COO^-$
S-Pro	=	S-Proline	 $\underbrace{NH-CH_2-CH_2-CH_2-\overset{*}{C}H}-COO^-$
CO_3	=	carbonato ion	 $O{=}C\begin{smallmatrix}O^-\\ O^-\end{smallmatrix}$
ox	=	oxalate ion	 $O{=}\underset{O^-}{\underset{\vert}{C}}-\underset{O^-}{\underset{\vert}{C}}{=}O$
mal	=	malonato ion	 $O{=}\underset{O^-}{\underset{\vert}{C}}-CH_2-\underset{O^-}{\underset{\vert}{C}}{=}O$
acac	=	acetylacetonato ion	$CH_3-CO-CH-CO-CH_3^-$

(contd.)

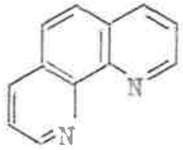
ABBREVIATIONS (contd.)

tfacac = trifluoroacetylacetonato ion $CF_3-CO-CH-CO-CH_3^-$

bipy = bipyridyl



phen = 1,10-phenanthroline



Tridentate Ligands.

dien = diethylenetriamine $NH_2-(CH_2)_2-NH-(CH_2)_2-NH_2$

4-Medien = 4-methyldiethylenetriamine $NH_2-(CH_2)_2-N(CH_3)-(CH_2)_2-NH_2$

4-Etdien = 4-ethyldiethylenetriamine $NH_2-(CH_2)_2-N(C_2H_5)-(CH_2)_2-NH_2$

tmdien = 1,4,7-trimethyldiethylenetriamine $CH_3-NH-(CH_2)_2-N(CH_3)-(CH_2)_2-NH-CH_3$

Et$_4$dien = 1,1,7,7-tetramethyldiethylenetriamine $(CH_3)_2N-(CH_2)_2-NH-(CH_2)_2-N(CH_3)_2$

RS-dipn = RS-dipropylenetriamine $NH_2-\overset{*}{C}H(CH_3)-CH_2-NH-CH_2-\overset{*}{C}H(CH_3)-NH_2$

2,3-tri = N-(2-aminoethyl)-1,3-propanediamine $NH_2-(CH_2)_2-NH-(CH_2)_3-NH_2$

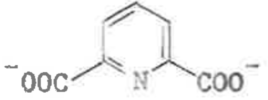
ditn = ditrimethylenediamine $NH_2-(CH_2)_3-NH-(CH_2)_3-NH_2$

IDA = iminodiacetate ion $NH(CH_2COO)_2^{2-}$

MIDA = N-methyliminodiacetate ion $N(CH_3)(CH_2COO)_2^{2-}$

S-Asp = S-asparto anion $NH_2-\overset{*}{C}H(COO)(CH_2COO)^{2-}$

PDC = pyridine-2,6-dicarboxylate ion



(contd.)

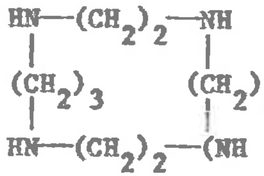
Tetradentate Ligands.

trien = triethylenetetramine $NH_2-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH_2$

4,7-diMetrien = 4,7-dimethyltriethylenetetramine $NH_2-(CH_2)_2-N(CH_3)-(CH_2)_2-N(CH_3)-(CH_2)_2-NH_2$

2,3,2-tet = 1,4,8,11-tetraazaundecane $NH_2-(CH_2)_2-NH-(CH_2)_3-NH-(CH_2)_2-NH_2$

cyclam = 1,4,8,11-tetraazacyclotetradecane



EDDA = N,N'-ethylenediaminediacetate ion $(CH_2COO)NH-(CH_2)_2-NH(CH_2COO)^{2-}$

eee = 1,8-diamino-3,6-dithiaoctane $NH_2-(CH_2)_2-S-(CH_2)_2-S-(CH_2)_2-NH_2$

Pentadentate Ligands.

tetraen = tetraethylenepentamine $[NH_2-(CH_2)_2-NH-(CH_2)_2]_2NH$

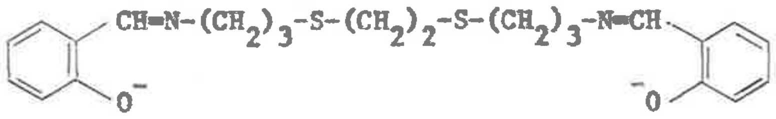
trenen = 4-(aminoethyl)-1,4,7,10-tetraazadecane $NH_2-(CH_2)_2-NH-(CH_2)_2-N(CH_2CH_2NH_2)_2$

(contd.)

ABBREVIATIONS (contd.)

Sexadentate Ligands.

lin-penten	=	linear pentaethylenehexamine	$[NH_2-(CH_2)_2-NH-(CH_2)_2-NH-CH_2]_2$
penten	=	N,N,N'N'-tetrakis(2'-aminoethyl)-1,2-diaminoethane	$(NH_2-CH_2-CH_2)_2N-(CH_2)_2-N(CH_2CH_2-NH_2)_2$
Me-penten	=	N,N,N',N'-tetrakis(2'-aminoethyl)-1,2-diaminopropane	$(NH_2-CH_2-CH_2)_2N-\overset{*}{C}H(CH_3)-CH_2-N(CH_2CH_2-NH_2)_2$
EDTA	=	ethylenediaminetetracetate ion	$(CH_2COO)_2N-(CH_2)_2-N(CH_2COO)^{4-}$
TET	=	1,10-bis(salicylideneamino)-4,7-dithiodecane	



CHAPTER 1

INTRODUCTION

1.1 PREFACE

The stereochemistry and general properties of cobalt(III) complexes form the major part of the knowledge of these aspects of octahedral complexes generally. Their preparation is in general simple, and a choice of the various methods available may allow different products to be obtained, depending on whether thermodynamic or kinetic factors are more important. Also, because of the inertness of the resultant complexes, geometric and optical isomers can be isolated, and investigations of mechanisms of reactions are relatively straightforward as ligand exchange is conveniently slow. The range of ligands employed is increasing continually, and the knowledge of the stereochemistry and properties of coordination compounds increases concomitantly.

A series of related ligands that has received particular attention is the linear polyethyleneamines. The complexes of Co(III) with ethylenediamine (en) have been studied extensively for many years. The stereochemistry of many Co(III) complexes of triethylenetetramine (trien) have been elucidated over more recent years,[1,2] and systems involving the linear tetraethylenepentamine (tetraen)[3] and linear pentaethylenehexamine (penten)[4] are at present being studied. However the complexes of the linear triamine diethylenetriamine (dien) have not been considered in any detail, and the present work is a detailed study of a number of aspects of the system bis(diethylenetriamine)cobalt(III), $[\text{Co dien}_2]^{3+}$.

1.2 NOTES OF NOMENCLATURE

The abbreviations used for ligands (although sometimes indicated) are not generally explained in the text of the thesis. A full list of all multidentate ligands mentioned throughout the work is given after the Index.

The symbols (+) and (-) refer to the sign of optical rotation measured at the Na_D line (589.3 nm), unless another wavelength is specified as a subscript.

R and S denote the absolute configuration about a tetrahedrally bonded carbon or nitrogen atom in accordance with recent recommendations.[5] The four atoms bonded to the asymmetric central atom are denoted A_1, A_2, A_3, and A_4 in the order of increasing atomic number. (If two atoms attached to the central atom are the same, their respective states of substitution are considered, in accordance with a set of sequence rules[5] to arrive at a priority order A_1-A_4.) Viewing the central atom from the side opposite the lightest atom A_1, the absolute configuration is designated R or S according to whether the decreasing atomic number sequence A_4-A_3-A_2 is clockwise, or anticlockwise, respectively.

The designations of five-membered chelate ring conformation and absolute configuration in octahedral systems are used according to the general proposals of the Commission on the Nomenclature of Inorganic Chemistry of IUPAC,[6] which are based on the principle that any two non-orthogonal skew lines constitute a helical system. Two skew lines AA and BB, viewed along their common normal, are designated Δ (for configuration) or δ (for conformation) for a right-handed helix, and

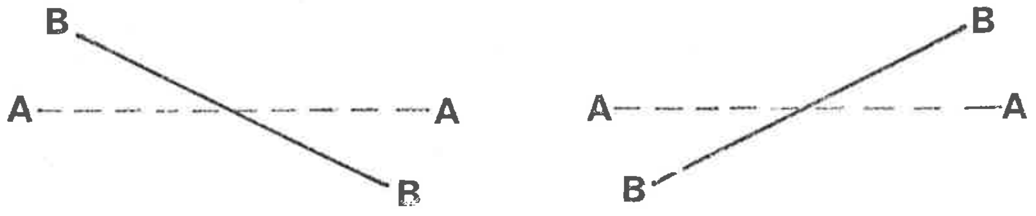
Λ or λ for a left-handed helix (Figure 1).

When applied to configuration, a chelate ring of a six-coordinated complex is represented by the octahedron edge determined by its donor atoms. Any two such edges, which are neither adjoining or opposite edges, will form a skew pair which can be associated with either (a) or (b) of Figure 1. Such a designation is independent of the molecular symmetry or pseudo-symmetry. With complexes of multidentate ligands, the "interactions" between all the chelate rings whose corresponding edges form skew pairs are considered, and either the dominant helicity Δ or Λ designates the absolute configuration, or preferably the helicities of all the skew line pairs should be stated,[6,7] in which case the order of citation is immaterial. For a case where all skew line pair helicities are identical, for example in tris(bidentate) complexes where the three helicities are ΔΔΔ or ΛΛΛ, the configuration is denoted Δ or Λ.

The conformations of five-membered chelate rings are designated δ or λ according to the rules given above, and shown for a Co-en ring in Figure 1.

In the discussions of molecular symmetry, the Schoenflies notation has been used, except in Chapter 9 where the Hermann-Mauguin terms have been used in the context of crystallography.

The designation of geometric isomers for various systems discussed in the thesis has been described at the particular place in the text. However, the empirical notation for the [Co trienX_2]$^{n+}$ system is given

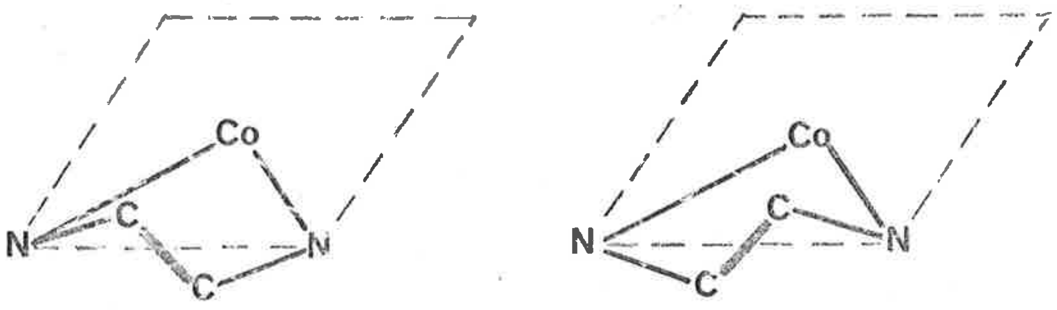


Δ or δ

right-handed helix

Λ or λ

left-handed helix



δ conformation

(a)

λ conformation

(b)

Figure 1. - Designation of absolute configuration and conformation using helicities of skew line pairs.[6]

here; the three possible topologies of the trien ligand have been designated as α, β, and trans, as shown in Figure 2.

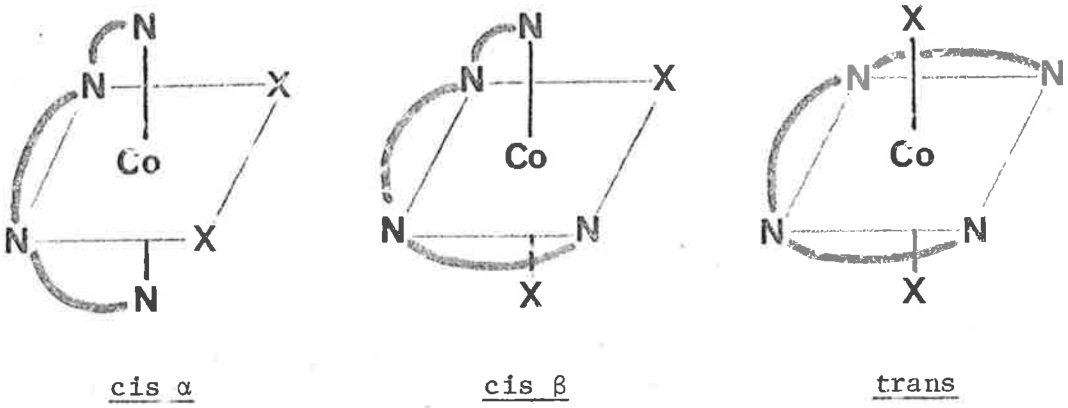
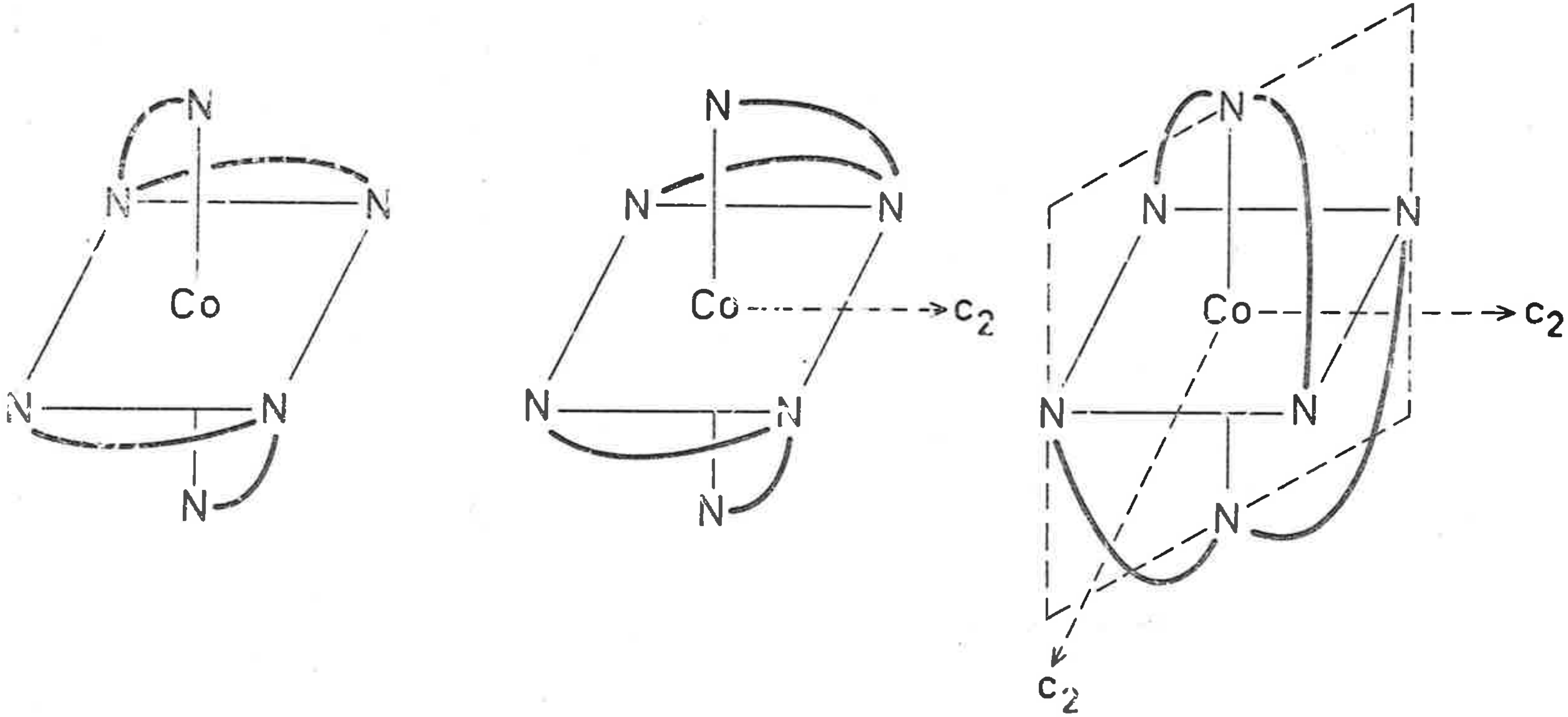


Figure 2. - Topological isomers of [Co trienX_2]$^{n+}$.

A further distinction β_1 and β_2 is used for the two possible geometric forms of β[Co trienXY]$^{n+}$.

1.3 ISOMERIC POSSIBILITIES FOR THE [Co dien$_2$]$^{3+}$ SYSTEM

The linear tridentate diethylenetriamine is a facultative ligand. It can be disposed about an octahedral metal centre in either of two ways, which are described as meridional and facial, or as trans and cis respectively, referring to the relative positions of the primary amino groups of the coordinated ligand. When two of these ligands are coordinated to the same metal, as in [Co dien$_2$]$^{3+}$, there are three topological possibilities. One of these (the trans form) arises from meridional coordination of dien, and the other two forms (s-cis and u-cis) from facial coordination. The three forms are shown in Figure 3.



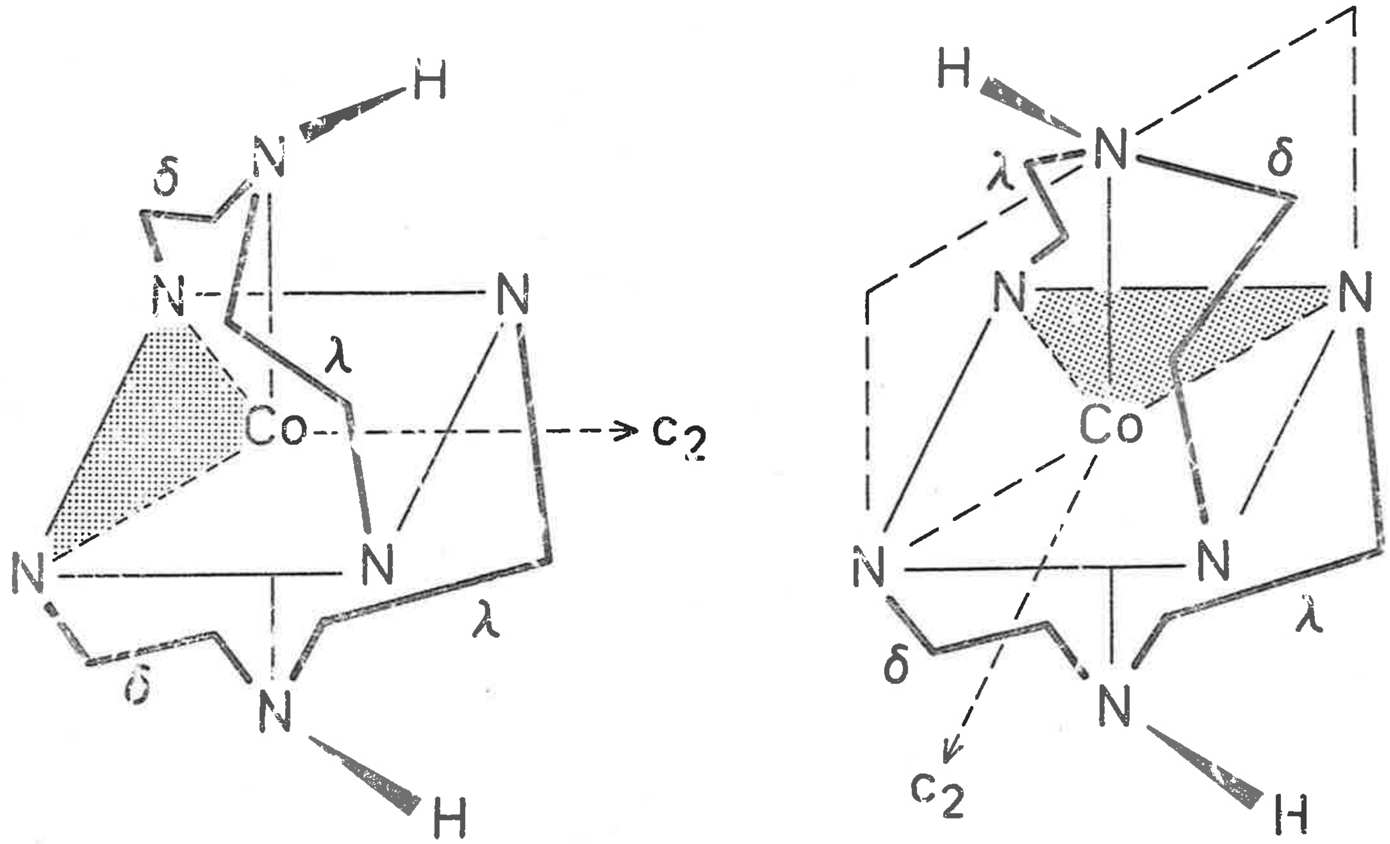
s-cis | u-cis | trans

s-fac | u-fac | mer

Figure 3. - Topological isomers of [Co $dien_2]^{3+}$.

The s-cis (symmetrical-cis) isomer has a centre and plane of symmetry, and is therefore not dissymmetric (point group C_{2h}). The u-cis (unsymmetrical-cis) form however has only a two-fold rotation axis and is therefore dissymmetric (point group C_2) and should be capable of optical activity. For the trans isomer, Figure 3 indicates that if the atoms of each chelate ring are taken to be coplanar, the structure has two planes of symmetry, two C_2 axes, and also an S_4 axis mutually perpendicular to the two C_2 axes shown in the figure. Consequently the complex will not be dissymmetric (point group S_2). However the chelate rings will be puckered rather than planar, and when the ring conformations are considered the planes of symmetry (Figure 3) disappear and the S_4 axis is destroyed. Only one C_2 axis remains and relates the two ligands of the molecule. The point group symmetry is thus reduced from S_2 to C_2 by the ring conformations, and the molecule is thus dissymmetric and will be capable of optical resolution if the rings remain in the fixed conformations. Figure 4 shows the chelate ring conformations which obtain in the two optical forms of trans$[\mathrm{Co\ dien}_2]^{3+}$, and also the mirror plane retained in each individual coordinated ligand.

A meridionally coordinated dien ligand will have such a plane of symmetry, and in isolation the two alternative dispositions of the $>N^2 - H$ bond cannot be distinguished. Only when other ligands present in the molecule create an appropriate point of reference for the two orientations of this $>N^2 - H$ bond can they be differentiated. For example in the two trans isomers (these are conformational isomers) of



trans-δ-NH

M(C_2)-NH

trans-λ-NH

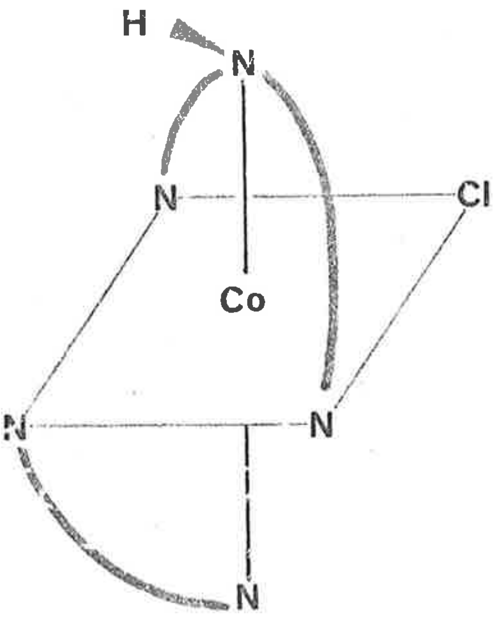
P(C_2)-NH

Figure 4. - Optical isomers of trans[Co dien$_2$]$^{3+}$.

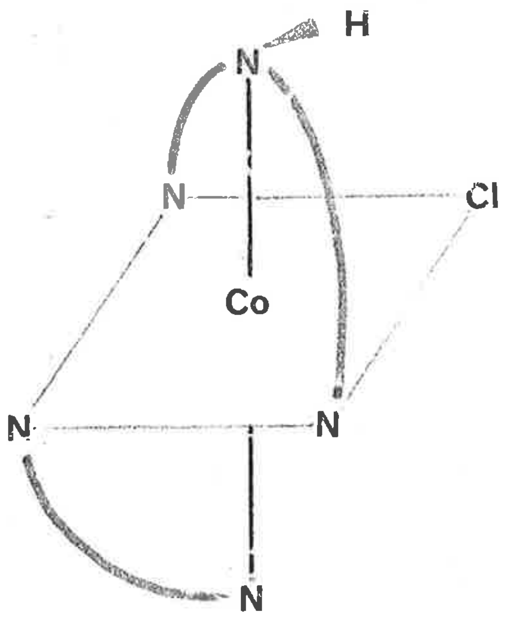
$[Co(dien)(en)Cl]^{2+}$ [8,9] (I and II, Figure 5), the Cl (or en) ligand can be used as a point of reference to distinguish the two dispositions of the $>N^2 - H$ bond. In the present system $[Co\ dien_2]^{3+}$, the orientation of one $>N^2 - H$ bond can be designated relative to the orientation of the other $>N^2 - H$ bond in the molecule, and in this instance the two forms are optical isomers, although each ligand separately contains a mirror plane (Figure 4). In a related system sym$[Co(trenen)X]^{n+}$ [10] (Figure 6), which also lacks configurational dissymmetry, the two possible orientations about the secondary nitrogen atom also correspond to the two enantiomers of the complex ion. This atom is asymmetric on coordination because the mirror plane present in coordinated dien has been destroyed by the presence of the coupled rings at one end of the ligand. In this situation the absolute configurations of the two optical isomers may be designated simply as R or S.

1.4 PREVIOUS STUDIES OF $[Co\ dien_2]^{3+}$, AND OTHER DIEN COMPLEXES

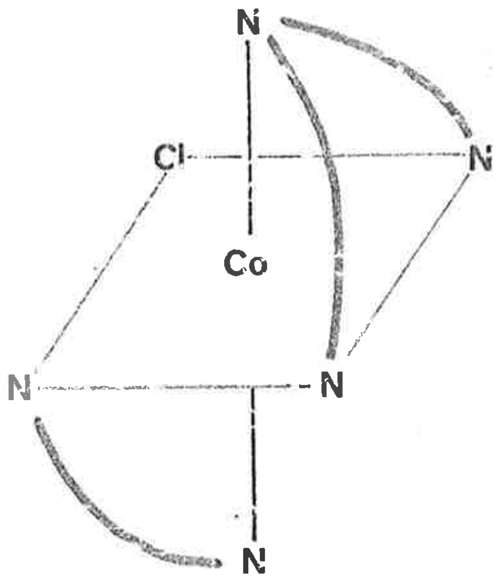
The bis(diethylenetriamine)cobalt(III) iodide complex was first prepared by Mann[11] in 1934 as part of an extensive programme involving the preparation of new multidentate ligands and their complexes, and the investigation of some aspects of the stereochemistry. It was found that dien, 1,2,3-triaminopropane and 2,2'-diaminodiethyl sulphide coordinated as tridentates. Despite the realisation that these ligands should be sufficiently flexible to be disposed facially or peripherally about an octahedral metal ion, no attempt was made to separate isomers and/or to



I

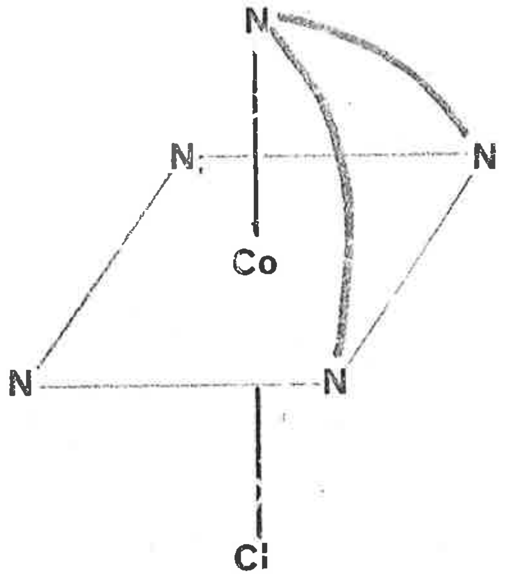


II



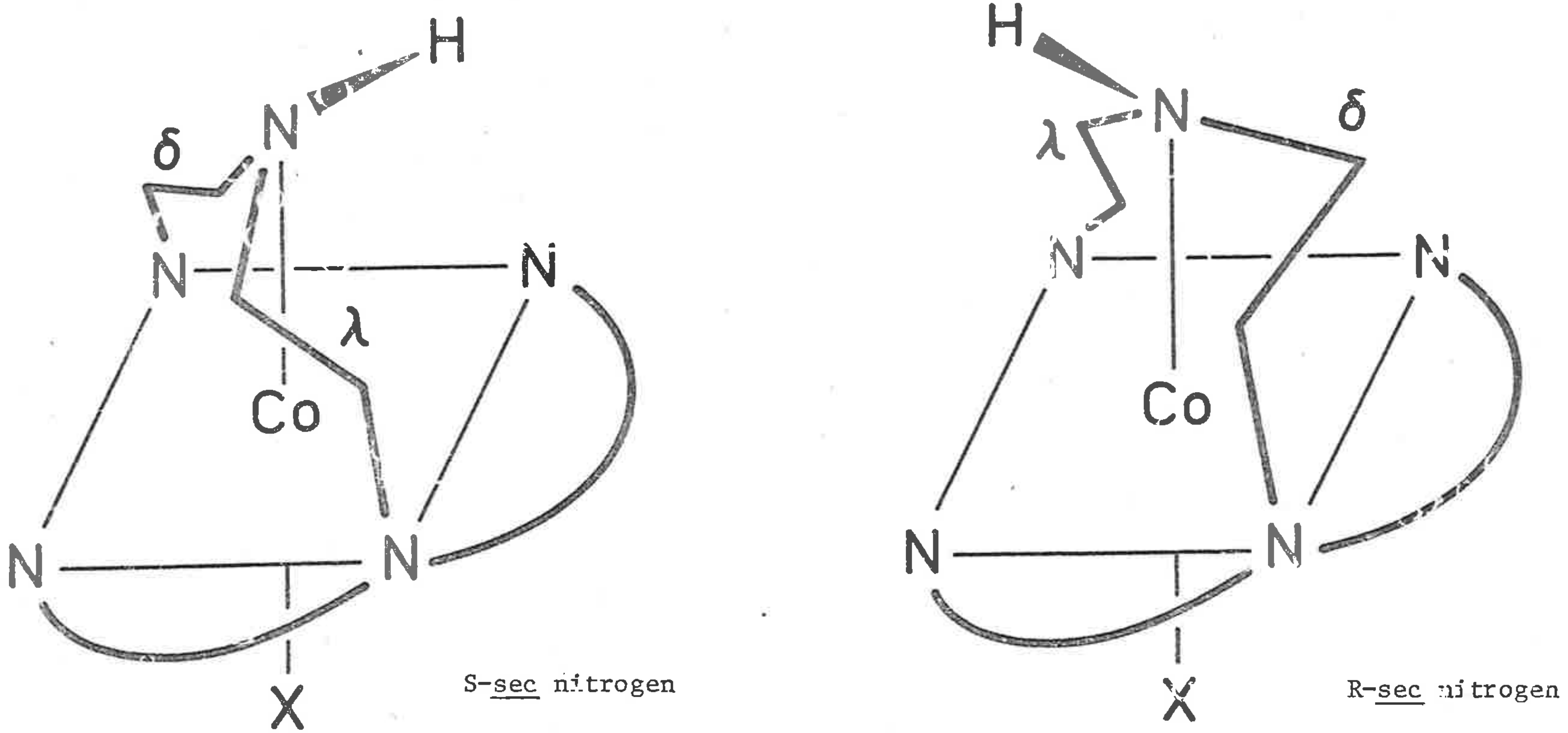
III

(dissymmetric)



IV

Figure 5. - Isomeric forms of $[Co(dien)(en)Cl]^{2+}$.



S-*sec* nitrogen

R-*sec* nitrogen

Figure 6. - Optical isomers of *sym*[Co(trenen)X]$^{2+}$.[10] (This geometric isomer of the trenen complex may alternatively be designated [Co(*sec*-trenen)X]$^{2+}$ where X is *trans* to the *secondary* amine group.)

assign a configuration to the system [Co $dien_2]^{3+}$.

A study of the basicity of several cobalt(III) hexamine-type complexes[12] included the [Co $dien_2]^{3+}$ complex which was prepared (in a similar way to that of Mann) and analysed, and the UV-visible spectral data quoted. The structure of the complex was drawn as the trans isomer without comment.

The nature of the stereochemistry of the [Co $dien_2]^{3+}$ system however remained unknown for many years. The problem was discussed several times in the literature,[13,14] but these various discussions were conflicting and all at least partly erroneous. The correct theoretical considerations were first given in 1967 by Sargeson and Searle[1] in their discussions of the stereochemistry of the cobalt(III) complexes of the linear quadridentate triethylenetetramine.

The only early attempt to assign a configuration to the system [Co $dien_2]^{3+}$ was by Crayton and Mattern[15] in 1960. These authors prepared a number of "inner" complexes of cobalt(III) of the type [Co $dienX_3]^{o}$, X = NO_2^-, SCN^-, Cl^-, and NO_3^-, and compared their electronic spectra with the spectra of the cis and trans isomers of the corresponding ammine species [Co$(NH_3)_3X_3$] to which configurations had previously been assigned.[16] On this basis they decided that dien was invariably coordinated meridionally or trans in these mono(dien) systems. Furthermore, in consideration of the [Co $dien_2]^{3+}$ system these authors stated that the u-cis form would be resolvable while the s-cis and trans forms would not, although at this stage there was little appreciation of the finer aspects of complex stereochemistry involving ring conformations. After unsuccessful attempts to resolve the complex, and considering the invariant existence of meridional dien in the above "inner" complexes of Co(III), they concluded that dien did not coordinate facially, and that the $[\mathrm{Co\ dien_2}]^{3+}$ complex was the trans isomer. On the basis of more recent knowledge their reasoning was invalid however. Firstly, the trans form should be resolvable, and secondly they supposed that only the most stable isomer would be isolated. Thirdly, failure to resolve a compound does not prove that it is not dissymmetric. The present work indicates however that their compound must have been an isomeric mixture with the trans isomer dominant, so that their configurational assignment was fortuitously essentially correct.

The isolation of the analogous Cr(III) complex, $[\mathrm{Cr\ dien_2}]\mathrm{Cl_3}$, has also been reported[17] but no comment was made on the isomeric possibilities.

After Crayton and Mattern's work in 1960, few studies of the geometry of coordinated dien were reported for several years. The complexes $[\mathrm{Au\ dienCl}]\mathrm{Cl_2}$ [18] and $[\mathrm{Pd\ dienCl}]\mathrm{Cl}$ [19] were prepared, both of which would be expected to have dien coordinated meridionally in a square planar complex. An X-ray crystal structure analysis of $[\mathrm{Mo\ dienO_3}]$ [20] showed dien to be facial for this system, whereas recent X-ray structural determinations of $[\mathrm{Co\ dien(NO_2)_3}]$ [21] and $[\mathrm{Cu\ dien_2}]\mathrm{X_2}$ ($\mathrm{X} = \mathrm{NO_3^-}$, [22] $\mathrm{Br^-}$ [23]) have indicated meridional dien in these complexes.

Since 1966 however, the knowledge of the stereochemistry of complexes of dien has increased considerably from the work of several research groups, whose various contributions are considered below. However, a significant advance at this stage was the demonstration by Halpern, Sargeson and Turnbull[24] of the properties of asymmetric coordinated secondary amines, and in particular their optical stability under sufficiently acidic conditions. These authors resolved $[Co(NH_3)_4sarc]^{2+}$ (whose dissymmetry arises solely from the coordinated secondary amino group of the sarc ligand) under acidic conditions, where the rate of N-H exchange with solvent protons is slow and consequently the configuration of the asymmetric nitrogen atom would be retained. The implications of this work, and of subsequent studies of donor atom asymmetry (which are discussed in detail in Chapter 8) were that, due to the fixed orientation of N-H protons of coordinated amines in acidic solution, the two enantiomeric forms of trans$[Co\ dien_2]^{3+}$ (Figure 4) should be resolvable under acidic conditions. Until this time the full stereochemical possibilities for $[Co\ dien_2]^{3+}$ could not be appreciated, and hence the justifiable errors of the early literature.

Schmidtke and Garthoff prepared the cis and trans isomers of $[Rh\ dienCl_3]$,[25] and in a subsequent paper[26] presented infrared spectral data for a range of $[M(III)\ dienX_3]$ complexes, some in both cis and trans forms, (M(III) = Cr, Co, Rh; X = halogeno anion). In this latter paper, the various infrared absorption bands of these complexes were assigned, and empirical rules formulated for the assignment of the configuration of dien in its complexes from infrared spectroscopy. These aspects will be discussed in detail subsequently (section 4.3.2), but of immediate interest is the demonstration of the ability of dien to adopt either of its two configurations for a range of complexes of Cr(III) and Rh(III). On this basis it seems surprising that a cis or facial disposition has not so far been observed in mono(dien) complexes of Co(III), [Co dienX_3] (where X = Cl^-, Br^-, SCN^-, NO_2^-, NO_3^-).

Concurrently, House and co-workers reported the two geometric isomers of [Cr dienCl_3] [27-29] and also the characterisation and interconversion of the [Cr dien$(OH_2)_nCl_{3-n}]^{n+}$ and [Co dien$(OH_2)_nCl_{3-n}]^{n+}$ species.[30] The latter part of this work was of particular interest because it proposed the formation (but in solution only) of the first cis Co-dien complexes, using aquo ligands (n = 1 to 3 in the above). Subsequently, these workers also demonstrated the significance of the configurational stability of the coordinated $>N^2$ - H bond under acidic conditions for coordinated dien by the isolation of the four geometric isomers of $[Co(dien)(en)Cl]^{2+}$ [8,9] (Figure 5), where the two meridional forms (I and II) differ only in the orientation of the $>N^2$ - H bond of the dien ligand.

Legg and Cooke meanwhile studied the stereochemistry of mono(dien) complexes of the type $[Co\ dienL]^+$,[31] where L = IDA, MIDA and PDC. These anion ligands are symmetrical tridentates of the form $O\frown N\frown O$, so that $[Co\ dienL]^+$ has the same geometric possibilities as $[Co\ dien_2]^{3+}$. The isomeric forms for each complex were separated by chromatographic procedures and the observed proportions discussed with reference to statistical and stereospecific effects. In the $[Co(dien)(IDA)]^+$ species, the three geometric forms were obtained, demonstrating the facultative character of the dien ligand. However the anionic ligands were observed to dominate the stereospecificity of these $[Co\ dienL]^+$ complexes in the following way. In $[Co(dien)(IDA)]^+$, the two _cis_ isomers were predominant because of the preference of IDA for the less strained facial coordination, even though dien itself favours a meridional disposition. Similarly for $[Co(dien)(MIDA)]^+$, the _s-cis_ isomer was formed in greater proportion than the _trans_ form, while the _u-cis_ could not be detected presumably because of instability caused by interaction of the methyl group with the dien ligand. The conjugation present in PDC constrained its coordination to meridional so that only the _trans_$[Co(dien)(PDC)]^+$ form was observed.

Yamasaki and co-workers, in studies of the chromatographic resolution of coordination complexes,[32-35] have considered the $[Co\ dien_2]^{3+}$ system, and the X-ray structural analyses of the three geometric isomers are in progress at present.[36] The separation of the system into its geometric isomers was achieved concurrently by the Japanese school and in these laboratories, as revealed in private correspondence. The work described in the thesis represents our own approach although Yamasaki's work is discussed where relevant with acknowledgement.

The $[Co\ dien_2]^{3+}$ system has also been reported in some other studies, where no mention was made of its stereochemical possibilities. Barclay and Barnard[37] demonstrated from magnetic susceptibility and conductance measurements that [Co dien_2]$^{3+}$ was six-coordinate and mononuclear. Basolo, Palmer and Pearson[38] used this complex in studies of the effect of chelation on the rate of proton exchange, and the PMR spectrum of [Co dien_2]$^{3+}$ in trifluoroacetic acid has also been reported by Japanese workers.[39] The results of these studies could not be adequately interpreted and it is now realised that the materials used were isomeric mixtures.

1.5 SIGNIFICANCE AND SCOPE OF THE PRESENT STUDY

The [Co dien_2]$^{3+}$ complex can exist in three geometric forms, and these have been separated and fully characterised in the present work. Because the donor groups are all amines, the complex is not easily substituted by other ligands so that it lends itself ideally to the study of certain aspects of octahedral complex stereochemistry. Also, the system is relatively uncomplicated structurally and the gross molecular features can be deduced without the need of structural determinations by crystallography.

Methods of predicting isomer stabilities and detailed geometries (conformational analyses) have been greatly developed recently for metal complexes, but experimental equilibrium data is to date very scant. This system of three geometric isomers presents a convenient comparison with the structures and stabilities determined from conformational analyses, especially since equilibrium isomer proportions have been experimentally determined under a variety of conditions. These aspects are discussed in Chapter 6.

Spectroscopic methods (electronic, IR and PMR), which are dependent on the molecular symmetry, reflect isomeric geometries and conformational situations existing both in the solid state and in solution. As the use of these techniques (in particular IR) can be somewhat empirical, this simple system provides a means of extending these correlations, as presented in Chapter 4.

Deductions of absolute configuration by spectroscopic means (CD) have been much in vogue recently, but these have been based largely on empirical rules and correlations and some errors have become apparent in the literature. Further exercises of this nature are required to test theories coupled with absolute structural analyses, and in the present system it was found one isomer (trans) could not be accommodated by the existing rules. Thus it has been inferred that another hitherto unrealised but quite general contribution to optical rotatory power may be present in complexes of certain puckered ring systems. The optical rotatory properties and configuration of active u-cis and trans-$[Co\ dien_2]^{3+}$ are given in Chapter 5.

Whereas tervalent nitrogen is configurationally unstable, the coordination of a nitrogen atom to a metal ion renders the inversion sufficiently slow under certain conditions for a kinetic study of the process. Certain aspects of the inversion mechanism are as yet uncertain, but the racemisation process for trans$[Co\ dien_2]^{3+}$ is particularly interesting since inversion about the bridging $>N^2 - H$ group of a meridional dien ligand (which is required for racemisation to occur) involves conformational inversion in each of the two attached chelate rings. The kinetics and mechanism studies of the proton exchange and racemisation process of this isomer are given in Chapter 8.

A variety of mechanisms has been proposed for intermolecular and intramolecular racemisation and isomerisation reactions in metal complexes, and in many instances a choice of mechanism is not unequivocal. The use of flexible tridentate rather than the more commonly studied bidentate complexes imposes restrictions on the mechanisms by which isomerisation can occur. The observed isomerisations for the system $[\mathrm{Co\ dien_2}]^{3+}$ (reported in Chapter 7), which are uncomplicated by the presence of more labile acido ligands, provide evidence for the existence of non-bond-breaking intramolecular "twist" processes.

Some of the problems associated with this system have not been fully investigated, and the features that remain (partly) unanswered are presented in the script. Several of these features result from the limited configurational stability of the coordinated secondary amine. The system $[\mathrm{Co(4\text{-}Medien)_2}]^{3+}$ has therefore been prepared and the isomers characterised (Chapter 10) with a view to such studies.

CHAPTER 2

CHROMATOGRAPHIC SEPARATIONS OF COORDINATION COMPOUNDS, WITH PARTICULAR REFERENCE TO THE SEPARATION OF THE $[Co\ dien_2]^{3+}$ SYSTEM

The preparation of the complex $[Co\ dien_2]^{3+}$, and the identification of the three geometric isomers is anticipated at this stage (from the following Chapter 3) since it is desirable to consider the chromatographic methods in a single chapter.

2.1 CHROMATOGRAPHIC PRINCIPLES AND METHODS

Chromatographic Mechanisms.

Two phases are involved in all chromatographic processes. The solvent or moving phase is either a liquid or a gas, and the adsorbent or stationary phase is either a solid or a liquid supported on a solid. The various forms of chromatography differ essentially in the nature of these two phases. All chromatography methods involve application of the mixture to be separated to a particular point of the stationary phase, and the separation of the constituents, because of their differing physical properties, on the passage of the moving phase through or past the stationary phase.

There are four basic mechanisms that can be involved in the variety of chromatographic methods: adsorption, partitioning, ion-exchange, and exclusion. Few chromatographic separations appear to depend on a single mechanism, and usually a combination of mechanisms operates simultaneously. The combination may be deliberately chosen for the situation or may be inherent in the nature of the method and materials selected for the separation. For an appreciation of the various methods used in this work the four mechanisms will be considered briefly in general terms.

Adsorption applies when the constituents of the mixture to be separated show different affinities for the adsorbent, or differing solubilities in the solvent. Thus the adsorbent and/or the solvent themselves may each play an active role in this mechanism. In the partitioning process however, the adsorbent itself is not involved in the separation but merely supports a liquid which constitutes the stationary phase. Substances may then be separated by the differences in partition coefficients of each constituent between the two liquid phases (stationary and moving). The ion-exchange mechanism allows separation of the constituents of a mixture according to differences in their polarities (or in the extreme, differences in their ionic charges). The fourth major principle is that of exclusion or molecular sieving effect, in which the particles of the adsorbent (as a gel in this chromatographic type) are permeable to molecules below a particular size. The smaller molecules penetrate the gel particles to a varying extent depending on size and shape, while the larger particles pass unhindered around the gel particles in the liquid phase. Elution is therefore in the order of decreasing molecular size.

Other mechanisms are of minor importance here, as they are concerned in more specialised techniques. Such principles include differences in vapour pressure (in gas chromatography), differences in the stabilities of complexes formed with a complexing agent (ligand-exchange chromatography), and differences in the mobilities of ions subjected to a potential gradient (electrochromatography, including electrophoresis).

Chromatographic Methods.

The types of chromatography used at various stages of this work were paper chromatography, thin-layer chromatography (TLC), and chromatography on the ion-exchange materials resins, celluloses, and dextrans. In all chromatographic procedures, the mobility of a compound is denoted by the R_F factor which is defined as the ratio

$$R_F \equiv \frac{\text{distance travelled by compound}}{\text{distance travelled by solvent front}} .$$

(a) Paper chromatography involves almost entirely the partitioning mechanism. The cellulose of the paper will absorb and strongly bind the most polar constituent (which is usually water) of the solvent mixture, to form a cellulose-solvent complex which constitutes the stationary phase. The solvents used in partition chromatography are (almost) invariably mixtures of liquids, and very often contain acids also.

As well as the dominant partition mechanism, the paper chromatography also operates by some ion-exchanging,[40] as cellulose has exchangeable hydrogen ions. When the cellulose is in contact with water, protons can be dissociated from the hydroxyl groups of the cellulose (or from the cellulose-water complex) leaving the paper with a negative charge and increasing the acidity of the solvent. Higher charged cations will thus be more tightly held to negatively charged groups on the cellulose. The use of acid in the solvent lowers the power of the cellulose-water complex to absorb cations and therefore increases their mobilities. These experiments of Yoneda[40] used an aqueous and basic solvent (1M ethylamine solution) chosen to promote ion-exchange and exclude partitioning effects. However with the mixtures of solvents as usually used in paper chromatography partitioning would be expected to be the dominant process. For example, in the separation of the _cis_ and _trans_-$[Co(en)_2(NO_2)_2]^+$ ions, paper chromatography[41,42] (_cis_ elutes first) and ion-exchange chromatography[43] (_trans_ elutes first) give a different order of elution. As the mobility of the ions has generally been observed to be greatest with the lowest charged ions in paper chromatography, it would appear that some ion-exchange effect is always present since such a mobility-charge dependence would not be anticipated for partitioning, which is considered to be the dominant process.

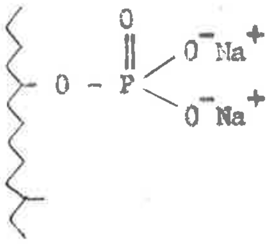
(b) _TLC_. The particular advantage of the TLC technique is its versatility and speed. The support consists of a thin film of finely powdered adsorbent applied on a flat glass plate. The adsorbent can be chosen to vary the mechanism as required. Any separation achieved using TLC can be transferred directly to chromatography using a column of the same adsorbent, and the same solvent, whence the separation can be achieved on a preparative scale. TLC can accommodate only small amounts of sample, but it is considerably more rapid and invariably more sensitive, for the same adsorbent-solvent system, than the use of a column.

Of the adsorbents used in this work, kieselguhr probably involves a purely partitioning mechanism, and cellulose a predominantly partitioning process with some ion-exchange processes operative in an analogous way to paper chromatography. Alumina usually (i.e. in the absence of water) involves a purely adsorption mechanism. Silica gel can use either predominantly partitioning or predominantly adsorption, both concurrent with ion-exchange, depending on the solvent system and the extent of activation or dehydration of the layers before use. The presence of water, which becomes strongly bound to alumina or silica gel adsorbents modifies the nature of the surface sites, and will promote partitioning as a mechanism. Activation, or drying of the layers of these adsorbents will then promote an adsorption process.

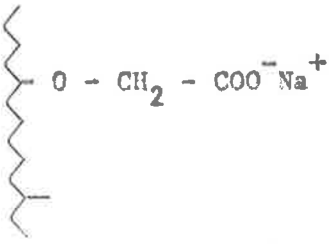
The function of silica gel as a weak cation exchanger has been rationalised[44,45] on the basis of the surface sites consisting of silanol groups which are weakly acidic and to which the cations will be weakly bound. Burwell et al.[44] have suggested that the nature of these surface sites is $\geqslant Si - O^-$ or $\geqslant Si(OH)_2^-$.

(c) Ion-Exchange Chromatography. The use of ion-exchange materials leads to perhaps the most sensitive of chromatographic methods for coordination compounds. As well as the ion-exchange process itself, partitioning, exclusion and adsorption effects may also occur to varying degrees by the particular resin particles. However the effects of the partitioning and ion-exchange processes may be opposing.

In this work, three types of ion-exchange media were used in the column form. Firstly, the strongly acid cation exchange resins (sulphonated polystyrene) in very small mesh size should lead to a dominantly ion-exchange mechanism with some exclusion and adsorption with aqueous solvents. The second type of medium was the cellulose ion-exchangers. In these derivatives of cellulose, phosphorylated (P)- or carboxymethyl (CM)- cellulose, the cation exchange properties are accentuated over the parent compound.

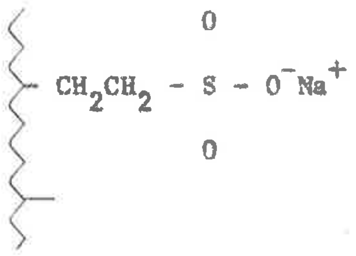


P-cellulose



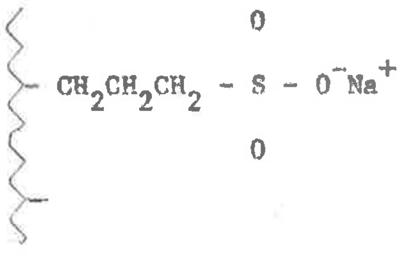
CM-cellulose

Because these adsorbents are celluloses, partitioning processes can also contribute. The third medium is similar to the ion-exchange celluloses as it is based on the polysaccharide dextran, but combines the advantage of resin-based exchangers in its higher capacity. The two dextran-based cation exchangers used in this work were the strongly acidic sulphoethyl (SE) and sulphopropyl (SP) derivatives.



$-CH_2CH_2-\overset{O}{\underset{O}{S}}-O^-Na^+$

SE-dextran



$-CH_2CH_2CH_2-\overset{O}{\underset{O}{S}}-O^-Na^+$

SP-dextran

Used with aqueous solvents, these substances would be expected to be predominantly ion-exchangers, but also to exhibit some exclusion and adsorption effects. The two types have very similar properties, but recently (from 1970) the SP- variety has replaced the earlier SE- form.

Separation of Optical Isomers by Chromatography.

The separation of geometric isomers by chromatographic means can be achieved because of differences in particular physical properties of the isomers. For a pair of optical isomers these physical properties are identical and the separation of enantiomers by chromatographic techniques relies on the premise that any differences between their properties will be evident only when the environment itself is dissymmetric. The celluloses and dextrans contain optically active centres, so that resolutions on these adsorbents should be possible. The use of an optically active solvent to resolve complexes chromatographically has also been proposed by Bosnich.[46]

2.2 HISTORICAL DEVELOPMENT OF CHROMATOGRAPHIC METHODS

Because of the empirical nature by which a chromatographic system is usually chosen for separation of any particular mixture, the different conditions proposed by authors in their studies of particular systems may not be generally applicable. The following brief survey of the trends in development of chromatographic separative procedures of inert charged coordination compounds is not intended to include a comprehensive listing of individual separations.

The use of chromatographic methods, particularly paper chromatography, for the separation of different metals in quantitative analysis, and the separation of different compounds of the same element, has been established for some time. Their use for the separation of geometric isomers and enantiomers of metal complexes is however a more recent achievement. In 1952, King and Walters[43] first reported the use of an ion-exchange resin to separate cis and trans$[\mathrm{Co\ en_2(NO_2)_2}]^+$. In 1954, Stefanovic and Janjic[41] separated these same isomers, and also the cis and trans forms of $[\mathrm{Co\ en_2Cl_2}]^+$, using paper chromatography. From their initial work and subsequent studies on other cobalt(III) tetramine complexes,[42] they observed that cis complexes were always eluted faster than the corresponding trans forms, whence they proposed this mobility as a criterion for the assignment of geometric configuration of such complexes. However there are exceptions to this proposed rule, and some of these are listed in a review by Druding and Kauffman.[47] Further, the dependence of order of elution on the mechanism involved makes this criterion doubtful.

Paper chromatography (and the mechanistically analogous chromatography on a column of cellulose pulp) received much attention after the initial work of Stefanovic and Janjic, and proved quite a sensitive procedure although somewhat slow. Many examples of its use are given in the literature.[47] As a general observation, the separation of geometric isomers was more difficult for complexes of higher charge than for +1 and -1 charged species.

Possibly the best demonstration of the sensitivity of partition chromatography was in the applications by Dwyer and co-workers,[48-50] where separations of isomers of more subtle differences than in the above *cis* and *trans* diacido complexes have been achieved. In their studies of stereospecificity in the complex system $[\mathrm{Co\ pn_3}]^{3+}$[48] they separated the internal diastereoisomers of $\Lambda[\mathrm{Co(-)pn_3}]^{3+}$, $\Lambda[\mathrm{Co(-)pn_2(+)pn}]^{3+}$ and $\Lambda[\mathrm{Co(-)pn(+)pn_2}]^{3+}/\Lambda[\mathrm{Co(+)pn_3}]^{3+}$ (all with their enantiomeric forms) on paper and on columns of cellulose pulp using n-butanol/water/HCl solvent. Similarly, these workers separated all the possible forms of $[\mathrm{Co\ en_x(-)pn_{3-x}}]^{3+}$ with the same solvent systems on the two media.[49,50] The separation on paper of the ΛRR-*α*, ΛSS-*β*, and ΛSR-*β* isomers of $[\mathrm{Co\ trien(NO_2)_2}]^{+}$ (with their enantiomers, the two *β* isomers being conformational forms) also demonstrates the sensitivity of the partition method.[51]

The spectacular growth of the use generally of TLC around 1960 included the separation of stereoisomers of coordination compounds. Although the subsequent advent of precoated plates has made the method even more attractive, the disadvantage of the small quantities that can be used has led to its decline in popularity in favour of the column techniques based on ion-exchange materials, which are discussed subsequently.

Apart from the various separations using TLC that were part of various individual studies there have been few very general works on the technique. Druding and Hagel[45] studied the separation of isomeric cobalt(III) amine complexes on silica gel using a methanol/dimethyl sulphoxide/perchloric acid solvent, this particular non-aqueous solvent being chosen to avoid solvolysis of the halo species of cations. They found that complex ions of different charge could be clearly separated, implying that the mechanism of separation was based on ion-exchange equilibria. They also found that cis and trans diacidotetraminecobalt(III) complexes could be separated one from another, and that almost invariably the trans ion had the higher mobility. This was rationalised by assuming that the linkage to the silanol group was through the acido group. By virtue of their stereochemistry, the two adjacent acido groups for the cis complexes can form two linkages, while the trans species can only form one linkage and would therefore be more loosely held. However if ion-exchange alone were the mechanism (rather than coupled with adsorption) the same trend in elution order would be anticipated, since the trans form might be expected to be less polar than cis and as a consequence less strongly attached and more mobile.

The use of ion-exchange resins for isomer separation had been limited since the original work in 1932, but their use has become very widespread since about 1965. The exclusion and adsorption effects, added to the ion-exchange process, produced some excellent separations.[47] Also at this time the resolution of a polynuclear Co(III) species was reported on a column of ion-exchange cellulose,[52] and this was in fact the first total resolution by a chromatographic procedure. Taylor and Busch[53] subsequently resolved a large macrocyclic Ni(II) complex on microcrystalline cellulose. These successful total resolutions were achieved with very large molecules whereas reported resolutions of small mononuclear coordination species on ion-exchange celluloses have been only partial. Legg and Douglas[54] (using $NaClO_4$ eluent) reported partial resolutions (degree of resolution of first eluant fraction ca. 60%) for a considerable variety of Co(III) complexes of tri- and tetradentate ligands, on CM-cellulose. Yoshikawa and Yamasaki[32,33,35] also reported the partial resolution (7%) of $[Co\ en_3]^{3+}$ on P-cellulose using an HCl eluent.

In an attempt to improve the degree of optical resolution obtained in the chromatographic resolution of Co(III) complexes on ion-exchange celluloses, Yoshikawa and Yamasaki[34] varied the eluent to include (+)-tartrate ion, either in aqueous or aqueous-butanol solutions. These variations improved the resolutions (80% and 92%, respectively, for $[Co\ en_3]^{3+}$ on P-cellulose), but they were never total.

However, the use of the dextran-based ion-exchanger Sephadex (which has the advantage of a greater capacity than the ion-exchange celluloses) provided total optical resolutions of $[Co\ en_3]^{3+}$ [34] and u-cis$[Co\ dien_2]^{3+}$,[35] with sodium (+)-tartrate solution as eluent. Such resolutions illustrate the very great sensitivity of these materials.

The evolution of chromatographic processes has resulted in a general preference for the use of ion-exchange resins and dextran-based ion-exchangers for separations of coordination complexes. However as no chromatographic method can be considered as universal in its application, and each separation required must be considered individually and empirically, paper and TLC techniques are still employed.

2.3 EXPERIMENTAL PROCEDURES

(1) Paper chromatography was carried out using Whatman 3MM chromatographic paper in glass tanks by the descending method. The papers were equilibrated with the saturated tank vapours for 12 hours before development.

(2) TLC was performed on glass plates coated with one of the following adsorbents: Whatman CC41 Microcrystalline Cellulose, Merck Kieselgel (silica gel) H or HF_{254}, Merck Kieselguhr G or Merck Aluminium Oxide H. (The H notation denotes no added $CaSO_4$ binder, G denotes with binder, and HF_{254} without binder and with a material fluorescent at about $\lambda = 254$ nm added.) The glass plates were cleaned with chromic acid, rinsed with distilled water, dried, and wiped with n-hexane (to remove grease) before use. The dimension of the plates was either 20 cm x 20 cm or 20 cm x 5 cm. The adsorbents were applied to the plates using established methods[56,57] with "Desaga" equipment, dried in the air for

several hours and stored in a desiccator over anhydrous $CaSO_4$. The alumina and silica gel plates were activated at 110°C for 1 hour before use.

The chromatograms were developed in glass tanks using the ascending method. They were dried in air and detection was accomplished either visually, or under ultra-violet light where the complexes absorb strongly due to charge-transfer transitions, and thus appear darker than the background adsorbent.

(3) Chromatography on ion-exchange resins. Resins used for chromatographic purposes were Bio-Rad AG 50W-X2, 200-400 mesh in the H^+ form, or its X-4 equivalent. The resins were packed in columns of appropriate length after soaking in distilled water for several hours. All resins were washed after use with 4M HCl, then with water. Samples were applied as dilute aqueous solutions. Some shrinkage of these resins occurs in the presence of an electrolyte compared with the size in distilled water, and column dimensions quoted in this work are the size of the resin bed in distilled water.

(4) Chromatography on ion-exchange cellulose. The celluloses used were the phosphorylated celluloses Bio-Rad Cellex-P (exchange capacity 0.765 meq gm^{-1} of dry weight) and Whatman P11 Cellulose Phosphate (exchange capacity 7.4 meq gm^{-1}), and the carboxymethyl substituted cellulose Bio-Rad Cellex-CM (exchange capacity 0.75 meq gm^{-1}). When these substances

were to be used with aqueous solvents, the columns were prepared by making a suspension of the cellulose in distilled water, de-aerating this suspension (by vacuum) and pouring the settled suspension into a column of appropriate size. For use with butanol-water solvent mixtures, ethanol was substituted for water in the above procedure, and the column washed with the solvent to be used for sample application. The samples were applied as either dilute aqueous solutions or as solutions in water-saturated butanol.

(5) Chromatography on dextran based cation-exchangers. The media used were SE- and SP-Sephadex C-25 Cation Exchangers (Pharmacia, Sweden), each of capacity 2.3 meq gm^{-1} of dry weight and particle size 40-120 μ (50-100 mesh), as the Na^+ forms. Columns of these adsorbents were prepared by de-aerating a suspension of the materials in distilled water and pouring the resultant suspension into the required columns. In the presence of water, these Sephadex materials swell to 6-8 times their dry volume. Column dimensions given in this work are those of the Sephadex bed itself in distilled water, as some shrinkage occurs in the presence of an electrolyte. Samples were applied as dilute aqueous solutions. After use the columns were regenerated by washing copiously with 2M NaCl, then with water. The Sephadex was stored in the columns in dilute sodium azide solution (0.02%) to prevent microbial growth.

2.4 CHROMATOGRAPHIC APPLICATIONS TO THE [Co $dien_2$]$^{3+}$ SYSTEM: RESULTS AND DISCUSSION

Various chromatographic procedures were examined for their ability to separate the geometric isomers of [Co $dien_2$]$^{3+}$. It was observed that the ion-exchange materials (resins, ion-exchange celluloses and dextrans) allowed a clear separation of the three geometric forms whereas chromatography on paper or thin-layers allowed only partial separations of isomeric mixtures. The best solvent mixtures found for each of the chromatographic media, and the orders of isomer elution are listed in Table 1, where 1 denotes the fastest moving band (highest R_F) and 3 the slowest or least mobile band. The Table also gives the approximate time for development of clearly separated bands in each chromatographic process.

Paper Chromatography.

The solvent mixture secBuOH:H_2O:HCl (70:20:10 by volume) was found to produce the best separation using paper (partition) chromatography. This system separated a mixture of the three isomers of [Co $dien_2$]$^{3+}$ into two bands, the faster moving (R_F = 0.38) containing both the *s-cis* and *trans* forms, and the slower band (R_F = 0.30) containing the *u-cis* form. No solvent mixture could be found that separated the three isomers on this support.

TLC.

TLC chromatography also would only allow separation of the *u-cis*

TABLE 1

Elution Orders for the Isomers of [Co dien$_2$]$^{3+}$ with Different Chromatographic Techniques

Stationary Phase	Solvent (ratios by volume)	Elution Order			Approximate Development Time
		s-cis	u-cis	trans	
Paper	secBuOH:H_2O:HCl (70:20:10)	1	2	1	36 hours
Thin-Layer Chromatography					
Cellulose	as above	1	2	1	3 hours
Kieselguhr	as above	1	2	1	4 hours
Silica Gel	EtOH:H_2O:HCl (90:5:5)	1	2	1	45 mins
	MEK:10M HCl (85:15)	1	2	1	30 mins
Alumina		No separation obtained			
Cation Exchange Resin					
Bio-Rad AG50W-X2	2M NH_4Cl	1	2	3	6 hours
Cation Exchange Cellulose					
Cellex-P (Bio-Rad), or P-cellulose (Serra, Germany)	nBuOH:H_2O:HCl (200:15:15)	2	3	1	12 hours[35]
P11 (Whatman)	0.5M HCl	3	2	1	12 hours
Cation Exchange Dextran					
Sephadex, SE- or SP-	0.3M Na_2(+)-tart	1	2	3	3 hours
SE-Sephadex	0.15M Na_2(+)-tart	Complete resolution of u-cis (long column)[34,35]			-

isomer from a mixture of the s-cis and trans forms. In no instances were the s-cis and trans isomers separated by this chromatographic method. With the solvent secBuOH:H_2O:HCl (70:20:10), layers of cellulose (R_F (s-cis + trans) = 0.34, R_F (u-cis) = 0.26) and kieselguhr (R_F = 0.71, 0.67 respectively) produced the same separation as paper chromatography using the same solvent, the partitioning mechanism predominating in all cases. On layers of silica gel, the best solvent systems (ethanol:H_2O:HCl (90:5:5), R_F values 0.39, 0.28; methyl ethyl ketone: 10M HCl (85:15), R_F values 0.36, 0.22) produced the same results as for the previous adsorbents. No isomer separations could be obtained with any solvents on alumina adsorbent.

The results indicate that the partitioning mechanism is important in the separation of the isomers of $[Co\ dien_2]^{3+}$. Under conditions where adsorption should predominate (alumina adsorbent), no separation could be achieved. Silica gel layers would be expected to promote the adsorption mechanism when a singly constituted solvent, rather than a mixture of solvents, was used. Because of the ion-exchange properties of these layers, the +3 complex was absorbed strongly, and only with an aqueous solvent did the complex move without considerable streaking. However when water is present the partitioning mechanism would be promoted at the expense of adsorption. Thus the identical order of elution for silica gel layers using these solvent mixtures, compared with the cases where partitioning would be the predominant mechanism (kieselguhr and cellulose), indicates a similar mechanism for all instances.

Detection of the complex was difficult on kieselguhr (and alumina) layers due to their absorption of ultra-violet light. Also, some elongation of spots was observed on silica gel layers. Thus the separation on cellulose was considered the most convenient TLC method to be used as a monitoring procedure for separations by fractional recrystallisations (section 3.2).

Ion-Exchange Resins.

All the ion-exchange media allowed the separation of $[\mathrm{Co\ dien_2}]^{3+}$ into the three geometric forms. With a column (80 x 2.0 cm) of Bio-Rad 50W-X2 cation exchange resin the isomers were eluted in the order s-cis, followed by u-cis and then trans using a 2M NH_4Cl eluent. If an ion-exchange mechanism alone were operative in this case, the isomers might be expected to be eluted in order of their increasing polarities, as has been observed for many $[\mathrm{Co\ N_4X_2}]^{n+}$ systems,[47] and for the $[\mathrm{Co(dien)(IDA)}]^{+}$ system[31] which has similar geometric isomeric possibilities to the $[\mathrm{Co\ dien_2}]^{3+}$ system. On perusal of these isomeric forms of $[\mathrm{Co\ dien_2}]^{3+}$ (Figure 3), the s-cis and trans isomers each have the secondary amine groups opposite, while in the u-cis form they are adjacent. Consequently, the u-cis would be expected to be the most polar, and therefore the least mobile isomer in an ion-exchange process. This is not observed however. In this case, the polarities of these isomers may not be that anticipated from these theoretical considerations because of solvation or ion-association. Alternatively some adsorption or exclusion effects occurring concurrently with the ion-exchange mechanism may modify the anticipated elution order.

Ion-Exchange Celluloses.

Of the two ion-exchange cellulose derivatives used, the phosphorylated derivatives were found to be more useful. Using a low capacity P-cellulose (made by Serra, Germany and equivalent to Bio-Rad Cellex-P, capacity 0.76 meq gm^{-1}), Yamasaki and co-workers[35] separated the three isomers using a partitioning solvent ($\underline{n}$BuOH:H_2O:HCl), the elution order being trans, s-cis, then u-cis. This order is consistent with that obtained on ordinary cellulose (paper and TLC), but in addition the s-cis and trans forms have now been separated. The similarity in elution order indicates the ion-exchange properties of P-cellulose may have been diminished to some extent by the use of the acidic solvent, so that partitioning effects have become dominant. The observation[47] that the two mechanisms individually may result in a different order of elution need not apply in this instance. Yamasaki also observed that the last fractions of the slowest moving u-cis isomer were optically active, indicating partial resolution on the P-cellulose medium.[33,35]

The three isomers could also be separated on a column (40 x 3.0 cm) of higher capacity (7.4 meq gm^{-1}) P11 cellulose using 0.5M HCl eluent. Under these conditions, ion-exchange effects would be expected to predominate and yet the elution order (trans, u-cis, then s-cis) is the complete reverse of that obtained on the resins. It appears therefore that the normally considered minor contributions (to the overall chromatographic mechanism) by adsorption and exclusion may considerably influence the observed separation in this instance. Thus any prediction of the order of elution may be dubious unless the mechanism is definitely known, and the present results imply that such a situation, where a unique mechanism is known to occur, may be rare.

Dextran-Based Ion-Exchangers.

The use of Sephadex materials (both SE- and SP- derivatives) allowed the easiest and best separation of the three geometric isomers of $[\text{Co dien}_2]^{3+}$. With 0.3M Na_2(+)-tartrate solution as eluent and a column of dimensions 40 x 0.9 cm, the order of elution was s-cis, then u-cis then trans, which is the same order as obtained with the ion-exchange resins. This medium was also used by Yamasaki and co-workers[34,35] for the optical resolution of u-cis$[\text{Co dien}_2]^{3+}$ on a long column (120 x 1.1 cm) with 0.15M sodium (+)-tartrate solution eluent. They observed that the use of sodium chloride or sodium sulphate solutions led to little or no activity in the first and last eluted fractions, indicating that resolution had not occurred.[34] In a similar way, no separation of the three geometric isomers of $[\text{Co dien}_2]^{3+}$ has been observed in the present work using 0.5M NaCl solution eluent.

It seems likely therefore that the mechanism of separation in these instances is influenced by differential association between the optically active tartrate anion and the enantiomeric forms of u-cis$[\text{Co dien}_2]^{3+}$ on the geometric forms of [Co dien$_2$]$^{3+}$. This chromatographic resolution is the closest approach to date to the use of an optically active solvent as proposed by Bosnich (section 2.1), but there may also be differential interactions between the optical isomers with the active centres of the adsorbent. These two effects, which are adsorption processes, coupled with exclusion and the basic ion-exchange mechanism, lead to the great sensitivity of these chromatographic materials.

CHAPTER 3

PREPARATION OF [Co dien$_2$]$^{3+}$, AND SEPARATION AND IDENTIFICATION OF THE ISOMERS

3.1 PREPARATIVE METHODS FOR Co(III) AMINE COMPLEXES

Introduction.

The extensive use of Co(III) complexes in stereochemical studies is due in part to the ease and versatility of their preparation. This unique situation arises because of the lability of the Co(II) state, the Co(III) complexes once formed are inert to substitution, and the rate of electron transfer between Co(II) and Co(III) species is relatively slow. Thus the methods of preparation can be placed in two broad categories - the stoichiometry required can be assembled in the labile Co(II) state and then oxidised, or the complex can be formed by substitution of the desired ligand into another Co(III) complex.

Oxidative Procedures.

There appears to be a quantitative relationship between the oxidised product and the mixture of Co(II) species expected prior to oxidation.[58] This occurs because although the Co(II) species may be oxidised at different rates, their lability does not imply that only the most easily oxidised species will be formed because the redox potential of the oxidising agent may make it more accessible to one Co(II) complex rather than another. Thus a thermodynamically unstable Co(III) species may be preserved because, once formed, it is inert to substitution and the electron transfer process to the corresponding reduced species is usually slow. In such an instance however the rate of electron transfer between the Co(II) species and the oxidising agent must be relatively fast.

The most common oxidising agents used are oxygen (air), hydrogen peroxide, and lead dioxide. Their reduction will produce hydroxyl ions (from O_2 or H_2O_2) or insoluble (weakly basic) lead oxide which will not interfere with the isolation of the oxidised Co(III) species. Because of the formation of basic by-products, pH control of the reaction is necessary. In the present work, the oxidising agent was oxygen, and the stoichiometry for the aerial oxidation procedure, where L denotes a tridentate ligand, is

$$4Co^{2+} + 8L + 4H^{+} + O_2 \rightarrow 4[Co\ L_2]^{3+} + 2H_2O.$$

In this type of reaction, the rate of oxidation, and the extent to which it occurs, are markedly increased by the presence of catalysts, and in particular charcoal.[58] Besides the acceleration of the oxidation process, the presence of charcoal also allows the establishment of equilibrium between the various possible Co(III) species. Thus such conditions preclude the dominance of thermodynamically unstable species mentioned above. The equilibration properties of charcoal have been demonstrated for several systems.[58,59a] Bailar and Work[60] first illustrated these properties, in a substitution process, by aerating a solution containing $[Co(NH_3)_6]^{3+}$ and NO_2^- in the presence of charcoal. The relative bonding tendencies to Co(III) of NO_2^- and NH_3 would appear similar,[60] but statistical considerations favour the $[Co(NH_3)_3(NO_2)_3]$

species (for 1:1 ratio of the two ligands), which was found almost exclusively (isomers not separated). Douglas[61] also demonstrated the marked catalytic effect of charcoal on the racemisation of $\Lambda[Co\ en_3]^{3+}$ in aqueous solution. The ion is optically stable almost indefinitely in aqueous solution, but on the addition of charcoal complete racemisation occurs within two minutes at 90^o.

Proposed Mechanisms for Equilibration on Charcoal.

The catalytic properties of charcoal, and the proposed mechanisms by which isomer equilibrations occur, are discussed in some detail as the principles are relevant to the study of the equilibrium preparations of $[Co\ dien_2]^{3+}$ under various environmental conditions, as reported in Chapter 6.

Charcoal in effect "labilises" the Co(III) state. The addition of Co(II) ions increases the effectiveness of the catalyst in many reactions of Co(III) complexes.[62] In situations not involving such addition of Co(II) species, the generation of some Co(II) has been demonstrated in Co(III) systems, presumably because the presence of charcoal causes some reduction of the Co(III) complex.[63,64] For example, Co(II) is generated to the extent of ca. 4% of the total cobalt in neutral conditions at room temperature during the racemisation of $\Lambda[Co\ en_3]^{3+}$. Dwyer[58] has proposed that charcoal may function by rendering the spin-free (high spin) state of Co(III), $t_{2g}{}^4e_g{}^2$, more accessible. Rearrangements and ligand dissociation are thereby facilitated as the transition from the spin-paired $t_{2g}^{6}e_{g}^{0}$ to the spin-free $t_{2g}^{4}e_{g}^{2}$ state involves expansion of the complex and bond labilisation. An alternative mechanism[58] for the equilibration arises as another consequence of the formation of the spin-free state. It is probable that electron transfer between Co(II), $t_{2g}^{5}e_{g}^{2}$, is more favourable under the spin-free Co(III) conditions, which itself confers mild reducing properties to the charcoal in allowing the formation of some Co(II). Equilibration can then occur by rapid electron transfer between the equivalent labile Co(II) complexes and the spin-paired Co(III) complex.

ELECTRONIC REARRANGEMENT

$$\begin{tikzcd}[column sep=huge, row sep=huge]
\begin{array}{c}\text{Co(III) } t_{2g}^{6}e_{g}^{0}\\ \text{low-spin state}\\ \text{(inert)}\end{array} \arrow[r, shift left, "\text{charcoal catalysis ?}"] & \begin{array}{c}\text{Co(III) } t_{2g}^{4}e_{g}^{2}\\ \text{high-spin state}\\ \text{(labile)}\end{array} \arrow[l, shift left] \arrow[d, shift right=6, "\begin{array}{l}+e\\ \text{REDUCTION}\\ \text{charcoal}\\ \text{reducing}\\ \text{agent?}\end{array}"'] \arrow[d, shift left=6, "\begin{array}{l}\text{ELECTRON}\\ \text{TRANSFER}\\ \text{charcoal}\\ \text{catalysis?}\end{array}"] \\
 & \begin{array}{c}\text{Co(II) } t_{2g}^{5}e_{g}^{2}\\ \text{(labile)}\end{array} \arrow[u, shift left=4]
\end{tikzcd}$$

It should be stressed however that the role of charcoal itself, or of the impurities adsorbed on its surface, in the equilibration process is still unknown. As yet no decision has been made between these proposed mechanisms, nor have any other satisfactory alternatives been presented. Circumstantial evidence[59a] may favour the second of Dwyer's proposals,[58] the electron transfer catalysis role of charcoal. For example, the charcoal catalysed racemisation of $\Lambda[Co\ en_3]^{3+}$ is inhibited by the presence of acid[64] although ca. 4% of Co(II) is formed, as it is under neutral conditions where racemisation occurs. This effect of acid is probably due to the reduced species being not $[Co\ en_3]^{2+}$ but $[Co(H_2O)_6]^{2+}$, thereby not allowing electron exchange with $[Co\ en_3]^{3+}$. The increased effectiveness of the catalyst in the presence of added Co(II)[62] also suggests an electron transfer process is operative between the Co(III) complex and the labile Co(II) complex. Despite such observations however, the mechanisms by which the catalysed isomerisations occur, and the role of the catalyst, are not unequivocal. Nevertheless, the ability of charcoal to catalyse the attainment of thermodynamic equilibrium in Co(III) systems is well known.

The relevance of these considerations to the present work, despite the uncertainty of the particular role of the catalyst, is that preparations in the presence of charcoal should yield an equilibrium distribution of the isomeric forms of $[Co\ dien_2]^{3+}$ under the environmental conditions used. Without charcoal present, a kinetically, rather than thermodynamically, controlled distribution of products may be obtained. Moreover any individual form, or mixture of the Co(III) species, can be equilibrated to give the equilibrium isomer mixture by equilibration in the presence of charcoal. Dwyer and co-workers used charcoal in this way in their studies of stereospecificity and dismutation (i.e. disproportionation) in the systems $[Co\ pn_3]^{3+}$ [65,48] and $[Co\ en_xpn_{3-x}]^{3+}$.[49,50] A detailed consideration of the factors affecting isomer stabilities, equilibration and isomerisation reactions of $[\text{Co dien}_2]^{3+}$ will be given in Chapters 6 and 7.

Non-Equilibrium Oxidative Procedure.

An essentially kinetically controlled oxidation preparation investigated in this work used dimethylsulphoxide (DMSO) to function both as a solvent and as an oxidant to oxidise the assembled Co(II) complexes to their Co(III) analogues. No charcoal catalyst is used. The method involves mixing solutions in dry DMSO at 40° of anhydrous cobalt chloride and (dien + dien.3HCl), the molar ratios being Co(II):dien:-dien.3HCl = $1:1^{2}/_{3}:^{1}/_{3}$. An exothermic reaction occurs, and after cooling to room temperature the Co(III) product can be precipitated in high yield by adding ethanol.

Substitution Procedures.

The second category of synthetic methods for Co(III) complexes involves substitution of one ligand for another in a Co(III) complex. Ligands commonly replaced in this way are NH_3, Cl^-, Br^-, NO_2^-, CO_3^{2-} and H_2O as these may be easily dispelled as gases or retained in the reaction solution as soluble salts.

The most common method, which has been used since Werner's time for the preparation of Co(III) complexes, is substitution of the desired ligand into the complexes $[Co(NH_3)_5Cl]^{2+}$ or $[Co(NH_3)_5(OH_2)]^{3+}$ in the presence of carbon, which establishes isomeric equilibrium in the product. The ammonia is dispelled from the solution once it has been de-coordinated, as the reaction is usually completed at steam bath temperature.

A second general preparative method by substitution is the reaction of the acid form of the ligand with $Na_3[Co(CO_3)_3].3H_2O$.[66-68] Charcoal may be used as a catalyst, and the reaction can be performed at any temperature. In a recent re-examination of this carbonato compound,[69] it was found that a substantial portion (ca. 20%) of the cobalt was Co(II) suggesting the substance was a sodium cobalt(II) salt of the required anion, as the overall composition was variable but approximated $Na_{2.8}\ Co(CO_3)_{2.8}\ .3H_2O$. The almost quantitative conversions to Co(III) complexes that have been observed[66,67] using this method occur presumably due to oxidation of the Co(II) component by atmospheric oxygen and catalysed by charcoal.

In an analogous way, direct substitution of the required ligand into $[Co(NO_2)_6]^{3-}$ can be carried out in the presence or absence of charcoal, where in both cases some NO_2^- will remain in solution as the complex counter-ion, and some will be dispelled from the solution as gaseous NO_2, particularly under acidic conditions.

The final preparative method used in this work is not a general procedure but involves substitution of dien into $[Co\ dienX_3]^{n+}$ ($X = Cl^-$, NO_2^-, H_2O) to form $[Co\ dien_2]^{3+}$ under non-equilibrium conditions. Both $[Co\ dienCl_3]$ [26] and $[Co\ dien(NO_2)_3]$ [21] have been shown (infrared[26] and X-ray[21]) to have the <u>trans</u> geometric configuration. $[Co\ dien(OH_2)_3]^{3+}$

has been claimed to exist in both cis and trans forms in solution, although neither isomer has so far been isolated.[30] It was thought that this triaquo complex might offer the possibility of preparation of predominantly cis or trans $[\mathrm{Co\ dien_2}]^{3+}$ by reaction of the corresponding $[\mathrm{Co\ dien(OH_2)_3}]^{3+}$ isomer with dien.

Summary.

The importance of the non-equilibrium preparative methods to the preparation of Co(III) complexes is that a kinetically controlled preparation might yield a different product distribution from the case where equilibrium is maintained by the presence of charcoal and the product isomer distribution is thermodynamically controlled. It is feasible for a thermodynamically unstable species of Co(III) to be a major product under non-equilibrium conditions.

3.2 EXPERIMENTAL: PREPARATIONS AND OPTICAL RESOLUTIONS OF $[\mathrm{Co\ dien_2}]^{3+}$ ISOMERS

Reagents.

Dien, from either Fluka (puriss) or Union Carbide Australia Ltd., was used without further purification. The corresponding amine trihydrochloride and trihydrobromide were prepared by slowly mixing cooled aqueous solutions of dien and the required acid (three molar ratio), and precipitating the acid salt (dien.3HX) by the addition of ethanol.

The charcoal used was freshly finely ground "BDH charcoal for gas absorption". Anhydrous $CoBr_2$ was obtained by heating the hygroscopic $CoBr_2.6H_2O$ (BDH) at 130° for 3 hours. The green anhydrous salt was cooled in a desiccator, weighed, and used immediately. $Na_3[Co(NO_2)_6]$ (BDH) was of laboratory reagent grade, and all other reagents were of analytical reagent quality where available.

$[Co(NH_3)_5Br]Br_2$,[70] $[Co(NH_3)_5Cl]Cl_2$,[71] and [Co dien$(NO_2)_3$] and [Co dienCl_3] [72] were obtained using methods given in the literature.

Preparation of [Co dien$_2$]$^{3+}$ by aerial oxidation. - To a solution of $CoCl_2.6H_2O$ (47.6 g, 0.20 mole) in water (250 ml) was added dien (34.5 g, 0.33 mole), dien.3HCl (14.5 g, 0.067 mole) and charcoal (25 g). Air was bubbled through the solution for 36 hours. After filtering, the solution was evaporated to a small volume using a rotary evaporator and the product was then precipitated as completely as possible by the addition of ethanol. The product was filtered off, washed with ethanol and acetone, and air-dried. Yield of [Co dien$_2$]$Cl_3.xH_2O$, 76.0 g (93% calculated for 2-hydrate).

The complex was prepared as the bromide in an analogous manner using $CoBr_2$ anhydrous (44.0 g, 0.20 mole), dien (34.5 g, 0.33 mole) and dien.3HBr (23.0 g, 0.067 mole) in water (500 ml). After aeration and filtration, the solution was evaporated almost to dryness, and the remaining product was precipitated with ethanol. Yield 99.0 g (95% calculated for [Co dien$_2$]$Br_3.H_2O$).

Preparation of $[Co\ dien_2]^{3+}$ from $[Co(NH_3)_5X]X_2$. - A slurry in water was prepared of charcoal (20 g), and either $[Co(NH_3)_5Cl]Cl_2$ (100 g, 0.40 mole) or $[Co(NH_3)_5Br]Br_2$ (154 g, 0.40 mole). Dien (91 g, 0.88 mole) was stirred in, and the mixture was heated on a steam bath for 4 hours. After filtering, the solution was evaporated almost to dryness and the product was precipitated as completely as possible with ethanol. The product was filtered off, washed with ethanol and acetone and air-dried. Yield of $[Co\ dien_2]Cl_3.2H_2O$, 153 g, 94%. Yield of $[Co\ dien_2]Br_3.H_2O$, 200 g, 95%.

Separation of geometric isomers from preparative mixtures. - The above bromide preparations were recrystallised from warm water by allowing the solution to cool and stand until about 10% of the material had separated. This was filtered off and fractionally recrystallised again from warm water (3 times its weight). As each fraction was filtered off it was washed with 70% ethanol, and the filtrate was evaporated in a rotary evaporator to induce crystallisation of the next fraction. The least soluble fractions comprised pure s-cis$[Co\ dien_2]Br_3$ as relatively large well-formed prisms and the point at which the more soluble trans isomer commenced to crystallise could be recognised visually from the very much smaller thin needles of trans$[Co\ dien_2]Br_3.H_2O$. This procedure allows essentially quantitative separation of the s-cis isomer from the mixture.

The trans and u-cis isomers in the remaining solution were separated by fractional precipitation by adding LiI in small amounts. The trans is the less soluble, but the precipitated products appeared (halide analyses) to be mixed bromide-iodides. (The halide analysis figures for the precipitated trans isomer were I = 32.4%, Br = 20.5%, indicating a 1:1 atomic ratio for these two anions. For the u-cis form, I = 43.7%, Br = 5.5%, giving a 5:1 proportion for I:Br.) This separation was monitored by running thin-layer chromatograms on cellulose of the various fractions (developing solvent sec-butanol:water:conc HCl = 70:20:10). The first and last fractions were isomerically pure trans and u-cis respectively, but middle fractions contained both isomers. The mixed halide precipitates of the separated isomers were converted to pure bromides or iodides using an anion exchanger. The trans and u-cis iodides are anhydrous.

Anal. Calcd. for s-cis[$Co(C_4H_{13}N_3)_2]Br_3$: C, 19.0; H, 5.19; N, 16.6; Br, 47.5. Found: C, 19.4; H, 5.40; N, 16.7; Br, 47.7. Calcd. for trans[$Co(C_4H_{13}N_3)_2]Br_3.H_2O$: C, 18.4; H, 5.40; N, 16.1; Br, 45.8. Found: C, 18.0; H, 5.12; N, 16.1; Br, 45.7. Calcd. for u-cis[$Co(C_4H_{13}N_3)_2]Br_3.0.5H_2O$: C, 18.7; H, 5.29; N, 16.3; Br, 46.6. Found: C, 18.6; H, 5.29, N, 16.2; Br, 46.5. Calcd. for trans[$Co(C_4H_{13}N_3)_2]I_3$: C, 14.9; H, 4.06; N, 13.0. Found: C, 14.9; H, 3.91; N, 12.9. Calcd. for u-cis[$Co(C_4H_{13}N_3)_2]I_3$: C, 14.9; H, 4.06; N, 13.0. Found: C, 14.7; H, 4.06; N, 13.0.

Isomeric purity was checked by chromatography on a column of SE-Sephadex C-25 cation exchanger (Na^+ form), column dimensions 50 cm x 0.9 cm. A dilute aqueous solution of a small portion (ca. 0.1 g) of a particular fraction was absorbed on the column and eluted with 0.3M sodium tartrate solution. Two hours were required to ensure a clean separation on the column of the bands of the three isomers (if present), the band order being s-cis (fastest moving), u-cis, and trans (slowest).

Fractionation with other anions, NO_3^-, Br^-, Cl^-, ClO_4^-, and NO_2^- gave less discrimination in solubilities between the u-cis and trans forms.

Preparation of $[Co\ dien_2]^{3+}$ by oxidation in DMSO solvent. - A solution of $CoCl_2.6H_2O$ (2.38 g, 0.010 mole) in DMSO (5 ml) was boiled for 5 mins to remove water. After cooling to 40°, it was added to a solution of dien (1.75 g, 0.013 mole) and dien.3HCl (0.75 g, 0.0067 mole) in a minimum quantity of DMSO (10 ml) at 40°. An exothermic reaction occurred and the mixture was kept at 65° for 5 minutes, and then cooled. A sample (ca. 1 ml) of this solution was diluted to 200 ml with water, and applied to a column (50 x 0.9 cm) of SP-Sephadex C-25 Cation Exchanger and eluted with 0.3M sodium (+)-tartrate solution for isomer analysis.

Reaction $[Co(NO_2)_6]^{3-}$ + 2dien. - An aqueous solution of $Na_3[Co(NO_2)_6]$ at 50° was added to a solution containing a 2.1 molar ratio of dien, also at 50°. An exothermic reaction occurred, and after cooling to room temperature the resultant solution was diluted and analysed chromatographically on a Sephadex column, as above.

Reaction trans[Co dien$(NO_2)_3$] + dien. - A suspension of trans-[Co dien$(NO_2)_3$] in water, and an equimolar quantity of dien was heated for 15 minutes on a steam bath. After cooling the solution was analysed chromatographically on a Sephadex column.

Reaction trans[Co dienCl_3] + dien. - An ethanol suspension of trans[Co dienCl_3] containing an equimolar proportion of dien was refluxed for 1 hour. The [Co $dien_2$]Cl_3 formed was filtered off, dissolved in water and refiltered (to remove unreacted [Co dienCl_3]), and analysed chromatographically on a Sephadex column.

This reaction has also been carried out by direct mixing of the two reactants at room temperature.[35]

Reaction cis[Co dien$(H_2O)_3]^{3+}$ + dien. - Cis[Co dien$(H_2O)_3]^{3+}$ was prepared and purified chromatographically by methods given previously,[30,73] except that the complex was eluted from Bio-Rad AG 50W-X4 cation exchange resin with a solution 2.9M $NaClO_4$/0.1M $HClO_4$ (replacing 3M $HClO_4$,[73] to reduce the acidity).

Dien was added dropwise to portions of the red-violet cis[Co dien$(H_2O)_3]^{3+}$ elute to adjust the pH to either 6 or 9; one set of these solutions was warmed on a steam bath (1 hour) and another set was allowed to stand at room temperature. The [Co $dien_2]^{3+}$ constituents of these yellow reaction mixtures were assessed by chromatography on Sephadex. A faster moving violet band of unreacted mono-dien species was also obtained from all reactions but was more prominent in the less complete reactions at pH 6.

In the purification of the cis[Co dien$(H_2O)_3]^{3+}$ species, an attempt was made to use phosphorylated cellulose (P11), to obviate the use of such a concentrated eluent as with the 50W-X4 resin above. However the aquo complexes were observed to bind strongly to the cellulose, even in the presence of 2M HCl solution. This affinity, which has also been observed for cis[Co $en_2(H_2O)_2]^{3+}$,[74] may either be due to a specific outer-sphere association between the cations and the phosphate group of the cellulose support, or inner-sphere coordination.

Resolution of u-cis[Co $dien_2]^{3+}$. - To a solution of u-cis[Co $dien_2]Cl_3.2H_2O$ (8.2 g, 0.02 mole) in warm water (200 ml) was added Ag[SbO(+)-tart] (23.6 g, 0.06 mole). After shaking, the precipitated silver chloride was filtered off and the filtrate volume was made up to 250 ml. Scratching the beaker induced crystallisation of the diastereoisomer (+)-u-cis[Co $dien_2$][SbO(+)-tart$]_3.2H_2O$ and after cooling at 0° for several hours it was filtered off, washed with 75% ethanol, absolute ethanol then acetone, and air-dried. Yield 9.2 g, 80% of one optical form. It was recrystallised from water (discarding the most soluble portions) until constant rotation was attained. $\alpha_D = +0.533^\circ$ for a 0.44% solution in water, whence $[\alpha]_D = 121^\circ$.

Anal. Calcd. for (+)-u-cis$[Co(C_4H_{13}N_3)_2][SbO(+)-(C_4H_4O_6)]_3.2H_2O$: C, 20.9; H, 3.65; N, 7.2. Found: C, 20.9; H, 3.65; N, 7.0.

This recrystallised diastereoisomer (2.6 g) was ground with NaI in an aqueous slurry, and the (+)-u-cis[Co $dien_2]I_3$ which separated was filtered off, washed with ice-cold NaI solution, ethanol and acetone, and air-dried. Recrystallisation from hot water did not increase the rotation. Yield 1.0 g, 8% from the starting racemate. $\alpha_D = +0.033^\circ$ for a 0.13% aqueous solution, $[\alpha]_D = +25.6^\circ$.

Anal. Calcd. for (+)-u-cis$[Co(C_4H_{13}N_3)_2]I_3$: C, 14.9; H, 4.06; N, 13.0. Found: C, 14.9; H, 3.95; N, 13.0.

The diastereoisomer remaining in the aqueous solution above was fractionally precipitated by gradually adding ethanol and cooling. The most soluble of these fractions (4.0 g) was ground with sodium iodide as before, and the (-)-u-cis[Co $dien_2]I_3$ obtained was recrystallised three times from water to give constant rotation. The optical isomer was less soluble than the racemate. Yield 1.3 g, 10%. $[\alpha]_D = -24.9^\circ$.

The total resolution of u-cis[Co $dien_2]^{3+}$ has also been achieved using a column of SE-Sephadex C-25 (120 cm x 1.1 cm) with 0.15M sodium (+)-tartrate solution as eluent.[34,35]

Resolution of trans[Co $dien_2]^{3+}$. - Trans[Co $dien_2]Cl_3.2.5H_2O$ (8.3 g, 0.02 mole) was dissolved in water acidified with acetic acid (100 ml water containing 0.5 ml of glacial acetic acid, giving a solution of pH 3-4). Ag(+)-[Co en $mal_2].2H_2O$ [1] (28.0 g, 0.06 mole) was added, and after shaking the solution in a stoppered flask, the precipitated silver chloride was filtered off. Water (100 ml) and methanol (200 ml) were added to the filtrate, then ethanol (about 500 ml) was added carefully to incipient crystallisation. Crystallisation of the diastereoisomer is somewhat difficult, but with the above conditions (+)-trans[Co dien$_2$](+)-[Co en mal$_2$]$_3$-.10H$_2$O crystallised on cooling the solution for several days in a refrigerator. Yield 7.3 g, 52% of one optical form. The diastereoisomer was filtered off, washed with methanol, ethanol and acetone, and air-dried. Because of the difficulty with crystallisation and the relatively poor discrimination between the two diastereoisomers with this resolving agent, optical purification of the diastereoisomer was difficult.

Anal. Calcd. for (+)-trans[Co($C_4H_{13}N_3$)$_2$](+)-[Co($C_2H_8N_2$)($C_3H_2O_4$)$_2$]$_3$-.10H$_2$O: C, 27.1; H, 5.8; N, 11.9. Found: C, 26.7; H, 5.2; N, 12.1.

The dextro isomer was obtained by dissolving the diastereoisomer in 0.1M HBr and absorbing the cation on a solumn of cation-exchange resin (Bio-Rad AG 50W-X2, 200-400 mesh, in H^+ form). The resolving anion was washed from the column with 0.1M HBr, then the (+)-[Co dien$_2$]$^{3+}$ cation was eluted with 3M HBr. (+)-trans[Co dien$_2$]Br$_3$.H$_2$O crystallised on evaporating the elute, and the product was recrystallised from 0.1M HBr four times to constant rotation, the active bromide being less soluble than the racemate. Yield 0.6 g. α_{546} = +0.089° for a 0.308% solution in 0.1M HBr, whence $[\alpha]_{546}$ = +28.9°.

Further diastereoisomer was crystallised from the cold solution by careful addition of further portions of ethanol over several days. The product was removed in fractions until the total diastereoisomer obtained was about 80% of the total (both optical forms). The solution which then contained essentially only (-)-trans[Co $dien_2$](+)-[Co en $mal_2$$]_3$ was passed through the cation exchanger as above, and (-)-trans[Co $dien_2$]$Br_3.H_2O$ crystallised from the 3M HBr elute. Recrystallisation to constant rotation gave $[\alpha]_{546} = -29.2^{\circ}$. Yield 0.8 g.

Anal. Calcd. for (-)-trans[$Co(C_4H_{13}N_3)_2$]$Br_3.H_2O$: C, 18.4; H, 5.40; N, 16.1; Br, 45.8. Found: C, 18.4; H, 5.30; N, 15.9; Br, 44.7.

The use of a more concentrated solution of HBr than 0.1M for the recrystallisation led to less discrimination between the active and racemic bromides. Use of $HClO_4$ rather than HBr in the isolation of the active isomer did not allow satisfactory optical purification as there appeared to be very little distinction between the solubilities of the perchlorates of the active and racemic forms of the cation.

The preparations of the following copper and nickel complexes were required for IR comparisons described in Chapter 4.

[Cu $dien_2$]$Br_2.0.5H_2O$. - A solution of $CuBr_2$ in ethanol was added to dien (2.1 molar ratio) in ethanol. After cooling the solution, the deep blue crystals were filtered off, washed with ethanol, and air-dried. The product was recrystallised slowly from hot methanol. Yield 70%.

Anal. Calcd. for [$Cu(C_4H_{13}N_3)_2$]$Br_2.0.5H_2O$: C, 21.9; H, 6.20; N, 19.2; Br, 36.4. Found: C, 21.7; H, 6.20; N, 19.0; Br, 36.4.

$[Ni\ dien_2]Br_2.H_2O$. - A solution of $NiBr_2.3H_2O$ in water was added to dien (2.1 molar ratio) in water. The product was precipitated by addition of ethanol, filtered off and washed with ethanol and acetone, and air-dried. Slow recrystallisation from hot water gave a yield of 70%.

Anal. Calcd. for $[Ni(C_4H_{13}N_3)_2Br_2.H_2O$: C, 21.7; H, 6.37; N, 19.0; Br, 36.1. Found: C, 21.7; H, 6.33; N, 19.0; Br, 36.0.

3.3 RESULTS AND DISCUSSION

$[Co\ dien_2]^{3+}$ was prepared as a mixture of the three geometric isomers by two general methods, the standard method of aerial oxidation of cobalt(II) chloride or bromide in the presence of dien, and by a substitution method involving reaction of dien with $[Co(NH_3)_5X]X_2$ (X = Cl, Br). All these preparations were carried out in aqueous solution at room temperature in the presence of charcoal catalyst to establish equilibrium.

The resulting mixtures contained all three isomers: the trans isomer was the major component and the s-cis isomer was present in smallest proportion. The presence of the s-cis isomer in both chloride and bromide preparations was demonstrated by separations of the product mixtures by a chromatographic procedure using Sephadex.

The same isomer distribution has also been observed[35] for the substitution of dien into "$[Co(CO_3)_3]^{3-}$" at 0°C in the presence of charcoal (equilibrium conditions). The similar isomer proportions obtained from aerial oxidation and by substitution in three different Co(III) starting complexes is good evidence that charcoal effects rapid equilibration between the [Co dien$_2$]$^{3+}$ isomers, especially since the carbonato procedure was carried out at 0°.

The three isomers could be separated by fractional crystallisation, but the s-cis could be isolated only from the preparations involving bromides, as the least soluble bromide. No s-cis isomer, though present (see above), could be separated by fractional crystallisation of the product mixtures from preparations involving chlorides. Even when the complex in a chloride solution was fractionally precipitated as complex bromide by adding lithium bromide, the least soluble fractions obtained were always predominantly the trans isomer. The inability to isolate s-cis by these methods from any preparation in the presence of chloride ion has also been noted by Yamasaki,[35] so that the presence of chloride evidently modifies the solubility relationships between the bromides of the three isomers. This may be due to crystallisation as mixed chlorides-bromides, since this effect was noticed with iodide precipitation of the u-cis and trans isomers from a solution of their bromides.

On a preparative scale the remaining trans and u-cis isomers (after removal of s-cis[Co dien$_2$]Br$_3$) were separated from the mixtures by fractional crystallisation as iodides, iodide giving a better discrimination than bromide. This separation required a chromatographic monitoring technique, and either thin-layer chromatography on cellulose or chromatography using a Sephadex column was suitable, although Sephadex was preferable for checking isomeric purity. The early and later fractions thus obtained were trans[Co dien$_2$]I$_3$ and u-cis[Co dien$_2$]I$_3$ respectively (these are actually mixed halides; see experimental section), and the intermediate mixed fractions were discarded.

The separated isomers were characterised by a number of methods, but of these only racemisation behaviour and PMR spectra (section 4.3.3) allowed unequivocal assignment of the geometric configurations.

The u-cis isomer was resolved into optical isomers through diastereoisomer formation with antimonyl (+)-tartrate. A solution of active u-cis in buffer pH 8 (collidine-HCl) showed no measurable change in rotation after standing for two months at room temperature. This isomer is resolvable by virtue of alternate configurations about the cobalt atom and therefore, like [Co en$_3$]$^{3+}$, is optically stable in base since racemisation would have to involve a gross rearrangement of the chelate rings.

The trans isomer was resolved with (+)-[Co en mal$_2$]$^-$ ion. The active trans[Co dien$_2$]$^{3+}$ complex should be handled in acid conditions to avoid racemisation, and although in principle acid conditions are not essential to obtain the solid less soluble diastereoisomer, such conditions were used throughout the resolution procedure to avoid racemisation of the more soluble diastereoisomer left in solution. Since both optical forms were obtained from the resolution and could be recrystallised to constant rotation, this was taken to indicate that optical purity had been achieved. Of the other resolving agents tried for the resolution of trans[Co dien$_2$]$^{3+}$, (+)-camphor-10-sulphonate and Cl (+)-tart (in combination) gave no crystalline diastereoisomer, and the crystalline salt obtained with (Br (+)-tart), (I (+)-tart), (SbO(+)-tart), (AsO(+)-tart), nitro-(+)-camphor, α-bromocamphorsulphonate, (+)-$[Co(en)(ox)_2]^-$, (+)-$[Co(EDTA)]^-$, (+)-$[Co\ ox_3]^{3-}$, and (-)-$[As\ cat_3]^-$ [75] did not yield active trans$[Co\ dien_2]^{3+}$.

Trans$[Co\ dien_2]^{3+}$ will be resolvable into its two optical forms (Figure 4) provided that the N^2-H bonds maintain a fixed disposition, thereby locking the ring conformations (section 1.3). It has been well established that, in acidic conditions, such N^2-H bonds in Co(III) complexes would be sufficiently inert to dissociation (and hydrogen exchange) to allow resolution of this isomer, although in solutions of higher pH, where the N-H exchange process is facilitated, racemisation will occur. Thus in contrast to the u-cis isomer, active trans racemises in basic media, and these observations allow the above assignments. The kinetics and mechanism of the exchange and inversion processes in the trans isomer are discussed in Chapter 8.

The equilibrium preparations of $[Co\ dien_2]^{3+}$ yielded the s-cis isomer in only small proportion. In seeking a non-equilibrium method to obtain the s-cis$[Co\ dien_2]^{3+}$ isomer in higher yield, the reaction of a solution claimed[30] to contain cis$[Co\ dien(H_2O)_3]^{3+}$ with excess dien was examined under various conditions of pH. The reaction was most complete in alkaline conditions pH 8-9 (as judged by the colour change), and product analysis by chromatography on Sephadex showed that the $[Co\ dien_2]^{3+}$ reaction products were almost all trans with only a trace of the u-cis isomer, and no evidence of any *s-cis*. This product proportion, while quantitatively similar to that obtained by synthesis, involves an even higher proportion of *trans*/*cis*. If the starting complex was in fact *cis*$[\mathrm{Co\ dien(H_2O)_3}]^{3+}$, these results would suggest that substitution of the second dien ligand on a *cis*-mono(dien) arrangement evidently leads to substantial isomerisation. This would accord with the greater stability of the *trans* configuration in the bis-complex as indicated by all other preparative methods.

The starting triaquo complex was obtained by the reaction sequence[30]

$$\textit{trans}[\mathrm{Co\ dienCl_3}] \xrightarrow{\mathrm{NaOH}} \textit{trans}[\mathrm{Co\ dien(OH)_3}] \xrightarrow{\mathrm{HClO_4}} \textit{trans}[\mathrm{Co\ dien(H_2O)_3}]^{3+}$$

and it is reported that on standing the *trans* triaquo isomerises completely to the *cis*.[73] The *cis* disposition of coordinated dien would thus appear to be considerably stabilised only by coordinated water. This might be attributed to more favourable hydrogen bonding between the aquo ligands all *cis*, as this factor may be used to rationalise the greater stability of *β*$[\mathrm{Co\ trien(H_2O)(OH)}]^{2+}$ compared with the *α* configuration.[76] The identity of the complex species purported to be *cis*$[\mathrm{Co\ dien(H_2O)_3}]^{3+}$ remains in some doubt however since it has been obtained only in solution.

Other non-equilibrium preparations involving the substitution of dien into *trans*$[\mathrm{Co\ dienCl_3}]$ and *trans*$[\mathrm{Co\ dien(NO_2)_3}]$ yielded a predominantly *trans* product (ca. 90%) with some *u-cis* and only trace amounts of *s-cis* present. Such an isomer distribution is not unexpected due to meridional coordination of dien in the initial complex. However on substitution of dien into $[\mathrm{Co(NO_2)_6}]^{3-}$ in aqueous solution, or the non-equilibrium oxidation procedure using DMSO as solvent, isomeric proportions of the product [Co $dien_2$]$^{3+}$ similar to those above were obtained. Thus in all non-equilibrium preparations, the kinetically controlled product was always even more predominantly trans than in the thermodynamically controlled preparations. The use of methanol as solvent, rather than water, gave similar results.

Preparative Methods Used by Other Workers.

In the previously reported studies of the system [Co $dien_2$]$^{3+}$, the preparative method used has been substitution by dien into $[Co(NH_3)_5(H_2O)]^{3+}$ (Mann,[11] Barclay and Barnard[37]) and $[Co(NH_3)_5Cl]^{2+}$ (Brigando,[12] Crayton and Mattern,[15] and Basolo, Palmer and Pearson[38]). The present work shows that all the products obtained by these researchers were isomeric mixtures.

CHAPTER 4

SPECTRAL PROPERTIES OF THE [Co $dien_2$]$^{3+}$ ISOMERS

4.1 INTRODUCTION

The three geometric isomers of [Co $dien_2$]$^{3+}$ were characterised by their spectroscopic properties in the electronic, infrared (IR) and PMR regions. In principle each of these spectral types, since they are dependent on detailed molecular symmetry, should enable the geometric configurations of the three isomers to be assigned. At this stage the detailed interpretations generally of these spectra still involve many uncertainties, but in the present system the geometric configurations are known unequivocally (from racemisation behaviour, section 3.3), and some of the chelate ring conformations can be reasonably inferred from molecular models. It was the purpose of the work in this chapter to attempt to interpret the differences in spectroscopic properties between the three geometric isomers in the light of the known structural features. It was hoped that these interpretations might be applicable and useful in studies of new similar systems, such as the [Co(4-$Medien)_2$]$^{3+}$ complex (Chapter 10), and the four geometric isomers possible for the [Co(lin-penten)]$^{3+}$ complex, which is currently being studied.[4]

4.2 EXPERIMENTAL

Electronic (visible-ultra-violet) spectra were measured on a Unicam SP700 recording spectrophotometer in 1 cm quartz cells against water as reference. The extinction coefficients agreed with those obtained on a

Shimadzu QR-50 manual spectrophotometer.

Infrared spectra were obtained on a Perkin-Elmer 457 grating infrared spectrophotometer using KBr discs against air reference. The discs were pressed, using a pressure of 25 tons, from ground mixtures of about 5 mgm of the complex bromide in 200 mgm KBr (for the spectral region 4000-600 cm^{-1}) or about 8 mgm complex in 200 mgm KBr (for the spectral region 600-250 cm^{-1}).

PMR spectra were obtained on a Varian HA100 spectrometer or a 60 MHz Jeol spectrometer using solutions of complex of about 10% concentration, with sodium trimethylsilylpropanesulphonate (TMP) as internal reference or trimethylsilane (TMS) as external reference.

4.3 RESULTS AND DISCUSSION

4.3.1 ELECTRONIC SPECTRA

The visible-ultra-violet spectra of the three geometric isomers of $[Co\ dien_2]^{3+}$, measured as the bromides, are shown in Figure 7. The two ligand field bands are closely similar in form for the three isomers, but there is a significant variation in intensities (Table 2). These differences in spectra could not be interpreted in terms of the structures. Nevertheless spectral comparisons between $[Co\ dien_2]^{3+}$ and the $[Co(lin\text{-}penten)]^{3+}$ systems could be useful in isomer assignments in the latter,[4] since each of the four isomers in the latter can be closely related to an isomer in the present system. Similar considerations apply to isomer assignment for the three geometric forms of the $[Co(4\text{-}Medien)_2]^{3+}$

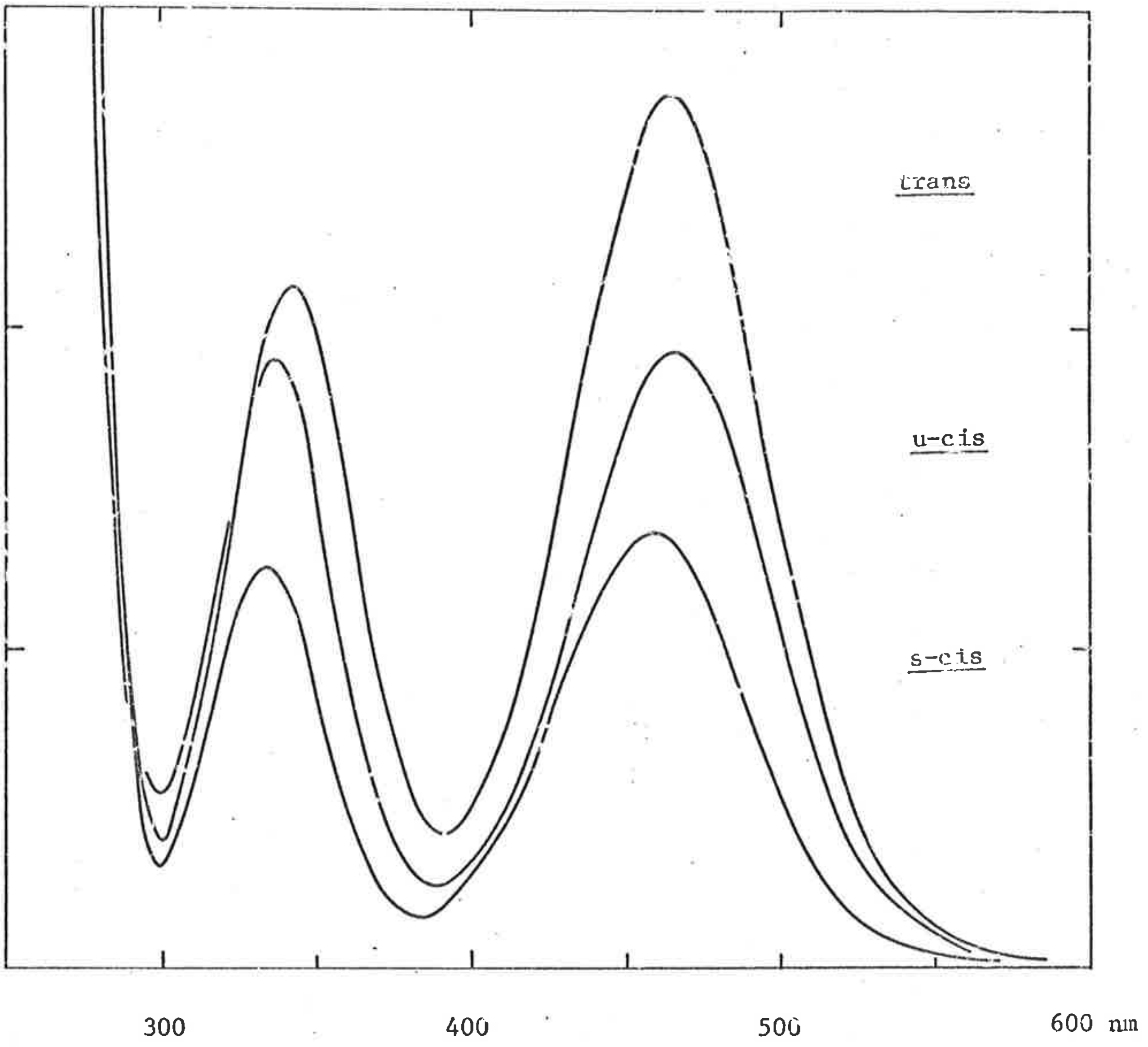


Figure 7. - Electronic absorption spectra of the [Co dien$_2$]$^{3+}$ isomers.

system (Chapter 10).

TABLE 2

Visible Absorption Maxima for the [Co $dien_2]^{3+}$ Isomers as Bromides

	Band 1	Band 2
s-cis	$\varepsilon_{461} = 68.5$	$\varepsilon_{333} = 65.0$
u-cis	$\varepsilon_{468} = 96.4$	$\varepsilon_{338} = 94.1$
trans	$\varepsilon_{466} = 137.0$	$\varepsilon_{341} = 103.0$

4.3.2 INFRARED SPECTRA

Introduction.

In the initial stages of this work it was considered possible that infrared (IR) spectroscopy alone might permit assignment of the three geometric forms of [Co $dien_2]^{3+}$, using the considerable information available concerning mono(dien) complexes.[9,19,26,30] The IR spectra of the three isomers were distinctly different (and thereby useful for characterisation), but isomer assignment by criteria established for the mono(dien) systems alone was not altogether unambiguous. The main contribution of the present work therefore was the extension of the previous work on the identification of the two topological forms of the coordinated dien ligand by IR methods, to complexes of lower conformation symmetry than the mono(dien) complexes.

Previous IR Studies on Complexes of Dien.

Only in recent years have detailed IR studies of dien complexes been used to establish the configuration of the ligand. Initially, Watt and Klett[19] assigned the absorption bands of the IR spectra (in the region 4000-200 cm^{-1}) for the planar systems [Pd dienX]X (X = I, Br, Cl) and [Pd(tmdien)I]I (tmdien = 1,4,7-trimethyldiethylenetriamine). Using these results, and the IR spectrum of [Co dienCl$_3$], which had been established as trans (or meridional) from electronic spectral comparisons (with the two [Co(NH$_3$)$_3$Cl$_3$] isomers) by Crayton and Mattern,[15] House and co-workers assigned geometric configurations to trans[Co dienBr$_3$] [27] and cis and trans[Cr dienCl$_3$] [27,30] by IR comparisons. Subsequently, Schmidtke and Garthoff[26] presented a wider study of the IR spectra of mono(dien) complexes, using the series [M dienX$_3$] (M = Cr, Co, Rh; X = halogen). These authors were able to empirically assign the various modes of vibration, and to deduce empirical rules to determine the configuration of coordinated dien as cis (facial) or trans (meridional). House and Garner[9] used these criteria to assign the four isomers of [Co(dien)(en)Cl]$^{2+}$. However, subsequent X-ray crystal structure determinations of two of these isomers[77] have shown these original assignments to be in error.

Band Assignments in Complexes of Dien.

The comprehensive work of Schmidtke and Garthoff[26] merits some discussion in relation to the use of this technique for the study of [Co dien$_2$]$^{3+}$. These authors found that the IR spectra of the various

[M dienX_3] complexes corresponded to one of two standard complexes, trans[Pd dienCl]Cl or cis[Mo dienO_3] (octahedral), whose configurations had been established by kinetic[78] and X-ray structural[20] studies respectively, so that structural assignments could be made.

The fundamental vibrations of the molecules were considered in the following regions which overlap in frequency.[79]

(i)	NH_2(NH), CH_2 stretching vibrations (ν)	(3500-2800 cm^{-1})
(ii)	NH_2(NH) deformations (bending δ, twisting γ, wagging ω, rocking ρ)	(1650-600 cm^{-1})
(iii)	CH_2 deformations	(1500-800 cm^{-1})
(iv)	skeletal stretching vibrations (ν_{C-C}, ν_{C-N}, ν_{C_2N} (for secondary amines))	(1100-800 cm^{-1})
(v)	skeletal stretching vibrations (ν_{M-N}, ν_{M-X}) and ring deformations ($\delta_{N-C-C-N}$, δ_{N-M-N})	(<600 cm^{-1})

Schmidtke and Garthoff[26] considered each of these regions and observed the differences in spectra corresponding to the alternate dispositions of the dien ligand. The band assignments were facilitated by the use of the N-deuterated [M dienX_3] species, and trans[Pd dienCl]Cl, trans-[Pd(Et_4dien)Br]Br and cis[Mo dienO_3].

(i) Cis isomers displayed a larger splitting (5 bands) than trans forms (3 bands, + shoulder or another weak band) of the ν_{N-H} absorbance (3300-3050 cm^{-1}). Also the intensities of the ν_{C-H} absorbances were considerably greater for the trans than for cis isomers, where they were barely detectable.

(ii) Between 1200-1100 cm^{-1} (ω_{NH_2}, γ_{NH_2}), cis isomers were observed to have three well-resolved approximately equally spaced bands, while the trans compounds showed only two absorptions. At ca. 1250 cm^{-1}, all trans complexes showed one medium-strong ω_{N-H} band which was absent or very weak for the cis counterparts. With the ρ_{NH_2} absorptions, two bands were observed at about 850 cm^{-1} in the spectra of trans isomers, while they were of higher intensities, and shifted to lower frequencies (800-700 cm^{-1}) for the cis forms. Also, although not specifically mentioned by these authors, the trans complexes possessed a rather distinctive quartet in the region 950-800 cm^{-1}.

(iii) The δ_{CH_2} absorption expected for all 1,2-disubstituted ethanes in the region 1500-1400 cm^{-1} was found for the trans dien complexes at ca. 1450 cm^{-1}, generally accompanied by another weak absorption. The cis forms showed a rather distinctive band triplet in this region.

(iv) Between 1100-1000 cm^{-1} there were high intensity bands due to C-C and C-N skeletal vibrations. The trans complexes in general showed 3-4 strong bands while the cis isomers had only two strong bands.

(v) The region below 600 cm^{-1} was not particularly distinctive for either isomer.

Three of these regions were found to be especially suitable for distinguishing the geometry of the dien ligand (Table 3).

TABLE 3

Spectral Regions for Detecting Geometry of Coordinated Diethylenetriamine[26]

	δ_{CH_2} (1500-1400 cm^{-1})	ω_{NH} (ca. 1250 cm^{-1})	ρ_{NH_2} (850-700 cm^{-1})
cis	3 bands	-	1-2 bands (800-700 cm^{-1})
trans	1 band	1 band	2 bands (at ca. 850 cm^{-1})

Furthermore, cis isomers were always observed to show more numerous bands and larger splitting in their spectra, presumably indicating their lower point symmetry than trans isomers.

IR Studies of the Isomers of [Co dien$_2$]$^{3+}$.

From this work on mono(dien) complexes, the technique of infrared spectroscopy seemed likely to be capable of distinguishing the cis and trans isomers of [Co dien$_2$]$^{3+}$. The infrared spectra of these three isomers were recorded, and also those of trans[Co dienCl$_3$],[15] trans[Cu dien$_2$]Br$_2$.$\frac{1}{2}$H$_2$0 (trans by X-ray),[23] and trans[Ni dien$_2$]Br$_2$.H$_2$0 (trans by X-ray).[55] The absorbances and their relative intensities in the regions listed above are given in Table 4. The band assignments shown are those given for [M dienX$_3$],[26] it being assumed that

TABLE 4

Infrared Absorption Bands[a] (cm^{-1}) of Diethylenetriamine Complexes (spectra run as bromides)

Assignment	trans- [Co dienCl$_3$]	s-cis- [Co dien$_2$]$^{3+}$	u-cis- [Co dien$_2$]$^{3+}$	trans- [Co dien$_2$]$^{3+}$	trans- [Cu dien$_2$]$^{2+}$	trans- [Ni dien$_2$]$^{2+}$
ν_{NH_2}, ν_{NH}	3290 s	3187 s	3140 vs, br	3175 vs, br	3332 m	3358 m
	3240 s	3095 s	3060 vs, br	3045 vs, br	3300 w	3325 s
	3150 s	3080 sh			3255 ms	3268 vs, br
	3115 sh				3235 sh	3190 sh
					3155 sh	3175 vs
					3138 s	3160 sh
ν_{CH_2}	2985 mw	2965 sh	2960 sh	2960 w	2950 sh	2945 s
	2965 mw	2935 vw	2892 vw	2945 sh	2922 ms	2918 s
	2955 sh	2892 vw	2850 vw	2882 vs	2875 ms	2876 s
	2918 mw	2865 vw				
	2885 mw					
δ_{NH_2}	1625 w, br	1578 ms, br	1601 ms	1610 w	1619 mw	1627 mw
	1588 sh	1555 sh	1587 sh	1562 sh	1568 s	1580 sh
	1582 s		1570 sh	1550 s		1564 ms
			1560 sh	1542 sh		

(contd.)

TABLE 4 (contd.)

Assignment	trans- [Co dienCl$_3$]	s-cis- [Co dien$_2$]$^{3+}$	u-cis- [Co dien$_2$]$^{3+}$	trans- [Co dien$_2$]$^{3+}$	trans- [Cu dien$_2$]$^{2+}$	trans- [Ni dien$_2$]$^{2+}$
δ_{CH_2}	1487 vw, sh	1486 m	1481 ms	1482 m	1472 m	1482 sh
	1457 s	1472 vw	1467 ms	1462 vw	1454 sh	1476 mw
	1412 m	1456 m	1450 ms	1454 mw	1449 s	1450 ms
		1439 m	1432 vw	1448 mw		
			1418 w			
ω_{CH_2}	1387 w	1388 w	1395 sh	1390 w	1388 m	1387 mw
	1371 w	1360 mw	1387 m	1380 sh	1365 vw	1375 sh
	1352 ms		1362 w	1361 w		1368 vw
			1354 vw			
ω_{NH_2}	1328 m	1331 w	1313 m	1328 ms	1326 s	1336 mw
	1308 ms	1322 m		1309 vw		1322 m
γ_{CH_2}	1290 w	1299 m	1292 m	1300 w	1304 mw	1308 mw
		1273 vw	1287 w	1272 sh	1290 w	1284 mw
			1264 w			
ω_{NH}	1249 s	1241 m	1233 mw	1261 m	1253 m	1254 m

(contd.)

TABLE 4 (contd.)

Assignment	*trans*- [Co dienCl$_3$]	*s-cis*- [Co dien$_2$]$^{3+}$	*u-cis*- [Co dien$_2$]$^{3+}$	*trans*- [Co dien$_2$]$^{3+}$	*trans*- [Cu dien$_2$]$^{2+}$	*trans*- [Ni dien$_2$]$^{2+}$
ω_{NH_2}	1137 s	1189 ms	1208 m	1205 vw	1147 ms	1145} d, ms
		1179 sh	1186 sh	1189 m		1140
			1173 ms	1146 w		
γ_{NH_2}	1119 s	1136 m	1148 m	1122 m	1135 ms	1121 vw
			1134 m	1117 vw		
C-C,C-N,C-N-C	1096 s	1087 ms	1082 sh	1099 s	1097 s	1089 vs, br
	1069 ms	1063 mw	1078 ms	1059 s	1078 s	1067 w
	1057 m	1050 s	1064 s	1037 s	1068 s	1059 mw
	1036 s		1046 s		1052 s	1031 vw
					1039 sh	1014 vs
					1029 vs	
γ_{NH_2}	994 s	1000 vw	1003 mw	1010 vw	993 w	978 vs
			988 w		981 s	

(contd.)

TABLE 4 (contd.)

Assignment	trans- [Co dienCl$_3$]	s-cis- [Co dien$_2$]$^{3+}$	u-cis- [Co dien$_2$]$^{3+}$	trans- [Co dien$_2$]$^{3+}$	trans- [Cu dien$_2$]$^{2+}$	trans- [Ni dien$_2$]$^{2+}$
ρ_{NH}, ρ_{NH_2}, ρ_{CH_2} and C-N	930 s, sp	912 vw	905 vw	930 w	944 s	910 w
	905 w	892 vw	884 w	898 m	919 w	892 s
	872 m	882 w	868 m	868 w	899 vs	868 w
	849 m	803 m	840 mw	839 mw	873 w	829 w
	827 m	779 mw	810 sh	761 m	861 mw	672 vw
	730 vw, br	758 m	802 m	742 w	835 vw	644 w
		683 m	777 w		822 vw	619 m
			755 w		660 m	
			743 sh			
			702 vw			
			667 w			
ν_{M-N}	576 ms	592 m	609 m, br	590 mw	559 w	578 sh
	522 w	516 mw	581 m	573 mw	540 w	555 w, br
	501 m		540 vw	568 mw	527 m	523 ms
			525 mw	528 m		
			501 w			

(contd.)

TABLE 4 (contd.)

Assignment	*trans*- [Co dienCl$_3$]	*s-cis*- [Co dien$_2$]$^{3+}$	*u-cis*- [Co dien$_2$]$^{3+}$	*trans*- [Co dien$_2$]$^{3+}$	*trans*- [Cu dien$_2$]$^{2+}$	*trans*- [Ni dien$_2$]$^{2+}$
δ_{ring}	458 vw	451 w	482 vw	487 m	471 s	456 mw
	422 m		457 w	471 w	443 s	412 mw
			445 sh	446 mw		
			432 sh	438 mw		
δ_{N-M-N}	360 w	389 vw	388 w	414 vw	375 w	387 w
	340 s	374 m	339 m	370 m	351 w	373 sh
	327 s	301 w	310 m, br	325 w		

---

[a] Relative band intensities: vs, very strong; s, strong; ms, medium-strong; m, medium; mw, medium-weak; w, weak; vw, very weak; sh, shoulder; sp, sharp; br, broad; d, doublet.

these assignments can be extended to bis(dien) systems.

Before consideration of the isomer assignment for bis(dien) complexes, the detailed symmetry of the three possible geometric forms should be appreciated. Schmidtke and Garthoff[26] deduced from the splitting present in the IR spectra of mono(dien) complexes that the less symmetric δδ (and λλ) forms (no plane of symmetry across the coordinated ligand) of facially coordinated dien existed in the solid state, and the symmetrical λδ combination (plane of symmetry) would be the form of dien in *trans* complexes. In bis(dien) complexes, the symmetry relationships present for the mono(dien) complexes may be further destroyed as the point symmetries of the $[Co\ dien_2]^{3+}$ isomers need not be as high in the solid state as those given earlier (section 1.3) - *s-cis* (C_{2h}), *u-cis* (C_2), and *trans* (C_2). The five possible conformational combinations for the *s-cis* species have varied symmetries, viz. λδ-λδ (C_{2h}), λδ-δλ (C_s), λλ-λδ (C_1), λλ-δδ (C_1), and λλ-λλ (C_2). Similarly for the *u-cis* species, for one configuration the combinations are λδ-λδ (C_2), λδ-δλ (C_1), λλ-λδ (C_1), λλ-δδ (C_1), and λλ-λλ (C_2). (The order of ring designation in this latter case has been chosen as that obtained as the molecule is rotated clockwise about the C_2 axis.) The two possible conformational combinations for the *trans* molecule are the two enantiomeric forms λδ-λδ/δλ-δλ (Figure 4).

Any lowering of the idealised symmetry for these molecules (from the symmetry above as deduced from models) implies that more splitting will be present in their IR spectra, thereby complicating structural assignments.

IR spectra may even provide in principle information on the conformational possibilities, however the interpretation would be difficult. X-ray crystal structure analyses of the various isomers of [Co dien_2]$^{3+}$ are in progress[36] and these will elucidate the conformational situation in the solid state. The problem of deducing the conformations that exist in solution is discussed subsequently (section 4.3.3, and Chapter 6).

When the infrared regions distinctive for mono(dien) complexes were examined for the [Co dien_2]$^{3+}$ species, it was found there were similarities but rarely identical band sequences, whence isomer assignment was difficult. The bis(dien) complexes in general had much more complicated spectra than the mono(dien) species, consistent with their having lower symmetry. It is worthwhile to consider in turn the regions discussed earlier, but neglecting those regions in the spectra of the bis(dien) complexes where extra bands and splitting have virtually meant loss of information.

(i) The ν_{NH} region (3500-3100 cm^{-1}) was broad and provided little information. However the ν_{CH} region (2900-2800 cm^{-1}) was of reasonable intensity for the trans isomer but barely recognisable for the two cis forms, and thus appears a reasonable criterion for the type of coordination by dien (Figure 8).

(ii) The trans isomer has a band (ω_{N-H}) at ca. 1260 cm^{-1} characteristic of meridionally coordinated dien. The s-cis form also has a reasonably strong band at 1234 cm^{-1} which was not present for cis mono(dien) complexes previously investigated,[26] and suggests that

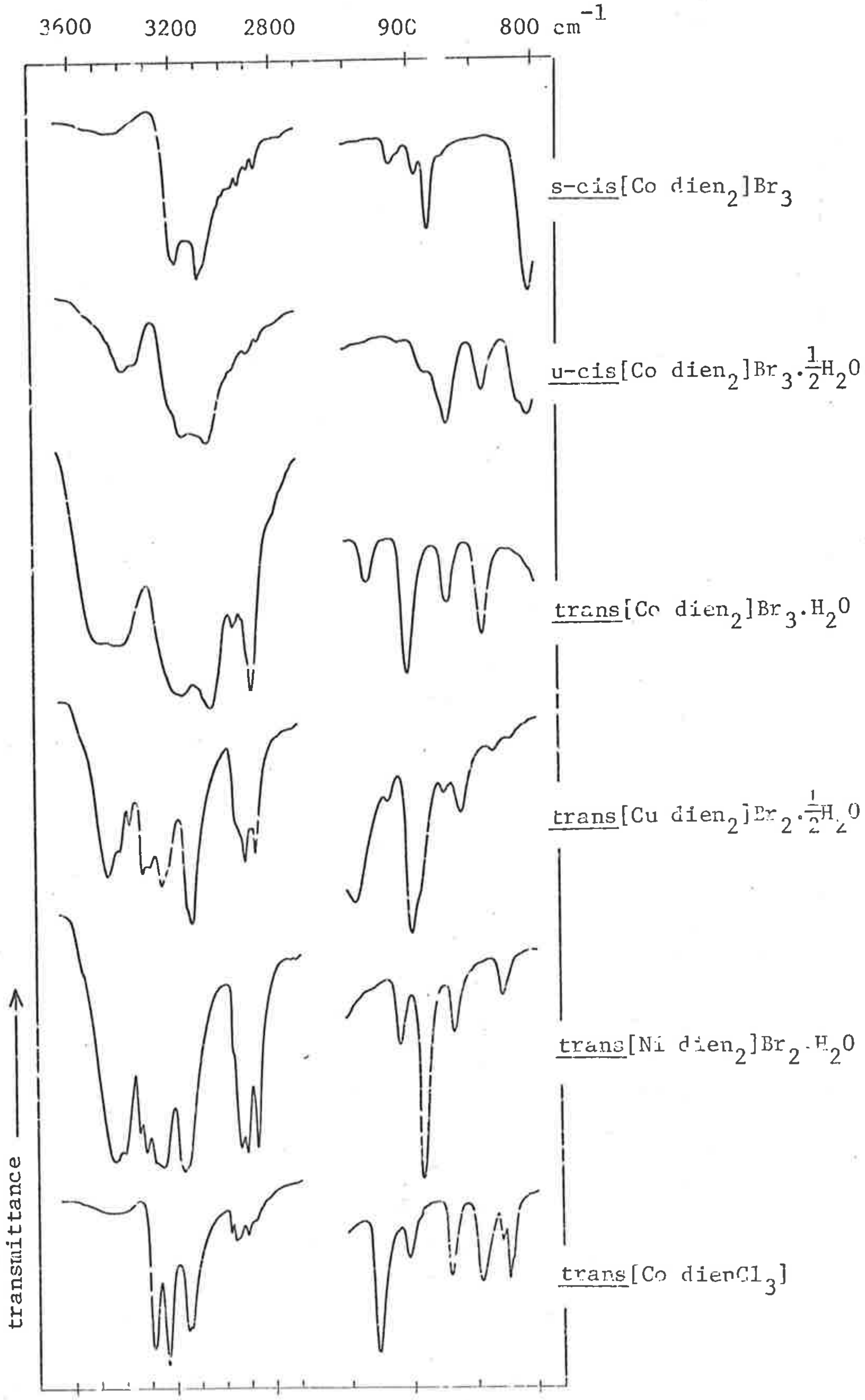


Figure 8. - Infrared spectral regions for characterising facial or meridional coordination of dien in [M dien$_2$]$^{n+}$ complexes.

the _s-cis_[Co dien$_2$]$^{3+}$ species may have considerable symmetry which is more consistent with _trans_ mono(dien) compounds. This band is absent in the _u-cis_[Co dien$_2$]$^{3+}$ isomer and all _cis_ mono(dien) complexes. In the spectrum of _trans_[Co dien$_2$]$^{3+}$, the quartet in the range 950-800 cm^{-1} characteristic of meridional dien was present, but only a triplet was observed here for the two _cis_ forms.

(iii) The region 1500-1400 cm^{-1} was complicated for all three isomers, although there were less bands for the _trans_ form than for the two _cis_ forms.

(iv) The region 1100-1000 cm^{-1} became too complicated in all isomers to provide any information.

(v) The spectra of the three geometric forms of [Co dien$_2$]$^{3+}$ in the IR range 600-250 cm^{-1} were distinctive, and although not useful for isomer assignment, they proved very useful for characterisation. (In the initial stages of the study of this system, IR spectra in this region were used for characterisation of the geometric form, and as a guide to isomeric purity. It was estimated that this method was capable of detecting 5-10% of one isomer as an impurity in another.)

As a general observation, there were more bands and more splitting in the spectrum of the _u-cis_ isomer compared with those of the _s-cis_ and trans forms, consistent with u-cis having the lowest symmetry. On the basis of these results therefore, the empirical criteria for the assignment of the geometrical configuration of dien by infrared spectroscopy appear to be, firstly, that the ν_{C-H} absorbance (ca. 2800 cm^{-1}) is much more intense for trans (meridional) coordination than for cis (facial), where it is barely recognisable. Secondly, the trans isomers show a characteristic quartet between 950-800 cm^{-1} and the cis only a triplet, and finally, the trans compounds have a sharp band at ca. 1250 cm^{-1} corresponding to the N^2-H wagging mode (ω_{N-H}).

To test these relationships, the IR spectra of both $[Cu\ dien_2]^{2+}$ [23] and $[Ni\ dien_2]^{2+}$ [55] (both of known configuration trans) were examined, and they were found to obey the three criteria. Figure 8 demonstrates the first two criteria for all the bis(dien) complexes studied, and also for trans$[Co\ dienCl_3]$. It is felt that these modified criteria will enable the geometric configurations of all dien complexes to be assigned, as well as N-substituted dien complexes (Chapter 10).

The initial assignment of the three forms of the system $[Co\ dien_2]^{3+}$ was not possible in an unequivocal way from the criteria of Schmidtke and Garthoff[26] given in Table 3. By closer study of other regions using their work on mono(dien) complexes, tentative geometric assignments could be made to the present system, and these subsequently proved to be correct.

The use of this present study however is to extend the information on the infrared spectra of dien complexes using the more varied symmetry possibilities associated with the bis(dien) complexes. It should be stressed however that assignments by IR methods must always be treated cautiously, because of the dependence of the observed absorptions on the detailed molecular symmetry.

4.3.3 PMR SPECTRA

Introduction.

NMR spectroscopy has been widely used in studies of Co(III) complexes for the distinction of geometric isomers, the elucidation of chelate ring conformations, and for kinetic studies involving N-H proton exchange. In the present study of the three geometric isomers of [Co $\text{dien}_2]^{3+}$, PMR was the only spectroscopic method used which could unambiguously assign these geometric forms, and the observed spectra were also rationalised in terms of possible conformational situations. The kinetic studies of proton exchange in trans[Co $\text{dien}_2]^{3+}$ are reported subsequently (Chapter 8).

Conformational Studies in [M $\text{en}_3]^{n+}$ Systems.

The knowledge of conformations of five-membered chelate rings in coordinated chelates such as en, both in solution and in the solid state, is now reasonably extensive and will be discussed in some detail subsequently in Chapter 6. Early conformational analyses[80] predicted that in the complex system [M $\text{en}_3]^{n+}$ the $\Lambda\delta\delta\delta/\Delta\lambda\lambda\lambda$ racemic pair would exist predominantly (59%, see section 6.1), so that the C-C bonds of each chelate ring would be essentially parallel to the molecular C_3 axis.

In the solid state, this has been verified in the X-ray crystal structure analysis of $[Co\ en_3]^{3+}$.[81] However subsequent crystal structures of $[Cr\ en_3]^{3+}$ with various anions[82-84] have realised all four possible combinations of conformations, δδδ, δδλ, δλλ, and λλλ due to lattice packing effects and hydrogen bonding rather than the thermodynamic stabilities of the isolated cations. Such X-ray determinations may give little idea concerning the most stable conformer in solution.

The PMR data available for the $[M\ en_3]^{n+}$ complexes (M = Co(III), Pt(IV), Ru(II), Ni(II), Rh(III), and Ir(III))[85,86] in D_2O solutions generally indicated that the chelate rings undergo rapid inversion, and that there is a conformational averaging so that the most abundant conformation in solution is Λδδλ/Δλλδ. It was observed also that the PMR spectrum of $[Co\ en_3]^{3+}$ was broad and featureless, presumably because of coupling with the Co nucleus (spin = $^7/2$), but this feature seems to be peculiar to that particular cobalt complex. As it is not observed for the $[Co\ dien_2]^{3+}$ species, their spectra can be considered without concern for such an effect.

PMR Spectra of the $[Co\ dien_2]^{3+}$ Isomers in D_2O Solutions.

For the system $[Co\ dien_2]^{3+}$ there are three possibilities for conformational changes in solution. Firstly, as with the $[M\ en_3]^{n+}$ complexes,[85] conformational inversion could be rapid and the relatively sharp resonance of the average conformer observed. Secondly, the conformational inversion could be very slow, in which case the superposition of the sharp resonances of the individual conformations would be observed. Finally, the rate of conformational inversion could be intermediate in terms of the NMR time scale, and a dynamic broadening of resonances would occur, and as there is no evidence for this case in the present spectra it will not be discussed further. As the en rings of $[M\ en_3]^{n+}$ are known to undergo rapid conformational interchange,[85] in conditions under which the N^2-H protons of the $[Co\ dien_2]^{3+}$ isomers can be dissociated (in neutral D_2O), free and rapid interchange would be expected for all three isomers. The molecules may thus possess essentially their maximum symmetries, <u>s-cis</u> (C_{2h}), <u>u-cis</u> (C_2), and <u>trans</u> (S_2) as rapid conformational inversion for the <u>trans</u> isomer implies two planes of symmetry as explained earlier (section 1.3).

In D_2O solution where all N-H protons will be deuterated, only the resonances corresponding to the methylene protons will be observed. Even when rapid conformational inversion occurs, the four protons of each ring ($-CH_2-CH_2-$) will have different environments in the two <u>cis</u> isomers, although the rings themselves may be related by symmetry to other ring(s). Thus an AA'BB', rather than A_2B_2, contribution from each ring would be expected, resulting in a complicated spectrum. With the effect of quadrupole relaxations from ^{14}N and ^{59}Co transmitted through the chelate ring, the observed resonances were somewhat broadened and although they did not show the detailed resonance pattern of AA'BB' there was some fine structure evident. On the symmetry considerations outlined above it would be anticipated that the CH_2 resonance observed for the u-cis form, where the two chelate rings of each ligand are non-equivalent, would be considerably more complicated than that for the s-cis isomer where the two chelate rings of each dien ligand are stereochemically equivalent (related by a plane of symmetry).

The CH_2 resonance of the trans isomer should be the least complex when rapid conformational inversion was occurring, as in this instance the four CH_2 protons α- to the N^2-D in each ligand then become equivalent and an A_2B_2 pattern would be anticipated.

Figure 9(b) shows the 60 MHz PMR spectra of the three isomers in D_2O, and verifies the above predictions. The 100 MHz spectra of the same region showed greater fine structure so that the general features are less apparent, but the overall conclusions remain unaltered.

PMR Spectra of the $[Co\ dien_2]^{3+}$ Isomers in Acidified D_2O Solutions.

In D_2O/D_2SO_4 solutions, coordinated amine protons do not undergo rapid exchange. The inertness of the $>N^2$ - H bond in particular implies that conformational interchange in the isomers of $[Co\ dien_2]^{3+}$ may not be as facile as when this bond dissociated (neutral solution, D_2O). However it seems a reasonable assumption that conformational inversion in the cis isomers is still facile even in acid solution since the interchange of conformations in these two isomers can occur without $>N^2$ - H dissociation. Consequently, the time average of the conformers

(a)

in D_2O/D_2SO_4 at 100 MHz

(b)

in D_2O (containing trace Na_2CO_3) at 60 MHz

Figure 9. - PMR spectra of [Co dien$_2$]Cl$_3$.xH$_2$O isomers.

would make all four -NH_2 groups equivalent for the s-cis isomer, and in the u-cis form there would be two different environments for the -NH_2 groups. With the rapid conformational flipping, the two individual protons attached to any one primary nitrogen atom will experience some environmental averaging. Furthermore, the amino proton resonances are broadened because of quadrupole relaxation in the ^{14}N nucleus, resulting in at least partial loss of possible fine structure in the observed -NH_2 resonances, including that due to coupling with the contiguous $>CH_2$ protons. Therefore a single -NH_2 resonance would be expected for s-cis[Co $dien_2]^{3+}$, and two -NH_2 resonances for the u-cis isomer. These were observed and are shown in Figure 9(a). The resonance assignments shown in the figure follow from the spectrum integration which gave peak area ratios 1:4:8 corresponding to NH:2(NH_2):4(CH_2).

In trans[Co $dien_2]^{3+}$, the -NH_2 groups on each dien ligand are in non-equivalent environments (Figure 4). In this isomer, conformational inversion of one ring would involve $>N^2$ - H dissociation, which does not occur readily in the acidic solvent. Thus as conformational interchange is severely restricted under these conditions, the four individual protons of the two primary amino groups of each dien ligand will be in different environments, and a complicated -NH_2 resonance would be expected. Any broadening of this resonance should result in either an unsymmetrical resonance or two separate resonances. Figure 9(a) shows a complex -NH_2 region in the PMR spectrum of this isomer, consistent with the above considerations. It will be shown later (Chapter 8) that inversion of the dien ring conformations in the trans isomer is slow under acidic conditions substantiating this proposal.

For all three isomers of [Co $dien_2]^{3+}$, both $>N^2 - H$ protons in each isomer would be expected to have the same environment and the observed $>N^2 - H$ resonance was single. The $>CH_2$ resonances were more complex under the acidic conditions than in D_2O because of coupling with $>N^2 - H$ and $-NH_2$ protons, but nevertheless the generalisations made for these $>CH_2$ resonances in D_2O were still valid. (Note that the spectra in Figure 9 (a) and (b) were recorded at 100 MHz and 60 MHz respectively.)

If the conformations of one dien ligand invert in a molecule of trans[Co $dien_2]^{3+}$, the product would be the enantiomeric form, which would have an identical PMR spectrum. However, a rapid conformational interchange in this system would produce a different PMR spectrum, as the symmetry of the molecule would effectively increase, with conformational averaging, from C_2 to S_2. Thus, in addition to the $>CH_2$ resonance being more complex in acidic solution than in D_2O because of coupling with adjacent amine protons, this region will be further complicated for the trans isomer by the decrease in molecular symmetry expected under acidic conditions. This latter consideration does not apply for the two cis isomers, where conformational averaging can occur in either solvent.

In summary, the assignment of the geometric isomers of [Co $dien_2]^{3+}$ was unequivocal from the PMR studies in aqueous solutions, and some conclusions as to the conformational situation in these isomers have been reached. In particular there appears to be rapid conformational inversion both in acid and D_2O solutions for both cis forms. In the trans isomer, conformational interchange becomes restricted in acid conditions.

PMR Studies in Non-Aqueous Solvents.

Two other solvents were investigated in the study of the isomers of $[Co\ dien_2]^{3+}$ by PMR methods. Yamasaki et al.[35] recorded the 100 MHz PMR spectra in d_6-DMSO. Although the $>CH_2$ resonances were somewhat masked by the $-CH_3$ impurity in the $(CD_3)SO$ solvent, there were two $-NH_2$ resonances for the u-cis isomer (5.08 and 4.68 ppm downfield from Me_4Si) and also two for the trans isomer (4.75, 4.18 ppm), but only one peak (4.80 ppm) for the s-cis form, consistent with the reasoning above.

The PMR spectra in trifluoroacetic acid (TFA) were qualitatively similar, but less useful. The 60 MHz spectra of the three isomers in this solvent showed all $>CH_2$ peaks to be broad and unsymmetrical, but the s-cis isomer showed a single symmetrical $-NH_2$ peak compared with unsymmetrical $-NH_2$ resonances in this region for the u-cis and trans forms. The 100 MHz spectra were similar in form, but showed more splitting as expected. The PMR spectrum of $[Co\ dien_2]^{3+}$ in TFA has been reported previously,[39] but it is apparent from the present work that the sample used was probably an isomeric mixture with trans predominating. The spectrum could not be interpreted by the previous authors.

The resonances observed in both d_6-DMSO and TFA solvents were broader than those in the less viscous D_2O solutions, and are consequently of less value for the present purposes.

CHAPTER 5

OPTICAL ROTATORY STUDIES ON THE [Co $dien_2$]$^{3+}$ ISOMERS

5.1 OPTICAL ROTATORY POWER AND THE ORIGIN OF OPTICAL ACTIVITY IN METAL COMPLEXES

The visible absorption spectra of octahedral Co(III) complexes of the type $Co^{(III)}N_6$ result from electronic transitions from the $^1A_{1g}$ ground state to the upper states $^1T_{1g}$ and $^1T_{2g}$ giving two absorption bands. However, lowering of the octahedral symmetry with chelating ligands or unsymmetric substitution results in a splitting of the degeneracy of the upper states. Theoretical calculations show that for the $^1T_{1g}$ state the splitting (which is dependent on the symmetry of the species) may be observable, but that the splitting of the $^1T_{2g}$ state is much less. Because of the nature of visible absorption spectroscopy, with characteristic broad bands arising from vibronic coupling, such small splittings are usually not detected as the broad absorptions are overlapped to such an extent that the split $^1A_{1g} \rightarrow {}^1T_{1g}$ band appears as a single peak.

If a complex is optically active however, such splittings may be observed using more sophisticated optical techniques. For an optically active compound the refractive indices and extinction coefficients for the passage of left- and right-circularly polarised light (denoted by subscripts L and R respectively) through the compound, or a solution, are different. Thus when plane-polarised light (which can be considered as being composed of the oppositely circularly polarised beams) is passed through such a medium, a difference in refractive index for one component relative to the other will result in differential velocities of the component light beams. On recombination to form plane-polarised light the plane of polarisation will have been rotated. The angle of rotation (α) is proportional to the difference in refractive indices ($n_L - n_R$), and the rotation phenomenon is therefore known also as circular birefringence. A plot of the rotation α as a function of the energy of the radiation is called optical rotatory dispersion (ORD). With the ORD technique however, because there are usually non-zero rotations at radiation energies far removed from the actual absorptions and because of the S-shape of the ORD curve (described as "anomalous", usually having both positive and negative signs) around the absorption maximum, it is difficult to resolve the curve into the individual contributions since these are often energetically very similar.

The consequence of different extinction coefficients for the passage of left- and right-circularly polarised light through an optically active compound (or its solution) is that instead of the two components combining to form plane-polarised light after traversing the medium, they form an elliptically polarised emergent wave. This ellipticity is a measure of the circular dichroism (CD), and is proportional to ($\varepsilon_L - \varepsilon_R$). For a compound to be dissymmetric, and hence optically active, it must contain no improper rotation axis (S_4) or plane (σ) or centre (i) of symmetry. The absence of these symmetry elements in a chromophore would imply that the rotational strength of any transition within that chromophore was non-zero, and therefore that the transition itself was optically active. The separate transitions constituting an unpolarised absorption maximum need not have the same sign or magnitude of rotational strength, and consequently the CD spectrum can often be resolved into the components corresponding to the individual transitions.

The appearance of a CD band as well as the anomalous rotatory dispersion associated with an electronic transition (or absorption band) is known as the Cotton Effect and can be positive or negative. For enantiomeric molecules the Cotton effects are of identical magnitudes but opposite signs.

5.2 THE ASSIGNMENT OF ABSOLUTE CONFIGURATION FROM OPTICAL MEASUREMENTS

5.2.1 INTRODUCTION

Optical activity arises from molecular dissymmetry, and is thus sensitive to molecular stereochemistry and is related to absolute configuration. However, to predict theoretically the configuration from the observed Cotton effect, the molecular factors which determine the sign and magnitude of the rotational strengths of the individual transitions must be known. While many theories of optical activity have been proposed,[87a] none are completely satisfactory in predicting the sign of the Cotton effect from first principles so that no general model is available. Nevertheless, because of the large amount of experimental information now available it is possible to determine absolute configuration from optical measurements using empirical relationships, and by reference to appropriate structures whose absolute configurations have been determined by X-ray methods.

The following discussion of such methods is intentionally brief, and sufficient only for their application to u-cis and trans[Co dien$_2$]$^{3+}$. A detailed discussion, and literature review, of these techniques is contained in a recent treatise by Hawkins.[87]

5.2.2 EMPIRICAL ASSIGNMENT OF ABSOLUTE CONFIGURATIONS USING OPTICAL METHODS

The basis of empirical methods of assignment of absolute configurations by optical methods has been (+)-[Co en$_3$]$^{3+}$, whose absolute configuration was determined by the anomalous X-ray scattering method.[81] For this ion, the first (lowest energy) ligand field absorption band $^1A_{1g} \rightarrow {}^1T_{1g}$ in the octahedral (O_h) [Co(NH$_3$)$_6$]$^{3+}$ is split into two transitions, $^1A_1 \rightarrow {}^1E_a$ and $^1A_1 \rightarrow {}^1A_2$, in the dihedral ($D_3$) field. From a single crystal CD study Mason and co-workers[88] have proposed that these transitions are polarised perpendicular and parallel, respectively, to the molecular C_3 axis. These authors deduced also that the $^1A_1 \rightarrow {}^1A_2$ transition was of slightly smaller magnitude and of opposite sign to the $^1A_1 \rightarrow {}^1E_a$ transition. This interpretation seems to have been generally accepted, but is not without its critics.[89] The present author notes however that the fundamental single crystal experiment was not extended by passing circularly polarised light through the crystal at right angles to the optic axis (and molecular C_3 axis) to excite the A_2 transitions only.

Once the transitions responsible for the observed Cotton effects had been identified, a solution (rather than a crystal) method of correlation of absolute configuration was suggested[90] using the observation[91,92] that polarisable oxyanions (such as phosphate and selenite) changed the areas of the CD bands of tris(diamine) complexes differentially by forming a conformationally ordered ion-pair (whose nature is elaborated subsequently in section 6.4.3), thus modifying the ligand field by changing the effective symmetry of the molecule. It was proposed[90] that the addition of an anion such as PO_4^{3-} to a solution of a tris(diamine) complex caused in the CD spectrum an increase in the area of the A_2 component and either a decrease or no change in the area of the E_a compound of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition.

The complexes (+)-cis$[Co(en)_2(NH_3)_2]^{3+}$ and (+)-$[Co\ penten]^{3+}$, although of lower symmetry (C_2) than (+)-$[Co\ en_3]^{3+}$ (D_3) showed the same form of CD band area changes as the tris(diamine) complex.[90] Mason proposed that although the experimental assignments of the electronic transitions of C_2 symmetry were not available, the sign of the CD band of mainly E_a (D_3) parentage (identified by the band area changes on the addition of polarisable anions) indicated that the absolute configurations of these three ions, as related by the proposed rules of the IUPAC Commission,[6] were identical.[90,93] In this way the absolute configurations of molecules can be related using measurements of optical rotatory power.

It should be noted that the above discussion pertains to five-membered chelate ring systems. The corresponding rules for six-membered ring systems appear to be less straightforward.

5.2.3 SOURCES OF OPTICAL ACTIVITY IN DISSYMMETRIC MOLECULES

The optical activity of dissymmetric metal complexes has hitherto been ascribed to three chiral sources,[94-97] whose contributions to the overall rotational strength of the d-d transitions are considered additive.

The configurational effect[87b] is due to the distribution of the chelate rings about the central metal atom. This effect is considered to arise in any molecule from any two chelate rings where the lines joining the donor atoms of each ring are skew (i.e. they have a sense of helicity or chirality). In multidentate complexes there may be several such pairs, which need not all have the same skew, and the sum of these skews constitutes the configurational effect of the molecule. This was clarified by the "ring-pairing" method proposed by Legg and Douglas,[98] and was later formulated in terms of general rules by the IUPAC Commission.[6]

The vicinal effect[87c] is due to an asymmetric atom in the chelate ring, or to asymmetry conferred on a donor atom by coordination.

The conformational effect[87d] is a contribution by the conformational chirality to the molecular dissymmetry. In some complexes (e.g. of active pn) the vicinal and conformational effects are coupled, since an asymmetric centre in the ligand may predispose the chelate ring to adopt a preferred conformation.

The CD in the visible wavelength region (ligand field absorption) is found to reflect primarily the stereochemical configuration of the chelate rings about the central metal ion. The magnitude of the CD in the UV region (charge-transfer absorption) is found to be influenced by the configurational effect, and in addition by the conformational and vicinal contributions.[95,96]

5.3 CD AND CONFIGURATION OF u-cis$[\mathrm{Co\ dien}_2]^{3+}$

It was stated earlier (section 1.3) that u-cis$[\mathrm{Co\ dien}_2]^{3+}$ (Figure 3) had only a two-fold rotation axis (molecular point symmetry C_2) and hence exists in optical isomers. The dissymmetry arises primarily from a configurational effect. The active forms of this isomer were found to be optically stable in basic conditions (section 3.3) in the same way as active $[\mathrm{Co\ en}_3]^{3+}$ whose dissymmetry is also ascribed predominantly to the configurational effect, whence racemisation would have to involve gross rearrangement of the chelate rings.

Some contribution to the chirality of u-cis$[\mathrm{Co\ dien}_2]^{3+}$ would also be expected from the conformations, as it is probable that there would be a stereospecific preference for one or more of the five possible conformational combinations (section 4.3.2). There should be no vicinal effect as there are no asymmetric centres in the ligands. However, in their studies of stereospecificity in the chelation of aspartic acid, Legg and Douglas[99] attributed the difference in the CD spectra of $[\mathrm{Co(NH_3)_3(S\text{-}Asp)}]^+$ and $[\mathrm{Co(dien)(S\text{-}Asp)}]^+$ to a (vicinal + conformational) contribution of coordinated dien resulting from the different conformations of the rings attached to the $>N^2$ - H atom.

u-cis[Co dien$_2$]$^{3+}$ was resolved into optical isomers (section 3.3) and the ORD and CD spectra for the (+)-enantiomer are shown (Figures 10 and 11). The results show that (+)-*u-cis*[Co dien$_2$]$^{3+}$ in aqueous solution gives a major positive and minor negative CD band, at a lower and higher frequency respectively, in the spectral region of the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption of the Co$^{(III)}$N$_6$ chromophore. The areas of these CD bands were diminished and enhanced, respectively, by the addition of the polarisable oxyanion selenite. The signs and relative frequencies and magnitudes of the lower energy CD bands of (+)-*u-cis*[Co dien$_2$]$^{3+}$, and the changes in band area on the addition of selenite are similar[90] to the analogous CD bands of (+)-[Co en$_3$]$^{3+}$, (+)-*cis*[Co(en)$_2$(NH$_3$)$_2$]$^{3+}$, and (+)-[Co penten]$^{3+}$, from which it is concluded that the (+)-*u-cis*-[Co dien$_2$]$^{3+}$ complex has the same configuration (Figure 12) as these complex ions which also contain the Co$^{(III)}$N$_6$ chromophore.

Absolute X-ray crystal structure analyses,[81,100] and CD studies[93] have shown that the (+)-[Co en$_3$]$^{3+}$,[81] (+)-*cis*[Co(en)$_2$(NH$_3$)$_2$]$^{3+}$ and (+)-[Co penten]$^{3+}$ [100] are configurationally related, (Λ,Λ, and ΛΛΔ(Λ) respectively,[6] where the brackets indicate the net or predominant configuration obtained by "ring-pairing" the three sets of skew lines in the (+)-[Co penten]$^{3+}$ molecule). On application of the nomenclature to (+)-*u-cis*[Co dien$_2$]$^{3+}$, Figure 12 shows that while the rings II and IV have a mutual Δ chirality, the two pairs I and IV, and II and III, have a

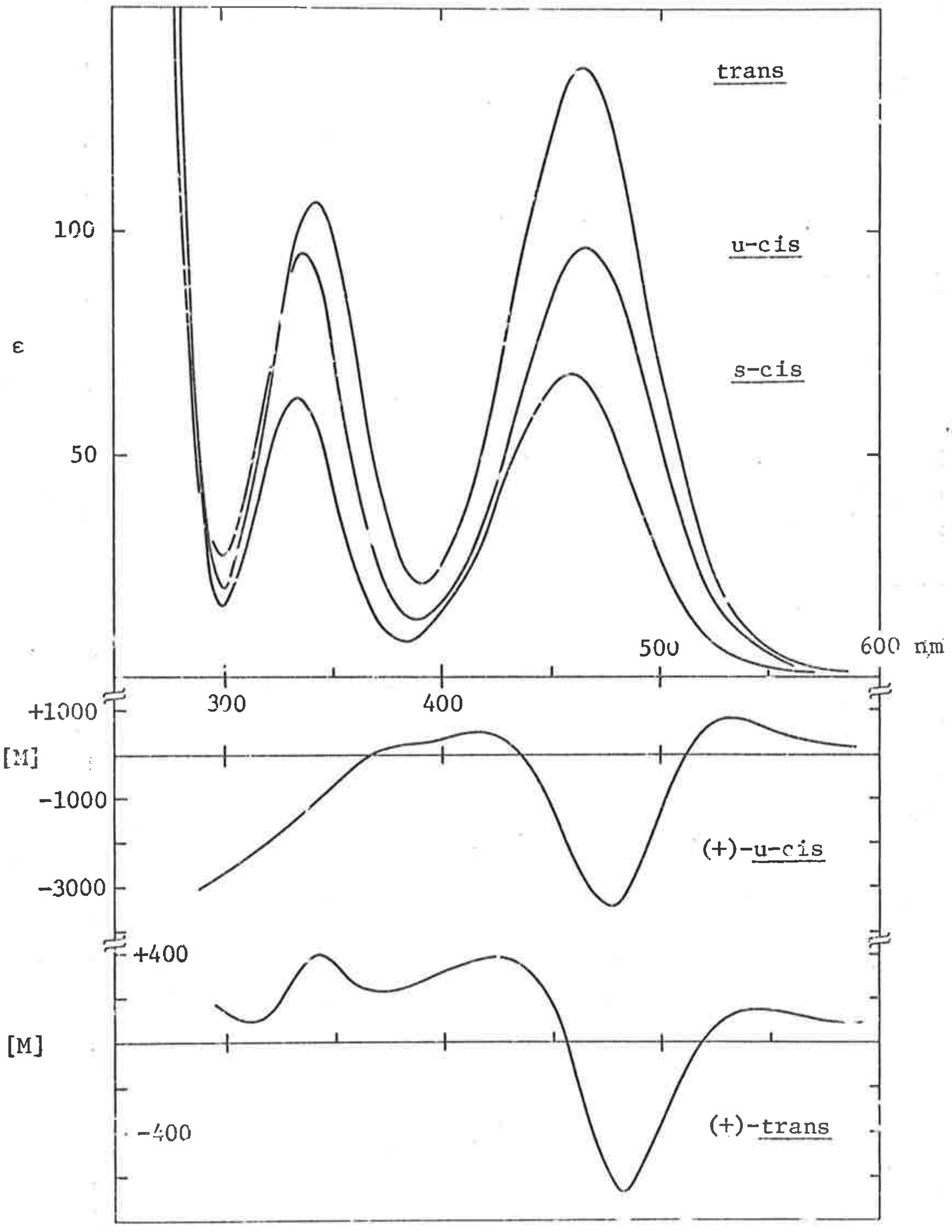


Figure 10. - Absorption and ORD spectra of the [Co $\text{dien}_2]^{3+}$ isomers.

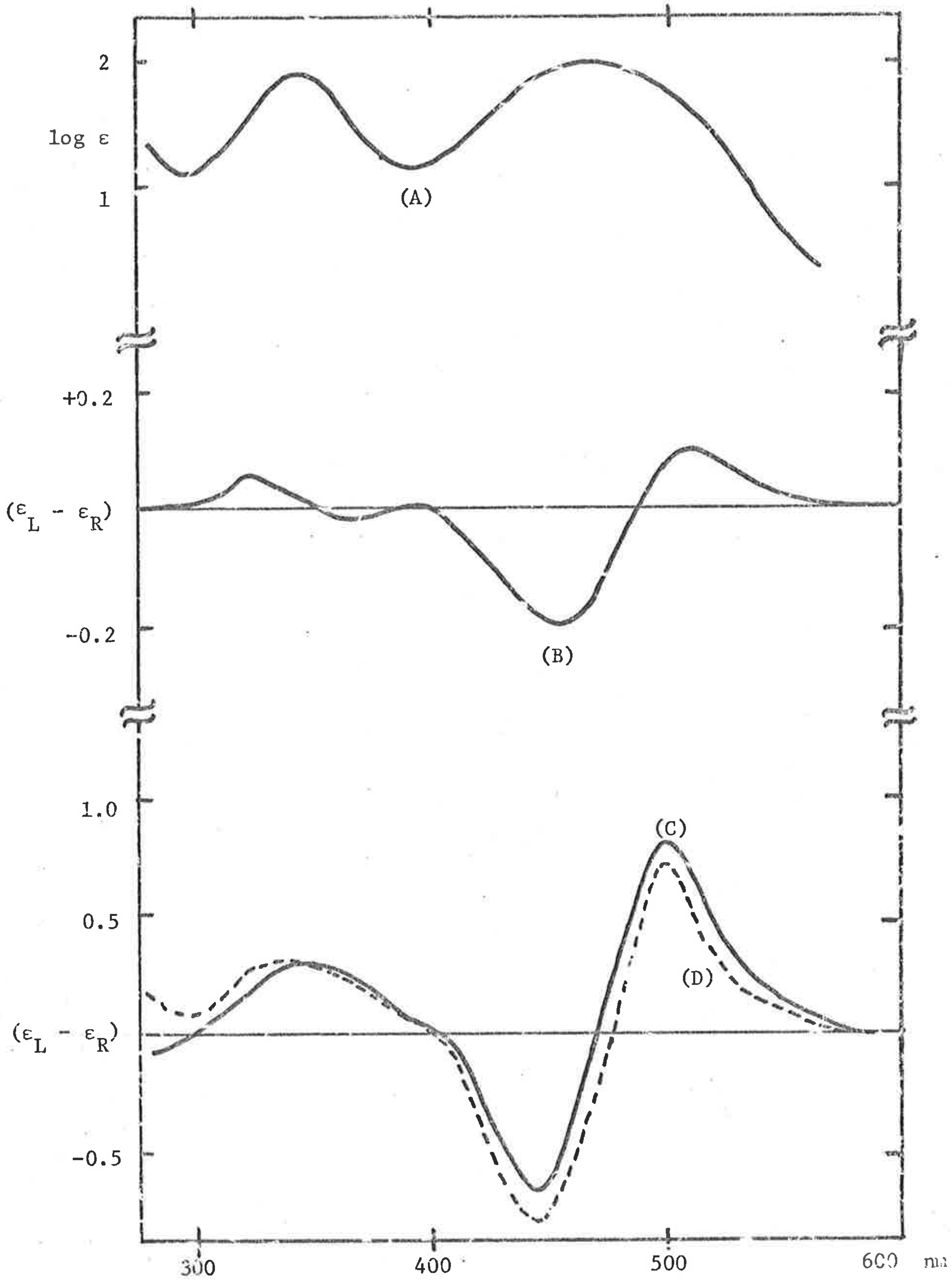
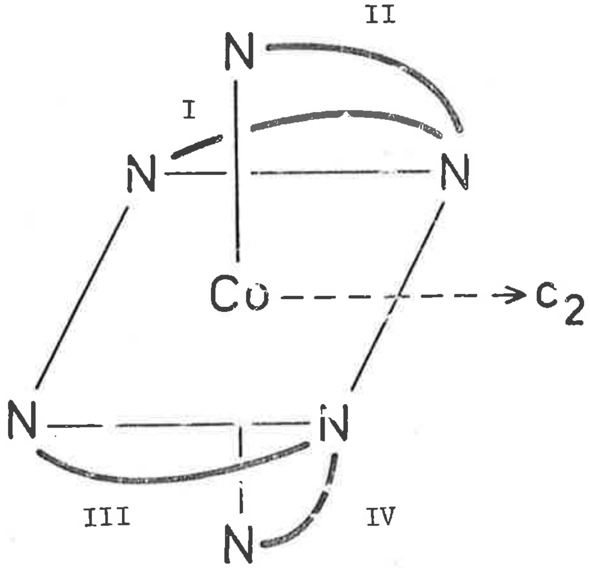


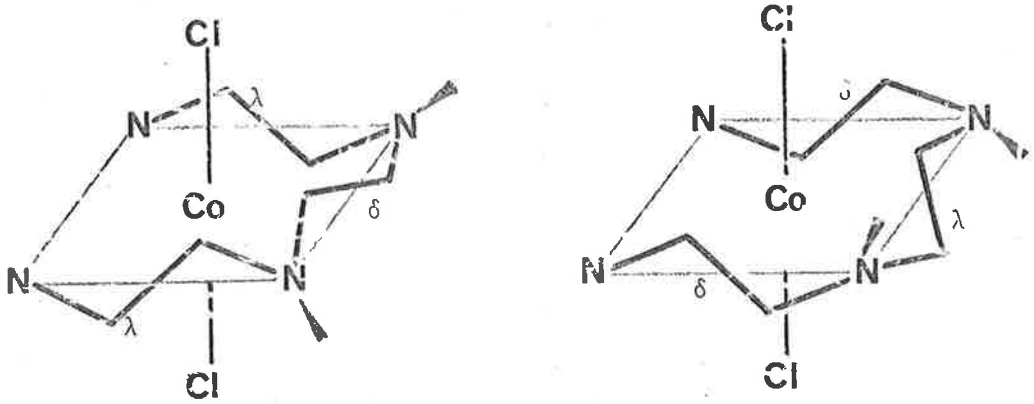
Figure 11. - The absorption spectrum (A) and the CD (B) of (+)-trans[Co dien$_2$]$^{3+}$ in 0.1M HClO$_4$, and the CD of (+)-u-cis[Co dien$_2$]$^{3+}$ in water (C) and in 0.2M sodium selenite (D).



(+) optical isomer

Λ absolute configuration

Figure 12. - The absolute configuration of (+)-u-cis[Co dien$_2$]$^{3+}$.



trans-RR-[Co trienCl$_2$]$^+$

trans-SS-[Co trienCl$_2$]$^+$

Figure 13. - Optical isomers of trans[Co trienCl$_2$]$^+$.

mutual Λ chirality, giving the configuration ΛΛΔ. By the ring-pairing scheme the overall configuration of the molecule *u-cis*[Co dien$_2$]$^{3+}$ shown in Figure 12 is Λ, like that of (+)-[Co penten]$^{3+}$ [100] where the ring-pairing relations are closely analogous,[93] the two complex ions differing only in that in [Co penten]$^{3+}$ there is a fifth chelate ring bridging the two secondary nitrogen atoms of *u-cis*[Co dien$_2$]$^{3+}$.

The determination of the absolute configuration of (+)-*u-cis*-[Co dien$_2$][Co(CN)$_6$] by X-ray structural analysis is in progress.[36]

5.4 CD AND CONFIGURATION OF *trans*[Co dien$_2$]$^{3+}$

Trans[Co dien$_2$]$^{3+}$ is capable of optical activity provided that the $>N^2 - H$ bonds remain in fixed dispositions (section 1.3). An aspect of particular interest with this molecule however is the origin of the dissymmetry, and to consider how far this can be expressed in terms of the conventional chiral sources (section 5.2.3).

In principle, the configurational and conformational effects are vanishing for this isomer. Figure 3 indicates that if the atoms of each chelate ring are taken to be coplanar, the structure has two planes of symmetry and two C_2 axes (there is also an S_4 axis mutually perpendicular to the two C_2 axes shown in the figure) so that the stereochemical disposition of the chelate rings about the metal ion is non-chiral. Figure 4 shows the chelate ring conformations which must obtain in the optical isomers. When these ring conformations are considered the planes of symmetry in Figure 3 disappear and the S_4 axis is destroyed (although each coordinated ligand retains a mirror plane as in Figure 4), but one of the C_2 axes remains and relates the two ligands in the molecule. The point group is thus reduced from S_2 (ring atoms taken to be coplanar) to C_2 by the ring conformations. A vicinal effect should not arise since the two chelate rings constituting each dien ligand are (in principle) mirror images. It is also evident that for each dien ligand the conformational effect is internally compensated, one chelate ring having a δ conformation and the other the λ conformation. Thus the conventional sources of chirality, configurational and conformational and vicinal effects, are not present in this molecule.

The dissymmetry of the molecule is due to another chirality type which is exemplified and uniquely described by the stereochemical relationship between the two trans N^2-H bonds of the secondary nitrogen atoms in the two ligands (Figure 4). These two N-H bonds form a segment of either a right-handed or a left-handed helix taking either N-H bond as the helix axis according to the IUPAC convention,[6] and the absolute configurations of the optical forms of the trans[Co dien$_2$]$^{3+}$ complex may be designated as trans-δ-NH and trans-λ-NH respectively (Figure 4). This source of chirality in such amine complexes can therefore be described as the "N-H chiral effect".

However the dissymmetry is not due solely to the presence of the N^2-H bonds as the structure would retain dissymmetry even if such bonds were absent, for example if a sulphur donor replaced the secondary amine group. The same type of symmetry relationship holds between any of the C_2-related C-H, N-H, N-C or C-C bonds in the two ligands and these individual bond chiralities should all contribute to the overall helicity of the molecule. The absolute configuration can therefore be described by any of these bond relationships (these are not all of the same skew, δ or λ) and the N^2-H bonds have been chosen as the simplest description for this complex as this means of nomenclature lends itself more generally to a wider variety of potential ligands. With sulphur donors for example, the lone pair directions might be employed in an analogous stereochemical situation. An alternative designation for the absolute configurations of the trans[Co $dien_2]^{3+}$ optical isomers could be in terms of the left-handed (minus) or right-handed (positive) helicity of the two N^2-H bonds about the C_2 axis, $M(C_2)$-NH or $P(C_2)$-NH respectively (Figure 4).

Such chiral effects as described above have not hitherto been realised as contributing effects to optical activity in metal polyamine complexes, but should be present in complex systems such as [Co $trienX_2]^+$ in addition to the conventional sources of chirality. The activity of resolved trans[Co $trienCl_2]^+$ (Figure 13) has been attributed to the conformations of the chelate rings and the two asymmetric secondary nitrogen atoms.[87e] The present work indicates however that these conventional sources of chirality will not fully explain the observed CD, and that there will be a contribution from a bond-pair chirality of the type described above and again typified by the stereochemical relationship of the two $>N^2$ - H bonds. In a similar way, for optically active cisα- and cisβ[Co $trienX_2]^+$, u-cis[Co $dien_2]^{3+}$, and all puckered ring systems of multidentate ligands such as linear-tetraen and linear-penten, this previously unrealised source of chirality would be expected to contribute overall molecular chirality.

Although the contribution of "N^2-H chiral effects" to optical activity of polyamine complexes has not previously been appreciated the stereochemical basis is not new. An N^2-H bond fixed in one of two alternative dispositions will confer isomerism providing these alternative dispositions can be distinguished. In trans[Co $\text{dien}_2]^{3+}$ the alternative dispositions of one $>N^2$ - H are distinguished with reference to one fixed disposition of the other $>N^2$ - H bond in the molecule. Due to the particular symmetry properties of this molecule the "N-H chiral effect" is the only contribution to the dissymmetry, since these coordinated nitrogen atoms themselves are not asymmetric. In complexes of N-Meen and sarc the secondary amine nitrogen becomes asymmetric on coordination (donor atom asymmetry) and the optical activity arises from vicinal and conformational effects. In these instances with only one $>N^2$ - H bond however the chiral effect does not arise since there is no second reference group or bond.

A similar situation to that in trans[Co $\text{dien}_2]^{3+}$ arises in the case where dien is coordinated meridionally in the system $[\text{Co(en)(dien)Cl}]^{2+}$, shown in Figure 5. Here the two alternative dispositions of the single N^2-H bond can be distinguished by reference to the chloro ligand which is cis to the donor secondary nitrogen. This creates two geometric isomers,[9] but optical isomers are not possible as there is no "N-H chiral effect" nor vicinal effect, and the conformational contributions in the coordinated dien cancel as in trans[Co $dien_2]^{3+}$.

Trans[Co $dien_2]^{3+}$ was resolved into its enantiomers under acidic conditions (section 3.2), where they are optically stable.

The ORD and CD spectra of (+)-trans[Co $dien_2]^{3+}$ are given in Figures 10 and 11. The CD spectrum has a minor positive and major negative CD band at a lower and higher frequency respectively in the spectral region of the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption of the octahedral $Co^{(III)}N_6$ chromophore. The bands have the same signs and similar magnitudes to those given by $[Co(+)pn(NH_3)_4]^{3+}$ [97] (no rotation sign was given for the complex in reference 97) or $(-)\text{-}[Co(N\text{-}Meen)(NH_3)_4]^{3+}$,[101] where the optical activity derives in each case from a single asymmetric centre in the ligand and a single puckered ring. The CD spectrum indicates that the trans "NH chiral" element gives rise to optical rotatory effects comparable in magnitude to those of the (conformational + vicinal) effect of a single fixed puckered chelate ring.

Although the measurements in the UV region were taken down to 185 nm (CD optical density detection limit 1 in 10^5), no CD response was recorded over this region for the trans isomer. Thus the CD in this charge transfer region, where ε_{max} = 39,000 at 222 nm, cannot be larger than about 0.3 compared with -30 for (+)-[Co $en_3]^{3+}$ or +12 for (+)-trans$[Co(-)pn_2(NH_3)_2]^{3+}$.[95] This indicates that the conformational contribution to the optical activity of trans[Co $dien_2]^{3+}$ is negligible, since any such contribution would be expected particularly in this region[95,96] (section 5.2.3), and justifies the assignment of the observed CD bands in the ligand field region to the "NH chiral effect".

The recorded CD does not however distinguish between the two structures of trans[Co dien$_2$]$^{3+}$ shown in Figure 4. Because of the unique symmetry properties of this molecule no suitable systems are available as references, so that at this stage only an absolute X-ray crystal structure analysis would allow the absolute configuration to be determined. An attempted crystal structure of (-)-trans[Co dien$_2$]Br$_2$-(ClO$_4$).2H$_2$O is reported in Chapter 9.

The molecular models indicate some crowding in one quadrant of trans[Co dien$_2$]$^{3+}$, shown shaded in Figure 4. Such crowding might be relieved by distortion of one chelate ring of each dien ligand. Optical activity could then arise from asymmetry of charge about the $>N^2 - H$ group since the helical contributions of the conformations δ and λ would not cancel (as the rings of each ligand would no longer be related by the plane of symmetry depicted in the Figure 4). Any such distortion in the solid state should be evident from a crystal structure analysis.[36] The solution CD has indicated however (see above) that any such distortion is evidently too small to be detectable by this means.

5.3 EXPERIMENTAL

ORD curves were recorded on a Perkin-Elmer P22 Recording Spectropolarimeter using ca. 0.3% solutions in 0.01M HBr.

The CD spectra were recorded on a Jouan CD 185 Dichrographe (by courtesy of Prof. S.F. Mason, School of Chemical Sciences, University of East Anglia, Norwich, U.K.*).

---

* Present address, Department of Chemistry, University of London,
King's College, U.K.

CHAPTER 6

EQUILIBRIUM ISOMER PROPORTIONS AND THEIR DEPENDENCE ON ENVIRONMENTAL PARAMETERS

6.1 FACTORS DETERMINING RELATIVE ISOMER STABILITIES

Introduction.

Some of the factors affecting relative isomer stabilities of coordination compounds have been appreciated for many years, but the quantitative estimation of these factors from theoretical considerations has been a relatively recent development. In coordination chemistry, the phenomenon of preference of one geometric isomer or internal diastereoisomer over another is termed stereospecificity. Such an effect is usually observed in situations where a dissymmetric chelate complex (e.g. of the tris(bidentate) type) contains an asymmetric (optically active) ligand of one configuration and the two optical forms of the complex, which are internal diastereoisomers, are not obtained in equal amounts. From early experimental studies,[102-104] such stereospecific effects were at first considered to be absolute, and the discussions of the free energy differences were in the qualitative terms of the gross steric effects, non-bonded interactions and bond angle strains, which were observable from models. However, the puckered nature of chelate rings[81,105-108] of many coordinated ligands, such as ethylenediamine, introduce more subtle conformational effects which contribute significantly to stereospecificity. It is proposed to outline in this section the development of ideas and methods to estimate the various factors involved, to provide a basis on which to discuss the present experimental results in the subsequent sections.

Corey and Bailar Calculations.

The first quantitative assessment of the energetics involved in the specificity caused by non-planar chelate rings was made in 1959 by Corey and Bailar,[80] using essentially the methods of conformational analysis which had been established for analogous flexible carbocyclic rings in organic chemistry by that time. The two possible enantiomeric conformations of the M-en ring, δ and λ (section 1.2, Figure 1), are equal in energy in isolation where they are geometrically equivalent (e.g. in $[M(NH_3)_4en]^{n+}$). In the tris-chelate M en_3 system however, the four possible conformational combinations for each optical configuration (Λ or Δ)[6] about the central atom (δδδ, δδλ, δλλ, and λλλ) will have different energies because they involve different non-bonded atomic interactions. The above authors using the potential function of Mason and Kreevoy,[109] assessed these interactions as giving rise to an "energy difference" between the most stable Λδδδ/Δλλλ and the least stable Λλλλ/Δδδδ conformers of 1.8 kcal $mole^{-1}$, or 0.6 kcal $mole^{-1}$ per chelate ring. In the former pair of conformers the C-C bonds of each ligand are parallel (<u>lel</u>) to the molecular C_3 axis whereas they are oblique (<u>ob</u>) to that axis in the latter case, so that the energy difference 1.8 kcal $mole^{-1}$ essentially represents the difference between three <u>lel</u> conformations and three <u>ob</u> conformations.

In the coordination of en analogues which form five-membered chelate rings, the same conformational possibilities have to be considered, but with amines substituted on either the C or N atoms another factor is involved in the determination of the stereochemistry. With active pn, the C-substituted methyl group can be either axial or equatorial to the overall plane of the ring (defined by the metal and two donor nitrogen atoms) depending on the ring conformation. Corey and Bailar[80] estimated that there would be a difference of at least 2 kcal $mole^{-1}$ between these axial or equatorial situations in favour of the methyl group being equatorial where non-bonded interactions of the methyl substituent are substantially less. With coordinated R(-)pn, where the ring conformation would always be λ to maintain the methyl group equatorial, regardless of the configuration Δ or Λ of ligands about the metal, there would be an expected energy difference between the optical forms $\Delta\lambda\lambda\lambda[Co\ en_2(-)pn]^{3+}$ (all conformations <u>lel</u>) and $\Lambda\delta\delta\lambda[Co\ en_2(-)pn]^{3+}$ (two conformations <u>lel</u>) of 0.6 kcal $mole^{-1}$ in favour of the Δ diastereoisomeric ion. Such a difference in energy would not lead to absolute stereospecificity (K_{calc} = 2.8/1) so that isolation of both ions should be possible. Stereospecific effects in the analogous complex systems $[Co(en/pn)_3]^{3+}$ were rationalised in a similar way.

In the theoretical predictions of Corey and Bailar[80] only non-bonded atomic interactions between the strain-free gauche conformations δ and λ were considered. No account was taken of the contribution to the free energy of what were referred to as the "entropy effects" of solvation,

ion-association, lattice forces, or statistical effects. Since the molecules being compared were similar in overall shape, size and nature it was suggested that such differences would be small.

Dwyer's Experimental Work on Stereospecific Systems of Bidentate Ligands.

At the same time, Dwyer was undertaking an extensive experimental study of stereospecific systems. In the equilibrium preparations of the systems $[Co\ pn_3]^{3+}$ [48,65] and $[Co\ en_{3-x}(-)pn_x]^{3+}$, [49] the close agreement between experimental free energy differences (ΔG^o) between pairs of isomers and the calculated enthalpy differences (ΔH^o)[80] tended to support the above contention of Corey and Bailar, after a statistical weighting favouring the "mixed ligand" complexes such as $[Co\ en_2(-)pn]^{3+}$ or $[Co(+)pn(-)pn_2]^{3+}$ had been applied to the calculations. The agreement, coupled with the substantially correct prediction of the shape of the M-en ring using methods of vector analysis,[80] led to wide acceptance of the Corey and Bailar method of conformational analysis at the time.

It is noted at this point however that subsequent calculations[110] on the $[Co\ en_{3-x}(-)pn_x]^{3+}$ system using energy minimisation techniques (which will be outlined later) have indicated that the ΔH^o values of Corey and Bailar[80] were probably overestimated. The contribution of the "entropy effects" to ΔG^o is probably not negligible therefore and the close agreement with Dwyer's results may have been somewhat fortuitous.

From the experimental figures of Dwyer for the energy differences between <u>lel</u> and <u>ob</u> conformations in these pn complexes, the conformer proportions in a solution of [Co en_3]$^{3+}$ may be calculated[111,112] as (for the Λ configuration) δδδ (tris-*lel*):δδλ:δλλ:λλλ (tris-*ob*) = 59:29:8:4. The proportion of the Λδδλ/Δλλδ (*lel lel ob*) form thus appears to be quite significant. The mixed conformers λλδ and λδδ should be favoured statistically over the forms δδδ and λλλ, but the above calculations have not included this statistical weighting. When such allowance is made the *lel lel ob* arrangement might become the most favoured, and this is discussed further below.

Bond Angle Strain in Multidentate Ligand Systems.

With multidentate ligand systems, the various geometric isomers must involve different bond angles at the donor atoms bridging adjacent chelate rings. Dwyer[14] applied the above mentioned gross steric effects qualitatively to the systems [Co $dien_2$]$^{3+}$ and [Co $trienX_2$]$^{+}$. For the dien system, consideration of bond angle strain about the secondary nitrogen groups of the dien ligands led to the prediction that the *cis* forms should be more stable than the *trans*. The *trans* isomer should be more favoured however on the basis of non-bonded atomic interactions only. As the relative magnitudes of these two effects, together with any conformational effect, was unknown it was concluded that there may be appreciable amounts of both *cis* (facial) and *trans* (meridional) forms present at equilibrium.[14] The present work indicates this to be substantially correct, and the greater stability observed for the *trans* form implies, on the basis of the above qualitative argument, that the bond angle strain factor is not the dominant effect.

For the [Co trienX_2]$^{n+}$ system (Figure 2), it was similarly deduced that on the basis of bond angle strains at coordinated sec-N, "angular" coordination of adjacent rings would be energetically more favourable than "planar" coordination, and accordingly the stability order of the three isomers should be cisα > cisβ > trans.[14] However non-bonded interactions would be expected to be greater for the cisα than the cisβ form. The opposing nature of these two steric effects suggests that the two cis forms could be of comparable stabilities. The above stability order has subsequently been established for [Co trien$(NO_2)_2$]$^+$ in aqueous media.[1] Although the cisα is generally more stable than cisβ, the α/β ratio is modified by the acido substituents, and in [Co trien$(OH_2)_2$]$^{3+}$ the cisβ isomer is favoured. Such dependence of relative isomer stabilities on acido substituents has also been noted in other cobalt(III)-quadridentate ligand systems.[113]

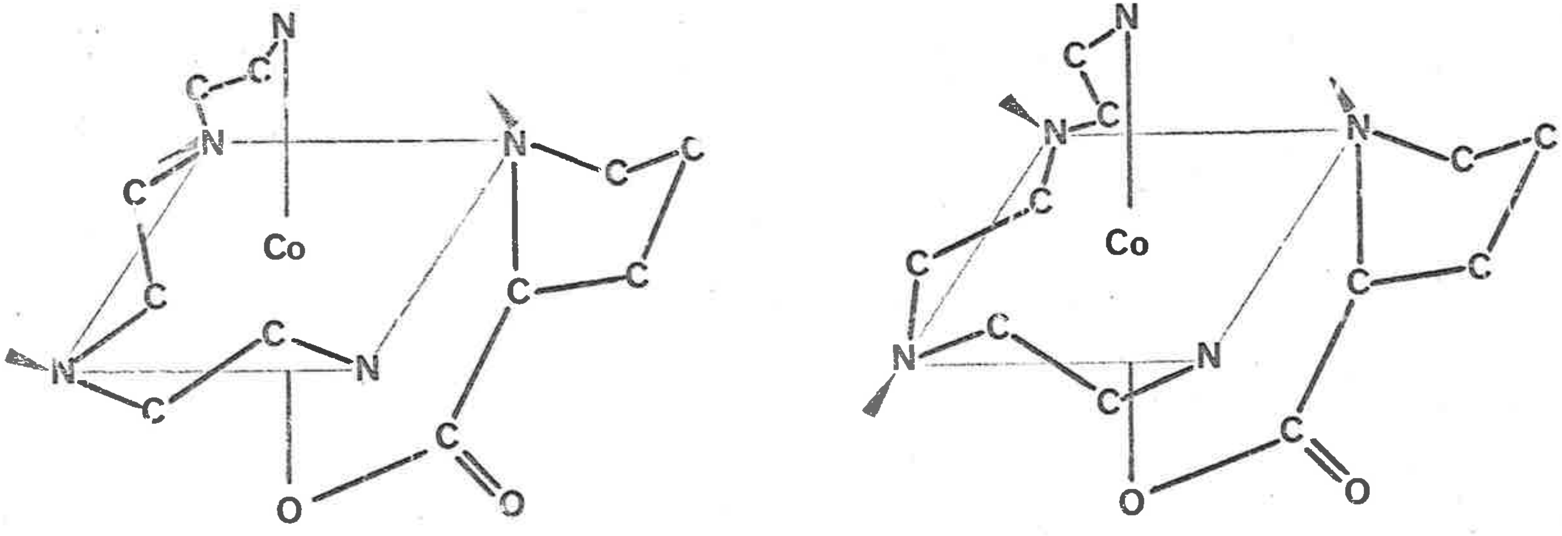
A priori Calculations of Non-Bonded Interactions.

Because of the apparent quantitative success of the Corey and Bailar method,[80] qualitative considerations such as those above were superseded by semi-quantitative a priori calculations[114] of enthalpies associated with non-bonded atomic interactions. This method involved measurement of these non-bonded distances from accurate scale models (Dreiding) assuming bond angles to be octahedral at the metal atom and tetrahedral around each C and N atom, and the various bond lengths to be average crystallographic distances. The most significant non-bonded interactions were minimised as much as possible in the model by rotation of substituent groups, and adjusting ring conformations within the flexibility allowed by the models, and the non-bonded distances were then measured directly. The repulsions associated with these non-bonded atomic interactions were computed using the potential function of Hill,[115] and summed for the molecule. This potential function, which is more conservative than that of Mason and Kreevoy[109] (used by Corey and Bailar[80]) was preferred as the Mason-Kreevoy expression may overestimate these repulsions.[116,117] Such calculations of energy differences have been made by Sargeson, Buckingham and co-workers for the systems $[\mathrm{Co\ en_2sarc}]^{2+}$,[118] $\Lambda\beta$-SS- and $\Lambda\beta$-SR-$[\mathrm{Co\ trienX_2}]^{+}$,[2] β_1- and $\beta_2[\mathrm{Co(trien)(sarc)}]^{2+}$,[119] $[\mathrm{Co(NH_3)_4}$-$\mathrm{(N\text{-}Meen)}]^{3+}$,[101] and trans, trans$[\mathrm{Co(N\text{-}Meen)_2(NO_2)_2}]^{+}$,[120] and by Gollogly and Hawkins for $[\mathrm{Co(Me\text{-}penten)}]^{3+}$.[117] For the above systems satisfactory agreement was obtained between the enthalpy calculations (ΔH^{o}) and the experimentally observed stereospecificity (ΔG^{o}). In the same way as for previous conformational analyses,[80] the *a priori* calculations considered only the contribution of non-bonded interactions to the enthalpy. The notable improvement of the *a priori* method was the quantitative assessment of every serious interaction and the use of a more appropriate function, and some minimisation of the interactions was achieved by the use of models.

As more complicated molecules were considered along the above lines some marked discrepancies emerged between the theoretical predictions of these calculations and experimental results. Maxwell et al. found that the two *β_2* isomers of $[Co(trien)(S\text{-}Pro)]^{2+}$ (S-Pro = S-Proline = $\overline{NHCH_2CH_2CH_2CH}COO^-$), shown in Figure 14, were formed in about equal abundance whereas *a priori* calculations had indicated that considerable stereospecificity was likely in favour of the (-)-*β_2* form of the complex.[121] X-ray crystal structures of these complexes,[121,122] showed that what were expected to be severe non-bonded interactions from models had been alleviated by slight bond twisting and small changes of bond angles. The validity of calculations based on rigid models with fixed bond lengths and angles thus became questionable.

Energy Minimisation Procedures.

Since Maxwell's work in 1969, the quantitative and more thorough approach of energy search and minimisation procedures has been developed, aided by advances in computer technology to allow the processing of a large number of variables. The most popular of these approaches for application to inorganic systems was originated by Boyd,[123] and the method has been developed and modified by Snow[124-126] and Maxwell,[126-128] and subsequently, independently by Hawkins,[129,130] and Dwyer,[131] and applied to the following systems: $[Co(tetraen)Cl]^{2+}$,[125,126] Co(III) complexes of tn,[132,133] *β_2*$[Co(trien)(S\text{-}Pro)]^{2+}$,[121,126] ring conformations in Co(III) *β*-trien systems generally,[127] $[Co(trien)(N\text{-}Me\text{-}(S)\text{-}ala)]^{2+}$,[128] ring conformations of coordinated en, pn and N-Meen ligands coordinated to Co(III),[129,130] *sym*$[Co(trenen)Cl]^{2+}$ [131] and *sym*$[Co(trenen)N_3]^{2+}$,[131] *sym*$[Co(Me\text{-}trenen)Cl]^{2+}$ [131] and *trans*, *trans*$[Co(N\text{-}Meen)Cl_2]^+$.[131]



$(-)$-$\underline{\beta}_2$-RRS-$[Co(trien)(S\text{-}Pro)]^{2+}$

$(+)$-$\underline{\beta}_2$-SSS-$[Co(trien)(S\text{-}Pro)]^{2+}$

Figure 14. - The diastereoisomeric forms of $\underline{\beta}_2[Co(trien)(S\text{-}Pro)]^{2+}$.[121]

The energy minimisation technique considers the total strain energy U of the molecule as being separable into several components:

$$U = E_B + E_{NB} + E_\theta + E_\phi + E_{other}$$

where E_B = bond length deformation terms

E_{NB} = non-bonded interaction potentials

E_θ = bond angle deformation terms

E_ϕ = torsional energy, and

E_{other} represents other terms contributing to the strain energy, but these are ignored in the calculations. Using a suitable force field, the total strain energy can be minimised by allowing the atomic coordinates to vary continuously. (The method of Hawkins[129,130] differs in that it considers the strain energy as a function of independent geometric variables which are varied one at a time.) Such calculations yield the equilibrium energy of the molecule and its detailed geometry, and although there is uncertainty in the arbitrary energy zero associated with U, similar molecules can be compared in terms of energy differences ΔU, which are equivalent to differences in enthalpy (ΔH^o).

The enthalpy differences thus calculated have generally been found to be close to experimental free energy differences observed in stereospecific systems.[124-128] The prediction of geometry by the method has generally been quite satisfactory where X-ray structural data is available, and some discrepancies have been satisfactorily correlated with the effects of lattice forces which can occur in the crystalline form.[125] The energy minimisation method is considerably more sophisticated than the previous methods as it considers all the major contributors to the force field. It will for example, explain the energy situation and geometry for the $\underline{\beta}_2[Co(trien)(S\text{-}Pro)]^{2+}$ system,[121,126] by which the *a priori* calculations were discredited.

Limitations of These Calculative Procedures.

Energy minimisation has so far been limited to calculating enthalpies arising from intramolecular effects only, $\Delta H^o_{intramolec}$, corresponding to a hypothetical isolated ion in the gas phase, and intermolecular interactions have not been considered. The experimental energy differences are however free energies, ΔG^o_{expt}, as assessed from the measured equilibrium position, K. They will therefore involve the terms which have been referred to earlier in this section as "entropy", and which will include solvation, ion-association, lattice effects and statistical considerations. The relationships may be set out in equation form as follows.

$$\Delta G^o_{expt} = \underset{\text{(calc from energy minimisation)}}{\Delta H^o_{intramolec}} + \text{"entropy terms"}$$

$$= \Delta H^o_{intramolec} - T\Delta S^o_{intramolec} + \Delta H^o_{intermolec} - T\Delta S^o_{intermolec}$$

The broad classification of these intermolecular interactions as "entropy effects" is somewhat misleading as the factors mentioned may involve contributions from both entropy and enthalpy. Experimental results do indicate that these intermolecular interactions with counter-ions and solvent may have a considerable bearing on stereospecificity, as discussed briefly below. Although the magnitude of these interactions individually cannot be estimated, their sum may be obtained from the difference between the ΔG^{o}_{expt} and the calculated $\Delta H^{o}_{intramolec}$ figures, but this difference cannot be divided into the enthalpy ($\Delta H^{o}_{intermolec}$) and entropy contributions ($T\Delta S^{o}_{intramolec} + T\Delta S^{o}_{intermolec}$). The thermodynamic consequences of intramolecular and intermolecular interactions will be discussed in the following section (6.2).

Recent PMR, CD, and X-ray Evidence on Preferred Ring Conformations.

The early calculations of Corey and Bailar[80] on the conformations of coordinated en indicated that lel rings were preferred. The most stable conformer of $[Co\ en_3]^{3+}$ was predicted[111,112] to be Λδδδ/Δλλλ (59%), although a significant proportion (29%) of the conformer Λδδλ/Δλλδ should exist in solution. However the PMR spectra of several $[M\ en_3]^{n+}$ complexes (M = Ru(II), Pt(IV), Ni(II), Rh(III), Ir(III), Co(III)) have recently been re-examined under high resolution,[85,86,134] and have been interpreted to indicate rapid conformational inversion, with the most abundant conformer being the racemic pair Λδδλ/Δλλδ and not Λδδδ/Δλλλ. This result is not unexpected from statistics, which would favour the mixed conformer situation (see above). The addition of polarisable anions such as PO_4^{3-}, SeO_3^{2-}, and SO_4^{2-} however, considerably modifies PMR[85,134] and CD[135] spectra, which suggests specific association by these ions. These two spectral techniques are the most important methods for study of conformations in solution as they are strongly dependent on molecular symmetry. In the PMR spectra of these complexes, the form of the $>CH_2$ resonance will depend on the number of different environments in which such protons are situated and thus depend on the molecular symmetry. A conformational change will alter this symmetry, and will be reflected in a change in the form of that resonance (section 4.3.3). Similarly for the CD spectra, a symmetry change of the molecule resulting from conformation change will alter the electronic energy levels and the CD spectrum will change, either in the relative intensities of bands or in the splitting of the band constituents (section 5.1).

The only other method available at present for conformational study is X-ray crystallography of ions in the solid state. By this method, $[Cr\ en_3]^{3+}$, in combination with various anions, has been shown to exist in the four possible conformer combinations in the solid state,[82-84] presumably because of specific stabilisation due to hydrogen bonding and lattice effects. The bulk of X-ray structural evidence on amine complexes to date however indicates that the tris-lel form is preferred in non-hydrogen bonded structures, but this is probably a lattice packing effect as it is apparently not the most stable conformer in solution (from PMR evidence, see above). These lattice effects, as part of the intermolecular contribution to free energy, are only involved in the solid state, so that preferred forms in the solid need not be the predominant forms in solution.

Effects of Solvation.

Solvation would also be expected to contribute to the free energies, especially in the case of cationic complexes which are likely to be highly solvated. The magnitude of this effect could be considerable as for example in the $[Co\ trienCl_2]^+$ system[1] where cisβ$[Co\ trienCl_2]^+$ isomerises to the trans isomer in methanol solution (cf. $[Co\ en_2Cl_2]^+$), whereas no trans$[Co\ trienX_2]^+$ species have been isolated from aqueous solutions to date.

Other Experimental Measurements of Isomer Stabilities.

Much of this discussion has involved bidentate amine complexes. Only in recent years have experimental determinations of equilibria, coupled with some form of calculation of stereospecific effects been made for more complex systems, and a number of these have been referred to above. Other instances of systems involving five-membered chelate rings which have been studied in this way include the following.

Legg and Cooke[31] considered the bis(tridentate) systems $[Co(dien)(IDA)]^+$ and $[Co(dien)(MIDA)]^+$, both of which have the same geometric possibilities as $[Co\ dien_2]^{3+}$, and they rationalised the observed equilibrium isomer proportions with qualitative conformational analyses and statistical arguments. The bis(tridentate) systems $[Co(dien)(S\text{-}Asp)]^+$ [99] and $[Co(IDA)_2]^-$ [136] have been studied in the same way.

For complexes of tetradentate ligands, stereospecific effects in $[Co\ trienX_2]^+$,[1] $[Cr\ trienX_2]^+$,[137] and Co(III) complexes of

N,N'-disubstituted ethylenediamines[113,138] (such as EDDA) have been considered with reference to qualitative predictions of stabilities. In a similar way, the proportions of isomers isolated for the Co(III) complexes of the trien analogue 1,8-diamino-3,6-dithiaoctane[139] (eee = $(NH_2\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-})_2$), and of various methyl-substituted triens[140,141] have been correlated with stabilities predicted by the study of models.

In all the previous studies, excepting $[Co(IDA)_2]^-$, the complexes involved mixed ligands or acido substituents and even in $[Co(IDA)_2]^-$, different donor atoms N or O were coordinated to the metal. In all these systems there will thus be factors other than those of environmental variations which may contribute to the observed stereospecificity.

Reasons for the Present Study on $[Co\ dien_2]^{3+}$.

Various experimental observations have thus shown that ion-association, solvation, lattice packing effects, and statistical factors contribute significantly to the ΔG^o between isomeric (and conformational) forms of metal complexes. Recalculations on $[Co\ en_3]^{3+}$ 110, 130 by energy minimisation methods have shown that the enthalpy differences between conformers calculated by Corey and Bailar[80] were too large so that in this instance the intermolecular factors are important. The relative magnitudes of the individual contributions are unknown, and the limited experimental data has not allowed estimates to be made, usually because of complications due to mixed ligands and acido substituents. In such cases the various contributions to the intermolecular interactions may not be varied independently. For example, disproportionation can occur with mixed ligand systems,[50] and ligand exchange and dissociation may occur with complexes containing acido ligands.[59b]

No temperature variation studies of geometric isomer proportions or environmental effects are apparent in the literature.

From this discussion, it would appear that a study of isomer proportions in the $[\mathrm{Co\ dien_2}]^{3+}$ system under conditions where thermodynamic equilibrium exists should be useful. The system is inert and free from the complications inherent with mixed ligand complexes and with acido substituents. It has a limited number of isomers (three geometric forms) which can be readily separated and characterised (sections 2.4 and 3.3). Moreover, by the preparation of the complex under conditions where equilibration occurs (section 3.1) this system lends itself to the variation of temperature, concentration, ion-association by a number of anions, and solvation. The immediate aim of the present work was to determine the effect on isomer proportions of varying the above parameters, and for this purpose an accuracy of ±1 in the isomer percentages was considered satisfactory. X-ray crystallographic studies of the isolated products[36] would allow assessment of the contribution of lattice effects.

In addition, the equilibrium isomer proportions between the three $[\mathrm{Co\ dien_2}]^{3+}$ isomers under various conditions were required for the subsequent studies of isomerisation reactions, reported in Chapter 7.

6.2 THERMODYNAMIC CONSIDERATIONS

For any system in equilibrium, the equilibrium constant K is related to the difference in standard free energies of the species by

$$\Delta G^o = -RT \ln K$$

where R = gas constant

T = absolute temperature.

This ΔG^o has contributions from the differences in the standard enthalpies and standard entropies between the species according to

$$\Delta G^o = \Delta H^o - T\Delta S^o.$$

Over a limited temperature range, it can be assumed that enthalpies and entropies are independent of temperature so that if an equilibrium is studied, and ΔG^o_{expt} evaluated from the experimental measurements of K at two temperatures, then ΔH^o_{expt} and ΔS^o_{expt} can be obtained for the system.

In the isomer equilibrium existing in the $[\text{Co dien}_2]^{3+}$ system, K can be determined for each isomer pair. For any given set of equilibration conditions, using values of the isomer proportions obtained at two temperatures, the enthalpy and entropy differences between each isomer pair can thus be evaluated.

The expression relating ΔG^o to ΔH^o and ΔS^o can be separated into further terms as follows:

$$\begin{aligned}\Delta G^o_{expt} &= \Delta H^o_{total} - T\Delta S^o_{total}\\ &= \Delta H^o_{intramolec} - T\Delta S^o_{intramolec} + \Delta H^o_{intermolec} - T\Delta S^o_{intermolec}.\end{aligned}$$

For any two preparative conditions, A and B, it is therefore possible to assess the differences between the contributions of the individual intermolecular interactions ($\Delta S^o_{total_A} - \Delta S^o_{total_B}$) and ($\Delta H^o_{intermolec_A} - \Delta H^o_{intermolec_B}$) from the difference in the experimental results under the two conditions A and B, if $\Delta H^o_{intramolec}$ may be assumed constant.

However if $\Delta H^o_{intramolec}$ were known (from energy minimisation calculations) for each isomer pair, then the contribution to each K value of $\Delta H^o_{intermolec}$ and ΔS^o_{total} for each of the individual environmental parameters could be evaluated directly.

6.3 EXPERIMENTAL

Equilibrium isomer proportions of the three geometric isomers of $[Co\ dien_2]^{3+}$ were determined under a variety of conditions from separate aerial oxidation preparations. The stoichiometry involved in all runs was

$$CoX_2 + 2dien + HX + \frac{1}{4}O_2 \xrightarrow{C} [Co\ dien_2]^{3+} + 3X^-.$$

All aerations were of 36 hours duration, and were carried out either at room temperature (18 ± 2^o) or over a steam bath (temperature 80 ± 2^o). Analytical grade reagents (Co(II) salts, added salts and acids), and freshly distilled dien, were used.

Equilibrium between the isomeric products was established by the presence of charcoal. Freshly finely ground "BDH granulated charcoal for gas absorption" was used for this work, and all determinations employed samples from the same batch, whose catalytic activity was tested to ensure that it satisfied the criterion of causing racemisation of $(+)$-$[Co\ en_3]^{3+}$

within 2 minutes at 90°.[64]

The following procedure was typical of most of the runs. It was the method used for Run 5 (Table 5) where anion was added in excess of the stoichiometry as required in the above equation.

$Co(NO_3)_2.7H_2O$ (0.29 g, 0.0010 mole) was dissolved in water (30 ml) in a two-necked 100 ml round-bottom flask fitted with a reflux condenser (to minimise loss of water by evaporation during the subsequent aeration). To this solution was added $NaNO_3$ (8.5 g, 0.10 mole) and the salt was dissolved as completely as possible before the addition of charcoal (2 g), and a mixture of dien (0.23 g, 0.0022 mole) and HNO_3 (1.1 ml of 1M, 0.0011 mole) in water (20 ml). The mixture was aerated for 36 hours and the charcoal was then filtered off under gravity.

The equilibrium preparations were carried out under a variety of conditions, including variation in the anion X^-, adding salts in some runs, and varying the cation concentration, temperature, the solvent, and pH. These variations are evident from Table 5.

In the preparations involving phosphate and selenite ions (runs 28-34, Table 5), the Co(II) salts of these anions were not used directly due to their low solubilities. Na_3PO_4 and Na_2SeO_3 were added to the solution of $CoCl_2$, as in the procedure above, and the aeration carried out on the resulting suspension of the sparingly soluble cobalt(II) salt which precipitated along with some cobalt(II) hydroxide. It was assumed that this Co(II) salt would dissolve as the reaction proceeded, so the preparation should remain under equilibrium conditions throughout the process.

The filtrate from each of the preparations was diluted so that the concentration of the +1 cations was less than 0.1M, and an aliquot of approximately one quarter of the total volume was applied to each of two columns (50 cm x 0.9 cm) of SP-Sephadex C-25 Cation Exchanger (Na^+ form) for duplicate isomer separations. The absorbed complex on each column was eluted with 0.3M sodium (+)-tartrate solution to separate the isomers in the order s-cis (eluted first), u-cis, then trans (last). The separated bands were collected in volumetric flasks which were subsequently made up to the standard volume (either 25 or 50 ml), and measured spectrophotometrically in 1 cm or 4 cm quartz cells.

The optical densities of the eluted isomers from each chromatographic separation were measured at the first band maximum (ca. 466 nm, Table 6) on a manual Shimadzu QR-50 spectrophotometer against water reference. It was established (section 4.3.1) that the separate isomers gave identical spectra and extinction coefficients if dissolved in water or 0.3M sodium (+)-tartrate solution (Table 6).

TABLE 6

Chromatographic Elution Order, and Visible Spectral Data for the Geometric Isomers of $[Co\ dien_2]^{3+}$

Isomer	Elution order from Sephadex with Na_2 (+)-tart	First band maximum
s-cis	1 (fastest moving)	$\epsilon_{461} = 68.5$
u-cis	2	$\epsilon_{468} = 96.4$
trans	3 (slowest)	$\epsilon_{466} = 137.0$

For each set of separated isomers, the eluted isomer quantities were calculated using the relationship

$$\text{number of moles} = \frac{Dv}{1000\ \varepsilon l}$$

where D = optical density,

v = volume of eluted solution (25 or 50 ml),

ε = molar extinction coefficient, and

l = path length (1 or 4 cm),

so that the percentage composition of the three component isomers could then be calculated. The values given in Table 5 for each run are the means of these duplicate determinations.

Before the chromatographic separative procedure on Sephadex had been developed, the isomer proportions were determined by the following alternative method. The $[\text{Co dien}_2]^{3+}$ equilibrium preparation was performed on a 0.1 mole or 0.2 mole scale, and the aerated solution, after filtering, was converted to the Br^- anion by a column of anion exchange resin. The s-cis isomer was crystallised quantitatively (section 3.2), using IR methods to determine the first appearance of the next least soluble trans isomer (section 4.3.2). The trans/u-cis ratio was obtained by quantitative paper chromatography (section 2.4) of a sample of the remaining solution (known volume), the eluted isomers being estimated spectrophotometrically. The isomer proportions thus calculated (assuming 96% formation of the complex in the aeration solution, section

TABLE 5

Isomer Proportions in Equilibrium Preparations of [Co $dien_2$]$^{3+}$ with Variations in Environmental Parameters

Run No.	Temp. ^oC	Solvent	Co^{2+} Anion	[Co^{2+}]	Added Salt and [salt]	Isomer proportions		
						s-cis	u-cis	trans
1	20	H_2O	ClO_4^-	0.2M	–	8	30	62
2	20	H_2O	ClO_4^-	0.02M	–	8	30	62
3	20	H_2O	ClO_4	0.02M	$NaClO_4$, 2M	9	30	61
4	20	H_2O	NO_3^-	0.02M	–	7	29	64
5	20	H_2O	NO_3^-	0.02M	$NaNO_3$, 2M	8	30	62
6	20	H_2O	OAc^-	0.02M	–	7	27	66
7	80	H_2O	OAc	0.02M	–	14	42	44
8	20	H_2O	OAc	0.02M	NaOAc, 2M	12	31	57
9	20	MeOH	OAc^-	0.02M	–	18	29	53
10	20	t-AmOH	OAc^-	0.02M	–	20	45	35
11	20	H_2O	Br^-	0.4M	–	7	28	65
12	20	H_2O	Br^-	0.2M	–	7	27	66
13	20	H_2O	Br^-	0.02M	–	7	27	66
14	20	H_2O	Br^-	0.2M	NaBr, 2M	7	25	68
15	20	H_2O	Br^-	0.02M	NaBr, 2M	7	26	67

(contd.)

TABLE 5 (contd.)

Run No.	Temp. ^{o}C	Solvent	Co^{2+} Anion	$[Co^{2+}]$	Added Salt and [salt]	Isomer proportions		
						s-cis	u-cis	trans
16	20	H_2O	Cl^-	0.4M	-	7	28	65
17	20	H_2O	Cl^-	0.2M	-	7	25	68
18	20	H_2O	Cl^-	0.02M	-	7	26	67
19	80	H_2O	Cl^-	0.02M	-	12	41	47
20	20	H_2O	Cl^-	0.02M	NaOH, 0.01M:pH~10	10	28	62
21	20	H_2O	Cl^-	0.2M	KCl, 2M	8	26	66
22	20	H_2O	Cl^-	0.02M	KCl, 2M	7	28	65
23	20	H_2O	SO_4^{2-}	.2M	-	19	34	47
24	20	H_2O	SO_4^{2-}	.02M	-	18	34	48
25	80	H_2O	SO_4^{2-}	.02M	-	22	44	34
26	20	H_2O	SO_4^{2-}	.2M	K_2SO_4, 2M	25	37	38
27	20	H_2O	SO_4^{2-}	.02M	K_2SO_4, 2M	24	39	37
28	20	H_2O	Cl^-	0.02M	Na_2SeO_3, 2M	59	28	13
29	20	H_2O	Cl^-	0.02M	Na_2HPO_4, 2M	37	38	25
30	20	H_2O	Cl^-	0.02M	Na_3PO_4, 1.2M (sat.)	59	29	12
31	20	H_2O	Cl^-	0.02M	Na_3PO_4, 0.01M	16	31	53
32	20	H_2O	Cl^-	0.02M	Na_3PO_4, 0.02M	26	33	41
33	20	H_2O	Cl^-	0.02M	Na_3PO_4, 0.04M	37	33	30
34	20	H_2O	Cl^-	0.02M	Na_3PO_4, 0.08M	55	25	20

6.4.1) were closely comparable to the present results obtained by a more direct method.

6.4 RESULTS AND DISCUSSION

6.4.1 DISCUSSION OF THE METHOD

In the course of these studies on the equilibrium proportions of the three geometric isomers of $[\text{Co dien}_2]^{3+}$, all results were obtained from aerial oxidation preparations under equilibrium conditions by the presence of charcoal. Variations of the parameters involved in the preparations, cobalt concentration, temperature, solvent, the presence of different anions (ion-association), and pH, could all be examined independently or in combination, and the results are set out in Table 5.

It was shown earlier (section 3.2) that the aerial oxidation method allows the crude $[\text{Co dien}_2]\text{Cl}_3$ complex as an isomeric mixture to be isolated in ca. 94% yield so that it can be assumed that in the present isomer proportion studies the complex is formed in solution in at least this yield. The maximum yield of Co(III) species anticipated would be ca. 96% because of reduction (ca. 4% to Co(II)) is known to occur in the presence of charcoal.[64] The isolation of the complex in high yields also precludes any inaccuracies in the determined isomer proportions due to adsorption by the charcoal of the complex.

Studies of isomerisation (no charcoal) from each geometric isomer, to be presented later (Chapter 7), allow an assessment of these isomerisation rates, and it is apparent that negligible isomerisation will occur separately (from the equilibration) between the isomers, once formed in equilibrium preparations, at 20° over the period of the aeration (36 hours). At 80°, the rates of isomerisation in water are still considerably slower than the rate of equilibration on charcoal at that temperature. Equilibration of each isomer separately in the presence of charcoal is known to be complete within 12 hours at this elevated temperature (section 7.4). The values in Table 5 can thus be considered as true equilibrium values since any isomerisation that occurred would be re-equilibrated in the duration of the aeration under the conditions used.

It might be argued that since equilibration of any isomer at 20° in the presence of charcoal is not complete within one week (Chapter 7), the aerial oxidation preparations at that temperature should be performed on a time scale consistent with the equilibration. However the isomer proportions obtained from the aerial oxidation procedure (36 hours) were identical (within experimental error) with the equilibration results, so that presumably the catalytic properties of charcoal are enhanced by the presence of the unoxidised Co(II) in the aerial oxidation preparations.[62] Furthermore at 80°, the aerial oxidation preparation (reported in this chapter), the charcoal catalysed equilibration process and the uncatalysed isomerisation process (both reported in Chapter 7) produced identical values of the isomer proportions. These results, in conjunction with the observation (section 3.3) that all charcoal catalysed preparations (both oxidative and substitution) gave products of similar isomeric distribution, form substantial evidence that charcoal markedly catalyses the attainment of a true thermodynamic equilibrium distribution of isomers in the complex preparations.

In all preparations the concentrations were adjusted to ensure that no product separated out, so that all results correspond to equilibria in solution. If some precipitation of the complex had occurred, the isomer proportions for the remaining solution might not be equilibrium values, although in principle the remaining solution would eventually equilibrate under the conditions.

6.4.2 QUALITATIVE CONCLUSIONS FROM THE EXPERIMENTAL RESULTS

The results (Table 5) allow some new conclusions to be made concerning the contribution of these intermolecular effects to the stereospecificity of this complex system. More work could be done however in the studies of solvation, and of temperature variations as the studies reported here are limited in scope. The main qualitative conclusions reached will be listed here, and discussed in the following section 6.4.3.

(i) The trans isomer of $[\mathrm{Co\ dien}_2]^{3+}$ is preferred to the two cis forms.

(ii) The concentration of cobalt [Co] in the 20-fold range of 0.4M to 0.02M had no effect on the isomer proportions (compare data from runs 11-13, and from runs 16-18). This effect will not be discussed further.

(iii) Changes of solvent, water and various alcohols, produced significant changes in the proportions of isomers.

(iv) The presence of the anions ClO_4^-, NO_3^-, Br^- or Cl^-, either in stoichiometrically required quantities or in excess, gave the same values for the proportions.

(v) The use of basic conditions in the preparation mixtures (e.g. excess acetate ion or added hydroxide ion) gave a slight increase in the proportions of the less stable *cis* isomers.

(vi) The presence of the anions PO_4^{3-}, SeO_3^{2-} (and to a lesser extent SO_4^{2-}) produced a marked increase in the proportion of the *s-cis* isomer at the expense of the *trans* form.

(vii) An increase of the temperature under which the aeration preparations were performed increased the proportions of the less stable *cis* isomers.

6.4.3 INTERPRETATION AND DISCUSSION OF QUALITATIVE CONCLUSIONS

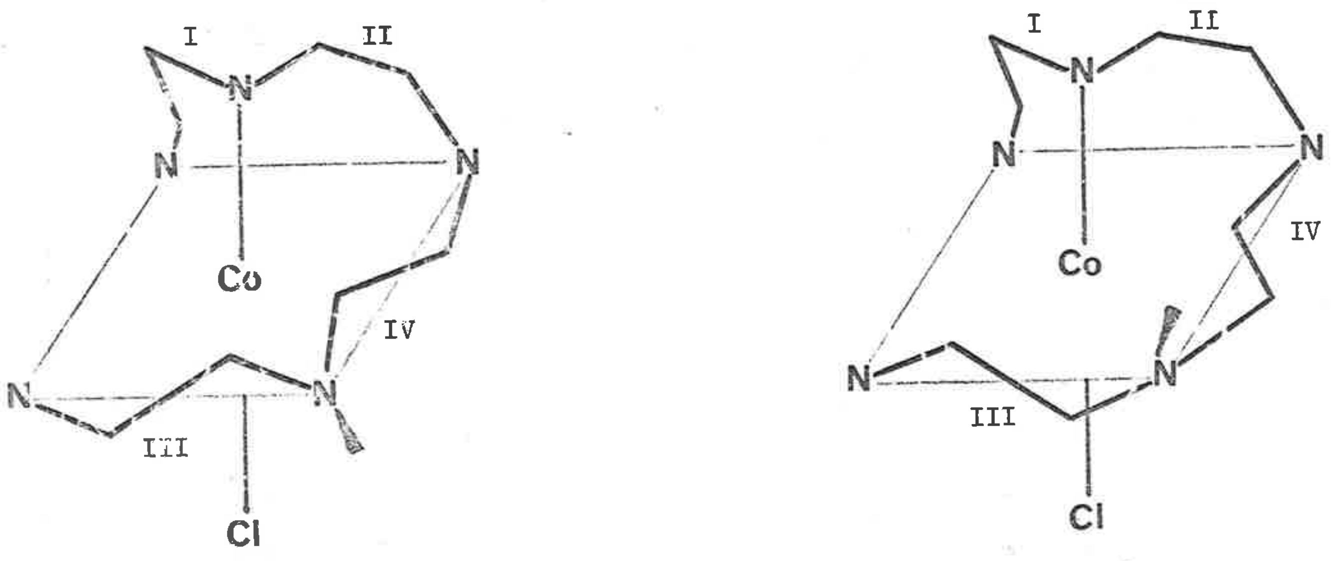
Preference for the trans Configuration.

It is not possible at this stage to compare the experimental values of the isomer proportions with theoretically calculated values since the energy minimisation calculations for the $[Co\ dien_2]^{3+}$ system are not yet completed.[142] Semi-quantitative *a priori* calculations were not considered worthwhile due to the inherent approximations in these calculations, as discussed earlier (section 6.1).

In a preliminary energy minimisation for coordinated dien, Snow[143] extrapolated the results of the energy minimisation calculations on two conformational isomers of αβ[Co tetraenCl]$^{2+}$ (one of the four geometric isomers) shown in Figure 15, to consider facially and meridionally coordinated dien by separate evaluation of interactions in rings I and II, and rings III and IV, respectively (Figure 15). It was found that such transferred results indicated the meridional coordination was preferred.[143]

This result concurs with experimental evidence on some mono(dien) complexes of Co(III), where the isolated complexes [Co dienCl_3],[15,26,27,30] [Co dien$(NO_2)_3$],[15,21] [Co dien$(NO_2)_2$Cl],[15] and [Co dien$(NO_2)_2(NH_3)$]$^{+}$ [15] were all found to be trans. Only in certain circumstances have cis mono(dien) complexes of Co(III) been observed. In the mixed bis(tridentate) systems [Co(dien)(IDA)]$^{+}$ [31] and [Co(dien)(S-Asp)]$^{+}$ [99] the predominance of the cis geometric forms was ascribed to the strong preference by these two amino acid ligands for the less strained facial coordination. Of the mono(dien) complexes involving three monodentate ligands however, only in [Co(dien)$(H_2O)_3$]$^{3+}$, and corresponding chloro/aquo complexes, have cis arrangements been reported.[30,73] It seems likely that aquo ligands enhance the stability of cis(dien) coordination, presumably by some form of intramolecular hydrogen bonding. These Co(III) mono(dien) complexes with aquo ligands have been reported only in solution however,[30,73] so that there may be some doubt as to the geometric assignments.

There thus appears to be a general preference for meridional coordination by dien in the above cobalt(III) complexes. It would thus be expected that the trans[Co $dien_2$]$^{3+}$ isomer should be favoured over the



αβ-R

αβ-S

Figure 15. Conformational isomers of αβ[Co tetraenCl]$^{2+}$.[143]

two <u>cis</u> forms, at least under conditions where there were insignificant intermolecular interactions, although the effect of the acido substituents is unknown in the previous examples. Under normal preparative conditions at 18° in the presence of Cl^- or Br^- (runs 11 and 16, Table 5) the proportions obtained were <u>s-cis</u>:<u>u-cis</u>:<u>trans</u> = 7:28:65, and these figures will be used as a standard with which the other data will be compared.

Effect of Solvation.

The present results are limited in the scope of the investigation of solvent effects on isomer proportions. However the change from the aqueous medium (run 6, Table 5) to alcoholic solvents (runs 9 and 10) affected the relative isomer stabilities, consistent with the differential solvation of the isomers, enhancing the proportions of the two <u>cis</u> isomers in the alcoholic solvents.

Effect of ClO_4^-, NO_3^-, Br^-, and Cl^-.

In conditions where the anions ClO_4^-, NO_3^-, Br^-, Cl^-, and OAc^- were present in stoichiometrically required quantities only, there was no variation in isomer proportions from those quoted above (compare runs 2, 4, 6, 13, 18). This latter observation is consistent with known association constants for outer sphere complexes with ions of the Co(III) hexamine type, which (for a given hexamine complex) are of the same order for all the above anions.[59c] The presence of a large excess of each of the anions ClO_4^-, NO_3^-, Br^-, and Cl^- did not cause any change in the isomer proportions (runs 3, 5, 14, 15, 20, 21). PMR[134] and CD[135] evidence indicate that these anions have only a small effect on changing the conformation population in systems such as $[Co\ en_3]^{3+}$, and therefore associate only to a small extent with these complex ions. However the present results with excess Cl^- anion make an interesting comparison with those of Gillow and Harris[144] who reported that the less symmetric (cis(dimethyl)) form of the trans-dichlorobis(N-methylethylenediamine)-cobalt(III) ion appeared to be stabilised in a solution swamped with Cl^- because this form "should be the more highly ion-paired". On this basis, it would be expected that u-cis$[Co\ dien_2]^{3+}$ might be the more favoured under such conditions. Since no change was observed in the proportions of isomers, a preferred association of the anion with the isomer of lowest symmetry does not seem to occur for the triply-charged species.

Effect of Excess Acetate; pH Effect.

Excess acetate ion slightly raised the proportion of s-cis$[Co\ dien_2]^{3+}$ (run 8). In all preparations involving ClO_4^-, NO_3^-, Br^-, and Cl^-, the measured pH of the reaction solution was ca. 4, but the solution containing excess sodium acetate was basic (pH ca. 8). To check that this was an effect of pH rather than OAc^- specifically, a preparation involving chloride ion was basified by the addition of OH^- (run 20) and a similar effect on the isomer proportions was observed to that of acetate. Increased pH thus has the effect of increasing the proportion of the least stable *s-cis* isomer to a small extent, from 7% to 12%. Basic conditions also obtained for preparations involving PO_4^{3-} and SeO_3^{2-} (runs 28-34) but the effects in these cases were due to specific associations by these ions (discussed below) which swamped any effect due to pH alone.

Specific Ion-Association with PO_4^{3-}, SeO_3^{2-}, and SO_4^{2-}.

The greatest effect on the equilibrium isomer proportions was shown by the addition of the polarisable anions SO_4^{2-}, HPO_4^{2-}, PO_4^{2-} and SeO_3^{2-} (runs 23-34), but the effect of SO_4^{2-} was less than that for the other species. The proportion of the *s-cis* isomer increased at the expense of the *trans*, and the *u-cis* proportion remained nearly constant. Over a range of PO_4^{3-} concentrations (runs 30-34) the proportions of isomers altered continuously until a constant value was reached when the PO_4^{3-}:Co ratio was about 4:1, when the *trans*:*s-cis* ratio had been almost reversed from the "standard" case. This suggests a specific interaction of these anions with *s-cis*$[Co\ dien_2]^{3+}$ enhancing its stability and to a lesser extent with the *u-cis* form, but considerably less association with the *trans* isomer.

Of many anions tested, PO_4^{3-} and SeO_3^{2-} (and to a lesser extent SO_4^{2-}) had a particularly marked effect on PMR[134] and CD[135] spectra of $M\ en_3$ complexes, caused presumably by alteration of relative conformer populations. Although larger association effects would be expected for these more highly charged anions in any case, the results have indicated that specific interactions occur so that in the presence of these anions the tris-lel conformer was even more strongly favoured. For these M en_3 complexes, the tris-lel conformer has two sets (at the opposite ends of the molecular C_3 axis) of three N-H bonds aligned nearly parallel to the C_3 axis, a situation which does not hold for any ob ring conformation. Mason[135] suggested that these tetrahedral polarisable anions could approach the cation along the C_3 axis to stabilise this particular conformation by hydrogen bonding to the N-H bonds (Figure 16). If, as suggested by PMR[85] studies, the original conformation in solution was not predominantly tris-lel, the addition of such anions to stabilise this lel form should simplify the $>CH_2$ resonance of the PMR spectrum[134] and change significantly the CD spectrum.[135] The recent X-ray crystal structure analysis of $[Co\ en_3]_2(HPO_4)_3.9H_2O$ [145] has indeed shown the three chelate ring conformations to be lel, with the phosphate ion positioned approximately on the C_3 axis of each molecule as proposed by Mason.

In a similar way, PO_4^{3-} has also been observed to cause a significant change in the cis $\rightleftharpoons$ trans equilibrium position for $[Co\ en_2(H_2O)_2]^{3+}$ in solutions of pH 7, and this was rationalised in terms of stabilisation of the cis isomer by specific ion-association.[146]

For the s-cis$[Co\ dien_2]^{3+}$ ion there are two sets of three N-H bonds appropriately placed at each end of the molecule (Figure 17) to allow hydrogen bonding in a similar way as that proposed above for M en_3. Furthermore, Dreiding models indicate that conformational changes in the four chelate rings would not affect these N-H dispositions significantly.

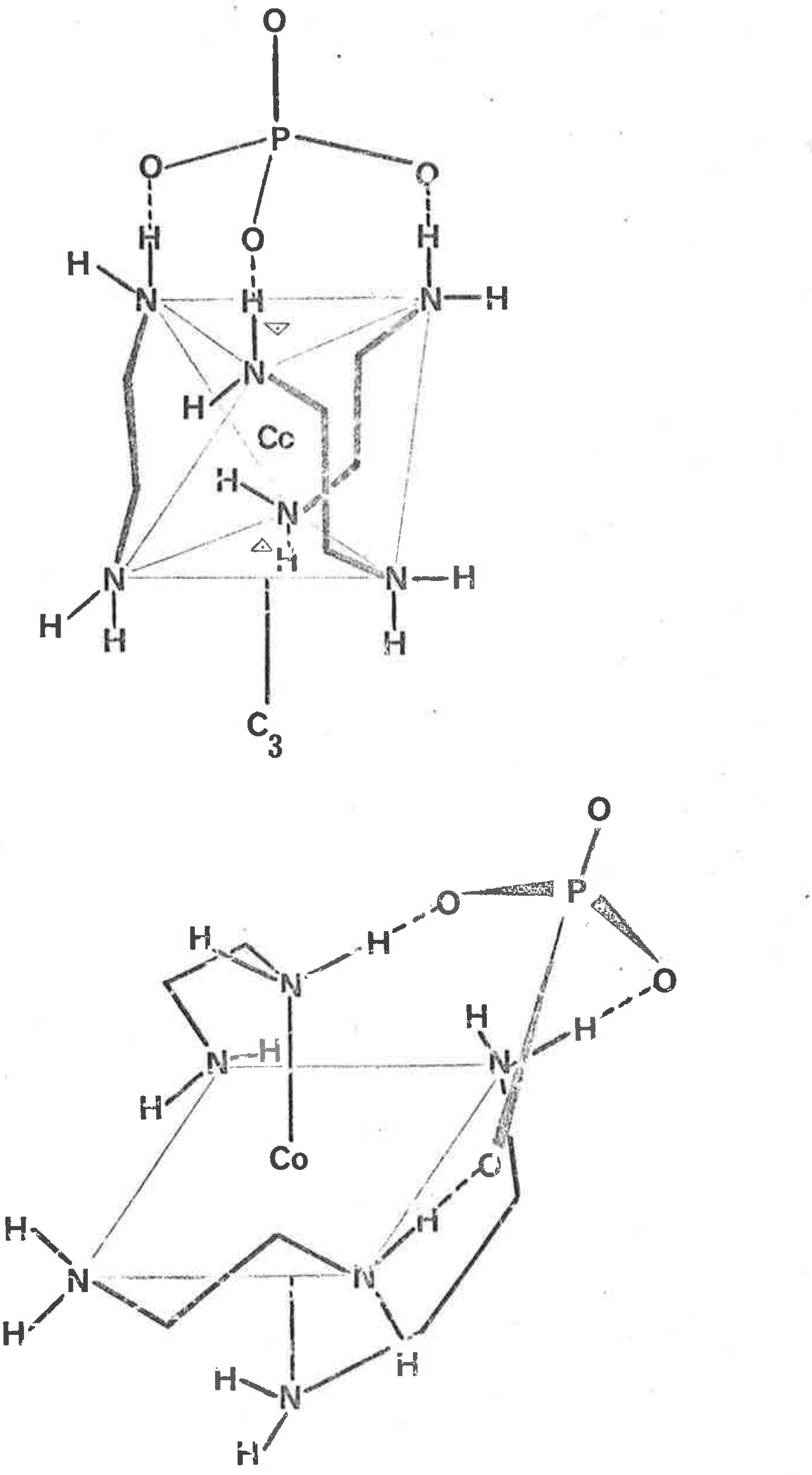


Figure 16. - The structure of the ion-pair between Δ[Co en$_3$]$^{3+}$ and PO$_4$$^{3-}$.[135]

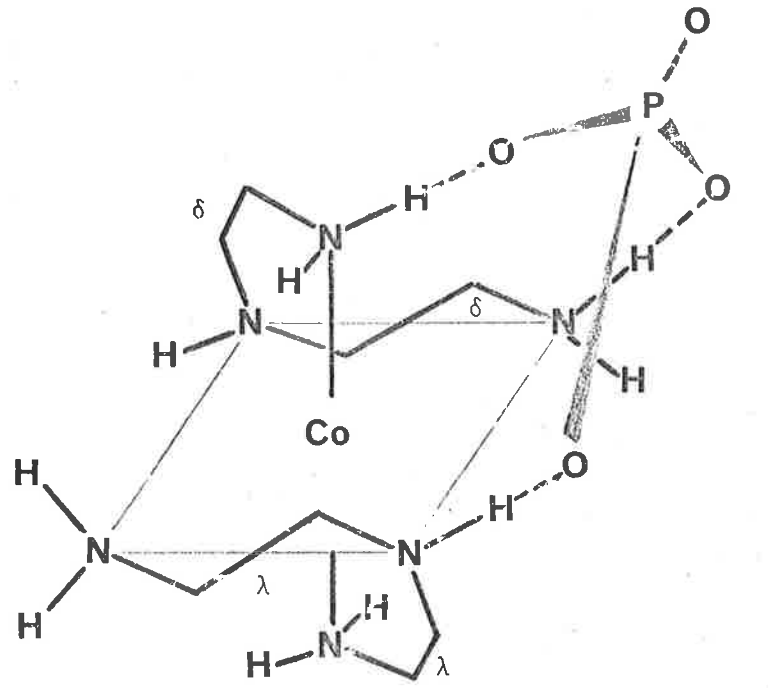


Figure 17. - The proposed ion-pair between s-cis$[Co\ dien_2]^{3+}$ ($\lambda\lambda$-$\delta\delta$) and PO_4^{3-}.

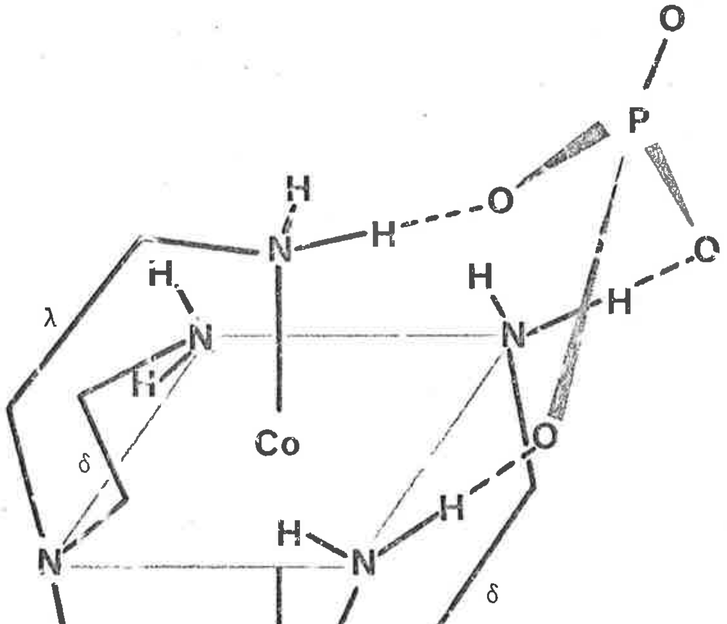


Figure 18. - The proposed ion-pair between u-cis$[Co\ dien_2]^{3+}$ ($\Lambda(\lambda\delta$-$\delta\lambda)$) and PO_4^{3-}.

Figure 17 is drawn for one particular conformer λλ-δδ (point symmetry C_1) which would seem a likely conformer in solution from a qualitative study of non-bonded interactions using models, and from statistical considerations. Stabilisation of the s-cis geometric isomer by ion-pair formation involving hydrogen bonding with these oxyanions could thus occur in the same way as conformational stabilisation for M en_3.[135]

In a similar way, u-cis$[Co\ dien_2]^{3+}$ has one set of three N-H bonds that could lead to formation of an ion-pair, but the particular orientation of these N-H bonds in this molecule seems considerably dependent on the particular conformations of the rings. Figure 18 shows the u-cis isomer in the λδ-δλ conformer (symmetry C_1) which is the form (indicated from models) giving the greatest stabilisation from the association according to the orientation of the N-H bonds, although this conformer, on the basis of qualitative studies of non-bonded interactions, would be one of the less stable forms of this isomer. The CD of u-cis$[Co\ dien_2]^{3+}$ changes on the addition of selenite ion (section 5.3), indicating a change in the symmetry of the molecule because of conformational change, implying that association of this cation with the anion occurs.

In the trans form of the complex there appears no such triple locations to favour such association with tetrahedral anions.

It is proposed therefore that a specific association occurs between these polarisable anions and the complex cations through hydrogen bonding with suitably disposed sets of N-H bonds. The study of models indicates that the existence of such sets would lead to stabilisation in the order s-cis > u-cis > trans, which is consistent with the present results. In the M en_3 system, the effect of such associations can only be inferred as conformational changes and a greater preference for one conformer. In the present system the association will be observed as changes in the relative stabilities of geometric isomers which can be directly measured, but these two effects are entirely analogous. In the latter case there will probably also be some conformational ordering, but this is of lesser importance compared with the preferential stabilisation of geometric forms.

It is not intended to consider in theoretical detail the conformational situation in these isomers. Because of the intermolecular interactions already discussed, and the complications of statistical preferences, any qualitative arguments must be employed cautiously until the relative stabilities of the various conformational combinations are known from the energy minimisation calculations[142] and X-ray crystal structure analyses[36] in progress. Further PMR and CD studies of these complexes may then allow a greater insight into the conformational changes occurring in the individual isomers. Nevertheless, some general discussions of the conformational situation in these isomers has already been made with respect to the IR studies (section 4.3.2), the PMR studies (section 4.3.3) and in the present chapter.

Effect of Temperature.

An increase in temperature was seen in all cases to enhance the proportions of the less stable cis isomers of the system (compare runs

6 and 7, 18 and 19, 24 and 25). However as little is known concerning the relative contributions of enthalpy and entropy to conformational and isomeric stability, the effect of temperature cannot be predicted.

A number of instances are known where higher temperatures may cause isomerisation from cis to trans octahedral complexes in aqueous solution, and it might appear at first sight that the trans isomers are stabilised at the higher temperatures. Examples of such changes in CoN_6 complexes are: cis$[Co\ en_2(NO_2)_2]^+$ changes to the trans on prolonged boiling in water,[59d] and cis$[Co(2,3,2\text{-tet})(NO_2)_2]^+$ isomerises to trans in a weak acid solution.[141] However in these cases the acido ligands and solvent are probably involved in the isomerisation mechanism so that the products under given conditions may depend on kinetic rather than thermodynamic factors, and these reactions occur more readily than isomerisation within the $[Co\ dien_2]^{3+}$ system.

It might be argued that increase in temperature would weaken the hydrogen bonding with the polarisable anions proposed above and that the equilibrium isomer proportions would tend to their values in a situation where association was not significant. However, an increase in temperature alone acts in the opposite direction and increases the proportions of the two cis forms, and for the anion SO_4^{2-} this temperature effect is dominant (runs 24 and 25). An observation of the effect of temperature on the hydrogen bonding could only be made on the individual isomers with a technique such as CD where the conformational changes could be measured directly, at least for the active forms of the complex. No such temperature variation studies of hydrogen bonding, using CD methods, in systems involving five-membered chelate rings, have been noted from the literature although the CD spectra of (+)-[Co $en_3]^{3+}$ and (+)-[Co(+)$pn_3]^{3+}$ have been recorded over the temperature range -78° to 57°C with the different aim of assessing the conformational populations in the former ion.[95] PMR studies might also provide information on the temperature variation aspect of hydrogen bonding.

In summary, the result of the present studies of the various contributions of intermolecular effects to the equilibrium between the isomers is that cationic concentration [Co] and added anion have little effect, except where association is very specific and stabilisation of particular isomers may result. There is also a significant effect due to solvation, and temperature.

6.4.4 ESTIMATION OF ENTHALPY AND ENTROPY FACTORS FROM VARIABLE TEMPERATURE RUNS

The present results (Table 5) do not allow a reliable quantitative analysis because of the limited scope of the variable temperature studies. However the following discussion illustrates the possibilities and limitations of this experimental approach.

The three isomeric proportions for the system [Co $dien_2]^{3+}$ at 18° and 80° allow the separation of the free energy differences between the isomers into enthalpy and entropy contributions (section 6.2). The only experimental errors involved in these determinations were in the temperature ($\pm 2^{o}$) and in the isomer proportion percentages which were in general observed to be reproducible to within ±1. While this error in the proportions appears at first sight reasonably satisfactory, it results in appreciable uncertainty in the calculated energy values. These uncertainties are quoted with the calculated energies in Table 7. The temperature uncertainty is of less importance.

In the three conditions in which temperature variations were studied (Cl^-, OAc^-, SO_4^{2-}), the results (Table 7) indicate large negative entropy differences (ca. -6 e.u.) for the equilibria <u>s-cis</u> $\rightleftarrows$ <u>trans</u> and <u>u-cis</u> $\rightleftarrows$ <u>trans</u>, but the entropy contribution to <u>s-cis</u> $\rightleftarrows$ <u>u-cis</u> was small. This is consistent with the <u>trans</u> form being the most ordered, which may be rationalised by the greater conformational freedom possible in the two <u>cis</u> (facial) isomers of the complex. This is also consistent with the PMR studies (section 4.3.3) which were interpreted on the basis of rapid conformational inversion in the two <u>cis</u> forms, whereas such inversion would be restricted for the <u>trans</u> isomer under the acidic conditions (pH ~ 4) obtaining in these preparations.

The equilibria between the isomers in the presence of Cl^- and OAc^- were essentially the same, as shown by the observed isomer proportions (runs 18 and 19, and runs 6 and 7, Table 5) and the resultant thermodynamic data (Table 7). For the equilibrium in the presence of SO_4^{2-} (runs 24 and 25, Table 5), where association occurs, the energy values (Table 7) indicate that the difference in proportions, compared with the

TABLE 7

Enthalpy and Entropy Contributions to Observed Isomer Equilibria in Aerial Oxidation Preparations of $[Co\ dien_2]^{3+}$

Isomer Pair	Anion	Temp.	K	ΔG^o kcal mole^{-1}	ΔH^o kcal mole^{-1}	$-T\Delta S^o$ kcal mole^{-1}	ΔS^o e.u.
trans/*u-cis*	Cl^-	291	2.32	−0.49 ± 0.03	−2.3 ± 0.5	1.8 ± 0.4	−6 ± 1
		353	1.15	−0.10 ± 0.03		2.2 ± 0.5	
	OAc^-	291	2.44	−0.52 ± 0.03	−2.8 ± 0.5	2.3 ± 0.5	−8 ± 2
		353	1.05	−0.03 ± 0.03		2.8 ± 0.6	
	SO_4^{2-}	291	1.41	−0.20 ± 0.03	−2.0 ± 0.5	1.8 ± 0.4	−6 ± 1
		353	0.77	+0.18 ± 0.04		2.2 ± 0.5	
trans/*s-cis*	Cl^-	291	9.29	−1.3 ± 0.1	−2.7 ± 1.2	1.6 ± 1.0	−5 ± 3
		353	3.92	−1.0 ± 0.1		1.9 ± 1.2	
	OAc^-	291	9.43	−1.3 ± 0.1	−3.6 ± 1.1	2.3 ± 1.0	−8 ± 3
		353	3.14	−0.8 ± 0.1		2.8 ± 1.2	
	SO_4^{2-}	291	2.67	−0.57 ± 0.05	−1.8 ± 0.6	1.2 ± 0.5	−4 ± 2
		353	1.55	−0.31 ± 0.05		1.5 ± 0.6	

(contd.)

TABLE 7 (contd.)

Isomer Pair	Anion	Temp.	K	ΔG^o kcal $mole^{-1}$	ΔH^o kcal $mole^{-1}$	$-T\Delta S^o$ kcal $mole^{-1}$	ΔS^o e.u.
u-cis/s-cis	Cl^-	291	4.00	-0.8 ± 0.1	-0.5 ± 1.1	-0.3 ± 1.0	1 ± 3
		353	3.42	-0.9 ± 0.1		-0.3 ± 1.2	
	OAc^-	291	3.86	-0.8 ± 0.1	-0.8 ± 0.8	0 ± 0.6	0 ± 2
		353	3.00	-0.8 ± 0.1		0 ± 0.8	
	SO_4^{2-}	291	1.89	-0.34 ± 0.05	+0.3 ± 0.5	-0.7 ± 0.5	2 ± 2
		353	2.00	-0.49 ± 0.05		-0.8 ± 0.6	

first two conditions, may be due mainly to enthalpy contributions. Such association is more usually considered as a contribution of entropy. However because of the limited accuracy possible with the present results, the energy differences in these cases are within the quoted extremities of experimental error, so that such conclusions must be treated with some caution at this stage. Further, in the case of such an association, temperature variation studies should ideally have been performed in the presence of excess of the anion so that the degree of association would remain as constant as possible throughout the temperature range used, as this factor would also contribute to the proportions of isomers observed. For this reason, the greater effects of association shown by the anions SeO_3^{2-} and PO_4^{3-} were not examined in this way as solutions containing these ions are strongly basic and at the higher temperature used in these studies (80°), the cobalt complex would therefore decompose. Nevertheless, temperature variation studies could be made of these effects using two controlled lower temperatures.

As the energy minimisation calculations of $\Delta H^{o}_{intramolec}$ for this system are incomplete,[142] the $\Delta H^{o}_{intermolec}$ values between isomer pairs cannot be obtained from ΔH^{o}_{total} (Table 7). At the present time, only such comparative studies of the energy values as given above, can be made. Future temperature variation studies on the effects of solvation, ion-association and other environmental parameters may yield useful information on the energetic contributions of their individual effects. However, it is evident that for these results measured at various temperatures to be interpreted in a meaningful quantitative sense, a high order of experimental accuracy in the proportions (say ± 0.2 in each percentage) is required.

In another approach to the evaluation of thermodynamic data in coordination complexes, the enthalpy differences (ΔH^{o}_{total}) may be measured directly by calorimetric techniques. This approach has only recently been undertaken, and for the equilibrium between $\underline{\beta}_2$-SR- and $\underline{\beta}_2$-SS-$[Co(trien)(gly)]^{2+}$, ΔH^{o} determined in this way was found to be very close to the experimental ΔG^{o} value, indicating only a small entropy difference between the forms.[147]

CHAPTER 7

ISOMERISATION REACTIONS IN THE [Co $dien_2$]$^{3+}$ SYSTEM

7.1 INTRODUCTION

Isomerisation and racemisation reactions of inert octahedral complexes have been observed since Werner's time. The majority of these studies have involved bidentate ligands, such as en, ox^{2-}, phen and bipy, often in association with monodentate acido ligands such as water or halide, and the detailed mechanisms involved have been reported for only a few systems. In many of these instances however the choice of mechanism has not been unequivocal.

The study of any observable isomerisation in the system [Co $dien_2$]$^{3+}$ may elucidate some of these problems; because of the restrictions imposed by the coupled chelate rings, the mechanistic pathways are more limited than for the bidentate complexes. Further, the system has no acido ligands so that isomerisation cannot be facilitated by easy ligand displacement and/or substitution.

7.2 SUGGESTED MECHANISMS FOR ISOMERISATION (AND RACEMISATION) IN CHELATE METAL COMPLEXES

The terms isomerisation and racemisation are used interchangeably as a general description for the processes considered in this chapter as racemisation is a special case of isomerisation. In the present context, the only difference is in the classification of the relationship of the product to the reactant.

There are two general types of isomerisation mechanisms, which are best termed as intermolecular and intramolecular.

Intermolecular Processes.

Ligand interchange, with complete dissociation of the ligand from the complex, is involved in an intermolecular process, and it is required therefore that the ligand exchange must be at least as rapid as the isomerisation (or racemisation). For example, in the racemisation of a tris(bidentate) complex $[M(AA)_3]$, the intermolecular pathway can be represented

$$\Lambda[M(AA)_3] \underset{+AA}{\overset{-AA}{\rightleftharpoons}} M(AA)_2 \underset{-AA}{\overset{+AA}{\rightleftharpoons}} \Delta[M(AA)_3]$$

where the exact nature of the intermediate $M(AA)_2$ is not defined. (It is suggested that solvent probably occupies, at least temporarily, the vacated coordination positions.) In a case where acido ligands are involved, an intermolecular mechanism requires dissociation of at least one of these acido groups with a subsequent rearrangement, presumably via a tetragonal-pyramidal or trigonal-bipyramidal intermediate. Such a mechanism has been proposed for the isomerisation/racemisation in the systems cis$[\text{Co en}_2\text{Cl}_2]^+$,[59d] cis$[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}$,[59e] and $[\text{Cr ox}_2(\text{H}_2\text{O})_2]^-$ (pH 3-7),[59f] which contain easily replaceable monodentate acido ligands. When only multidentate ligands are present such a mechanism would appear less likely, although an intermolecular process has been shown to occur in the racemisation of the nickel complexes $[\text{Ni phen}_3]^{2+}$, $[\text{Ni phen}_2\text{bipy}]^{2+}$, $[\text{Ni phenbipy}_2]^{2+}$, and

$[\mathrm{Ni\ bipy_3}]^{2+}$.[59g]

Intramolecular Processes.

Although intramolecular mechanisms for isomerisations of complex ions have been demonstrated in several instances, the mechanistic details have not always been clear. There are two classifications for mechanistic pathways that are considered intramolecular, dissociative or "twist" mechanisms.

The dissociative or bond-rupture process could occur for a complex of the type $[\mathrm{M(AA)_3}]$ in two ways (Figure 19), depending on whether one or two one-ended dissociations are involved. Several systems have been reported which have been proposed to racemise or isomerise in this way, since no total dissociation (i.e. an intermolecular process) of the ligand(s) could be proved. For example, the isomerisation of cis$[\mathrm{Co(en)_2(NH_3)(OH)}]^{2+}$,[59h] and the racemisation of both $[\mathrm{Cr\ ox_3}]^{3-}$ [59i] and $[\mathrm{Co\ acac_3}]$ [59j] are consistent with the bond rupture process to give intermediate (i) (Figure 19). In the Co(III) complex of Dwyer's sexadentate ligand TET (Figure 20), the green form can isomerise to the brown form, and does so with no loss of optical rotation, strongly supporting an intramolecular process of the type shown in Figure 20.[59k] The difference between this process and an intermolecular process is that the unattached atom is held within the coordination sphere as part of the ligand molecule while the rearrangement of the sexadentate is proposed to occur via the trigonal-bipyramid.

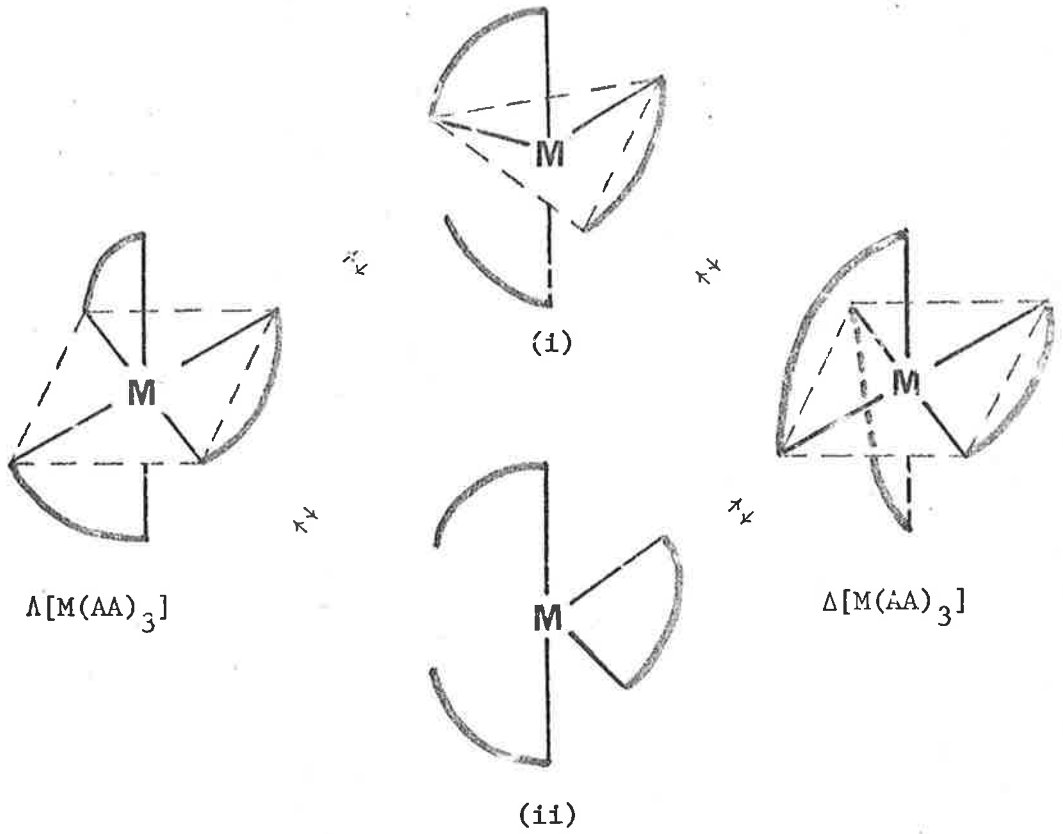


Figure 19. - Pathways for racemisation of $[M(AA)_3]$ via an intramolecular dissociative process.

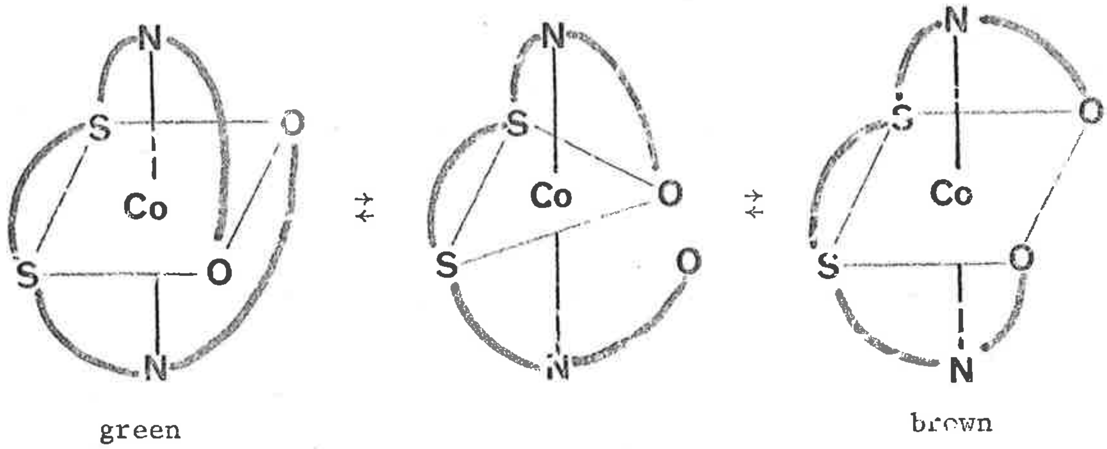


Figure 20. - Intramolecular isomerisation of $[Co(TET)]^+$ by a dissociative mechanism.

The twist mechanisms have been proposed to explain isomerisation reactions where no dissociation is apparent. For example, the racemisation of [Fe phen$_3$]$^{2+}$, [Fe bipy$_3$]$^{2+}$ (in part),[591] and [Co(EDTA)]$^-$ [591] have been rationalised by this mechanism, and also the isomerisation/-racemisation behaviour of cis[Co(en)$_2$(OH)$_2$]$^+$.[148] Many examples remain however where the choice between intramolecular dissociative mechanisms and the twist process is equivocal, as in the isomerisation reactions of cis[M(III)(tfacac)$_3$],[59m] where M = Al, Ga, In, Co, Rh.

There have been several proposals invoked for twist mechanisms. Ray and Dutt[149] suggested that [M(AA)$_3$] could racemise if one chelate ring remained fixed in space while the remaining two rings rotated 90° in opposite directions about axes through the metal ion, and perpendicular to their ring planes (Figure 21). This mechanism is called the Ray and Dutt twist, or "rhombic" twist (referring to the geometry of the intermediate).

In an alternative proposal Gehman,[150] Seiden,[151] and Bailar[152] formulated a mechanism for racemisation of [M(AA)$_3$] by rotation of 120° about the molecular C_3 axis of one octahedral face (containing one end of each ligand) relative to the face containing the other ends of the ligands. This proposal is often called the "trigonal" twist mechanism,*

---

* This process has also been termed the "Bailar twist" although the idea was proposed prior to Bailar's paper.

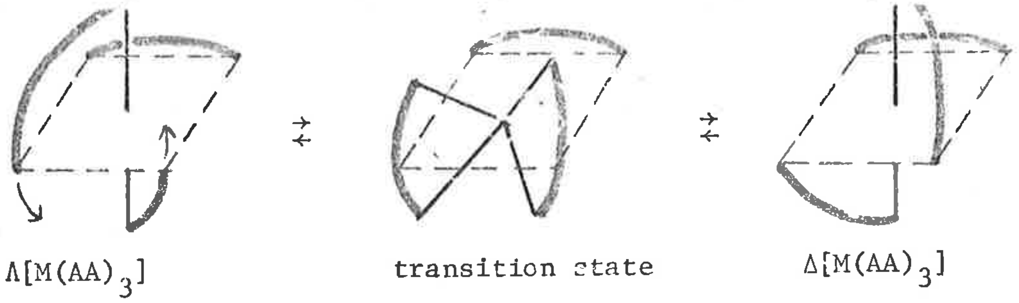


Figure 21. - The Ray and Dutt, or rhombic-twist mechanism for the racemisation of $[M(AA)_3]$.

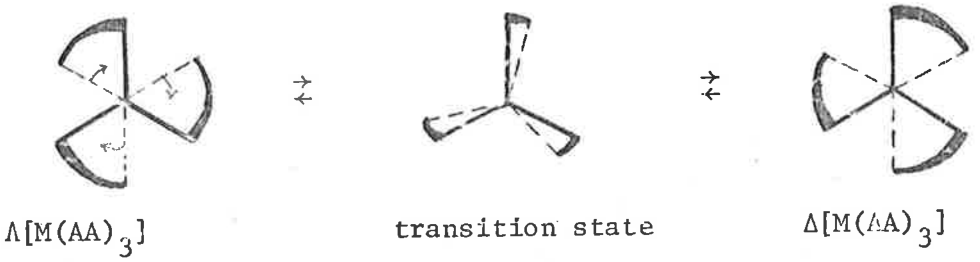


Figure 22. - The trigonal twist about the C_3 axis for the racemisation of $[M(AA)_3]$.

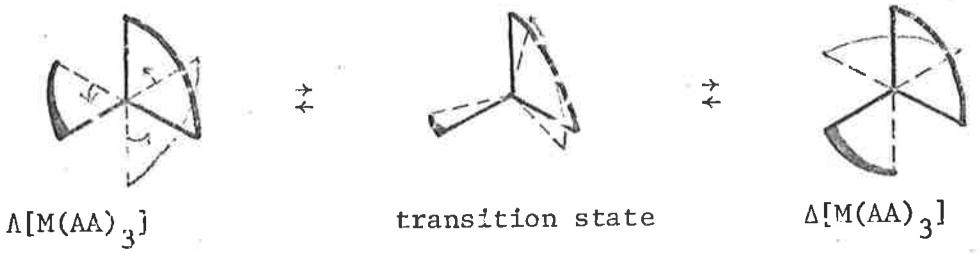


Figure 23. - The trigonal twist about a pseudo-C_3 axis for the racemisation of $[M(AA)_3]$.

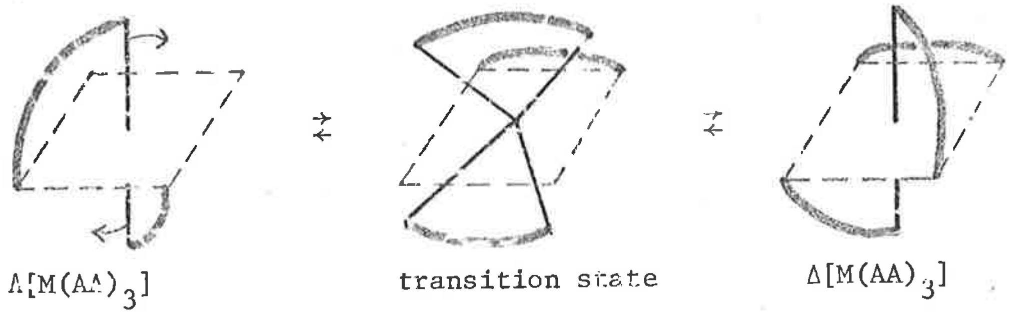


Figure 24. - The Springer and Sievers mechanism for the intramolecular racemisation of $[M(AA)_3]$.

since it passes through a symmetrical trigonal prismatic transition state, and it is shown in Figure 22. Although these authors suggested only rotation about the molecular C_3 axis, the same rotation involving another pair of octahedral faces would also cause racemisation (Figure 23). This process is henceforth called the trigonal (pseudo-C_3) twist, to distinguish it from the trigonal (C_3) twist process (Figure 22).

Springer and Sievers[153] suggested a further twist mechanism for the racemisation of $[M(AA)_3]$, in which one chelate ring is considered fixed in space (as in the Ray and Dutt mechanism) while the other two rings revolve past each other, continually changing planes, as shown in Figure 24.

The intermediate or transition state for both the Springer and Sievers mechanism and the trigonal (C_3) twist process is the same (Figure 25a), although the A-M-A angles would be different. In the former process, the ring angles would remain fixed at 90°, while during the trigonal (C_3) twist this angle would reduce to 81° 48', which is the calculated A-M-A angle for a trigonal prism. In a similar way, the rhombic and trigonal (pseudo-C_3) twists involve a common geometry of intermediate (Figure 25b), the rhombic twist retaining the ring A-M-A angles at 90° while the latter mechanism would lead to ring compression.

While all the above processes lead to racemisation of the $[M(AA)_3]$ species, when an unsymmetrical bidentate ligand AB is involved there is a difference between the processes. The Springer and Sievers and trigonal (C_3) twist mechanisms which involve the symmetrical intermediate (Figure 25a)

(a) (b)

Figure 25. - Trigonal prismatic intermediates involved in twist mechanisms:

(a) Springer and Sievers, or trigonal (C_3) mechanism transition state, and

(b) rhombic, or trigonal (pseudo-C_3) mechanism transition state for the racemisation of $[M(AA)_3]$.

will account for racemisation of $[M(AB)_3]$ but not <u>cis</u> $\rightleftarrows$ <u>trans</u> isomerisation, as these two pathways cannot alter the relative disposition of the ligands. Conversely, the rhombic and trigonal (pseudo-C_3) twists (intermediate (b), Figure 25) will both produce isomerisation simultaneously with configurational change. These changes could be observed by using an unsymmetric ligand in Figures 21-24, and are further elaborated in analyses of intramolecular rearrangements in six-coordinate species given in the literature.[148,154,155]

The difference between the Springer and Sievers mechanism and the trigonal (C_3) process (which both involve the same intermediate) is conceptual however, and they are actually identical as pointed out by several workers[148,155] and particularly by Brady.[156] The essential difference in the proposals was that in the Springer and Sievers process the A-M-A ring angles remained at 90° whereas they were compressed in the trigonal twist process. This presumes that in the trigonal twist the distance between rotating octahedral faces remains fixed, but this would seem to be an unnecessarily stringent condition to be imposed on an intramolecular rearrangement when bonds are being distorted. Should the distance between these faces expand during the twist process so that the ring angles remain at 90°, then these trigonal (C_3) and Springer and Sievers mechanisms become identical and the intermediates (Figure 25a) are also identical. In a similar way, the rhombic and trigonal (pseudo-C_3) processes (intermediate (b), Figure 25) are also identical. In summary therefore, there are only two basic twist mechanisms, represented by the two different possible trigonal prismatic transition states (Figure 25). The apparent differences with the other presentations is conceptual only since the detailed variations in bond angles to achieve the transition state should have no bearing on overall stereochemical changes.

Significance of $[Co\ dien_2]^{3+}$ in the Study of Twist Mechanisms.

Most of the studies where intramolecular mechanisms have been proposed have involved complexes of bidentate ligands. For mechanistic appraisal, such systems are not ideal as the observed results may not always be explained unequivocally. Moreover, the presence of different ligands ("mixed ligand" systems) can lead to disproportionation[50] so that interpretation may be complicated. Also the presence of acido ligands may facilitate isomerisation because of easier dissociation of these ligands. Isomerisation in [M trienX_2]$^{n+}$ compounds, for example, could conceivably occur by a wide range of mechanistic types. The [Co dien$_2$]$^{3+}$ system has none of these disadvantages. Further, it has a limited number of geometric isomers which are well characterised (section 3.3), and two of these can exist in optical forms. Because of the more restrictive nature of the tridentate ligands (compared with bidentates) on the possible modes of isomerisation, it was hoped that observation of isomerisation in this system might allow an unequivocal assignment of the mechanism involved.

7.3 EXPERIMENTAL

All isomerisation reactions were carried out using the acetate salts of the isomers of [Co dien$_2$]$^{3+}$, because of their appreciable solubility in many organic solvents. They were prepared by shaking the corresponding chloride with a 3.0 molar quantity of silver acetate for 1 hour, filtering off the silver chloride and evaporating the filtrate to dryness on a rotary evaporator (40°). These salts were stored in vacuo over anhydrous $CaCl_2$.

The solvents used are listed in Tables 8 to 10, together with the reaction conditions. The complex concentration was in all cases ca. 0.4 g complex in 50 ml solvent (ca. 0.02M), and the solutions were kept at either 25 ± 1° (immersed in a constant temperature bath), or at steam bath temperature (82 ± 1°). Samples (10 ml) were withdrawn at appropriate times and applied to columns of SP-Sephadex C-25 cation exchanger

(50 x 0.9 cm) and eluted with 0.3M sodium (+)-tartrate solution (as outlined in section 6.3). The analyses were performed singly.

In some cases decomposition products were found to be present. These red-purple compound(s) had an R_F factor intermediate between those of s-cis and u-cis[Co $dien_2]^{3+}$ and were not totally separable from those isomers, leading to some inaccuracy in the spectrophotometrically determined [Co $dien_2]^{3+}$ isomer percentages (s-cis and u-cis high). The runs so affected are indicated in the tables with a footnote. An average discrepancy of ±3 might therefore be expected in each isomer percentage, rather than ±1 as quoted for the isomer proportion studies (Chapter 6) where decomposition was not observed and duplicate analyses were available.

7.4 RESULTS AND DISCUSSION

The use of complexes of bidentate ligands in previous isomerisation studies has limited the possible observable isomerisation to cis $\rightleftarrows$ trans only. The use of higher multidentates in isomerisation studies can potentially afford more mechanistic information as there are more geometric forms possible, and some stereochemical restrictions may be imposed on possible pathways between these forms. However, no higher multidentate systems (involving amine donors only) have been studied in this way. Even studies of multidentate systems involving acido ligands have been limited to reactions of systems such as [Co $trienX_2]^{n+}$.[76]

The following results are from a study of the isomerisations of the three geometric isomers of [Co $dien_2]^{3+}$ under various experimental conditions (temperature, solvent, anion, charcoal catalysis), and it is believed that the present studies are of especial interest in that they are the first of their type. It is emphasised at the outset however that the present studies are preliminary in nature. The closest comparison for isomerisation in a hexamine system is the racemisation of $[\mathrm{Co\ en_3}]^{3+}$ which has been studied under a limited range of conditions[59a,61,64,137] (in water, with conditions acidic, neutral, or basic; presence or absence of charcoal; presence or absence of $[\mathrm{Co^{II}en_3}]^{2+}$, or Co^{2+} only, or en only) and about which reasonable mechanistic proposals have been advanced. These ideas should be reasonably applicable to the present system. In the absence of charcoal, for example, $\Lambda[\mathrm{Co\ en_3}]^{3+}$ did not measurably lose optical activity after 24 hours at 90°,[61] so that any isomeric change from a particular $[\mathrm{Co\ dien_2}]^{3+}$ isomer was expected to be slow. Each run undertaken was therefore exploratory in that it was difficult to predict the most appropriate intervals for sampling and analysis.

It was expected that each run would eventually yield an equilibrium mixture of the three isomers (hence the necessity of the extensive studies on the equilibrium isomer proportions in Chapter 6). However, the sampling was also important in the early stages of each run to assess whether the equilibrium mixture was being formed directly from the particular starting isomer used in each run, i.e. concurrent reaction routes

$$\begin{tikzcd} & B \\ A \arrow[ur, shift left] \arrow[ur, leftarrow, shift right] \arrow[dr, shift left] \arrow[dr, leftarrow, shift right] & \\ & C \end{tikzcd},$$

or whether the other two isomers were being produced (or being produced

TABLE 8

Isomerisation Reactions of *s-cis* and *trans*[Co dien$_2$]$^{3+}$ at 25°

Run No.	Isomer	Solvent	Time	Isomer Proportions (%)		
				s-cis	*u-cis*	*trans*
1-7	*s-cis*	H_2O, MeOH, EtOH, t-BuOH, HOAc (glacial), DMSO, collidine/HCl buffer (pH 8).	3 months	No observable isomerisation		
8-14	*trans*	H_2O, MeOH, t-BuOH, HOAc (glacial), DMSO, collidine/HCl buffer (pH 8), 1M aqueous Na_2SeO_3.	3 months	No observable isomerisation		
15	*s-cis*	dien (+ water to dissolve complex (0.5 ml)).	1 month	93	2	5
			3 months	79	6	15[a]
16	*trans*	dien (+ water to dissolve complex (0.5 ml)).	1 week	4	8	88
			1 month	8	14	78[a]
			3 months	25	31	44[a]
17	*s-cis*	H_2O/activated charcoal.	1 day	92	4	4
			1 week	69	11	20
			1 month	51	17	32
			3 months	9	30	61
18	*trans*	H_2O/activated charcoal.	1 day	2	13	85
			1 week	5	29	67
			1 month	9	31	60
			3 months	10	30	60

(contd.)

<u>TABLE 8</u> (contd.)

Run No.	Isomer	Solvent	Time	Isomer Proportions (%)		
				<u>s-cis</u>	<u>u-cis</u>	<u>trans</u>
19	<u>trans</u>	1M aqueous Na_2SeO_3/-activated charcoal.	1 day	17	41	42
			1 week	52	33	15
			1 month	60	29	11
			3 months	58	31	12

[a] Red-purple decomposition products observed.

TABLE 9

Isomerisation Reactions of the Isomers of $[\mathrm{Co\ dien_2}]^{3+}$ in Non-Aqueous Solvents at Steam Bath Temperature (82°)

Run No.	Isomer	Solvent	Time	Isomer Proportions (%)		
				s-cis	*u-cis*	*trans*
20	*s-cis*	t-BuOH	2 hours	89	4	7
			12 hours	64	20	16
			24 hours	51	32	17
			3 days	38	45	17
21	*u-cis*	t-BuOH	2 hours	5	80	15
			12 hours	11	72	17
			24 hours	16	67	17
			3 days	19	64	16
			2 weeks	40	42	18[a]
22	*trans*	t-BuOH	2 hours	3	5	92
			12 hours	7	13	80
			24 hours	10	18	72
			3 days	20	38	42
			2 weeks	32	42	26[a]
23	*s-cis*	MeOH	2 hours	92	2	6
			12 hours	44	31	24
			24 hours	35	37	27[a]
			3 days	33	39	27[a]
24	*u-cis*	MeOH	2 hours	5	78	16
			12 hours	8	68	23[a]
			3 days	13	59	28[a]
25	*trans*	MeOH	2 hours	4	4	92
			12 hours	6	9	85
			24 hours	7	13	80
			3 days	14	23	63[a]

(contd.)

TABLE 9 (contd.)

Run No.	Isomer	Solvent	Time	Isomer Proportions (%)		
				s-cis	u-cis	trans
26-28	s-cis u-cis trans	HOAc (glacial)	2 weeks	No observable isomerisation		

[a] Decomposition products observed.

TABLE 10

Isomerisation Reactions of the Isomers of $[Co\ dien_2]^{3+}$ in Aqueous Solvents at Steam Bath Temperature (82°)

Run No.	Isomer	Solvent	Time	Isomer Proportions (%)		
				s-cis	u-cis	trans
29	s-cis	H_2O	24 hours	69	7	24
			3 days	32	23	44
			7 days	18	37	45
			2 weeks	15	41	44
30	u-cis	H_2O	3 hours	6	84	10
			24 hours	7	62	31
			3 days	9	49	42
			7 days	12	45	43
			2 weeks	14	44	42
31	trans	H_2O	3 hours	4	7	89
			24 hours	9	33	58
			3 days	13	40	47
			7 days	13	44	43
			2 weeks	13	43	44
32	trans	H_2O/activated charcoal	12 hours	15	42	44[a]
			36 hours	16	41	43[a]
33	s-cis	0.1M HCl	2 days	No detectable isomerisation		
34	s-cis	0.1M NaOH	2 days	Complex decomposed		

[a] Decomposition products observed.

in part) by consecutive routes $A \rightleftarrows B \rightleftarrows C$.

Conclusions from Experimental Results.

The results of the isomerisation reactions of the isomers of $[\mathrm{Co\ dien_2}]^{3+}$ are given in Tables 8, 9 and 10, representing a classification of the different conditions used: Table 8 - at 25°; Table 9 - at 82° in non-aqueous media; Table 10 - at 82° in aqueous media. Due to the slowness of these reactions, most of the runs were carried out at 82°. The observations can be summarised as follows.

(i) Under conditions where isomerisation did occur, all three isomers were found from each isomer separately.

(ii) The isomerisation reactions were pH dependent. Isomerisation occurred under neutral and basic conditions (pH 6-9) but was not observed under acidic conditions ($\mathrm{pH} < 3$).

(iii) In most cases where isomerisation occurred, "decomposition products" were observed, and such decomposition was more rapid for the s-cis and u-cis forms than for the trans form.

(iv) In all runs at 82°, the final proportions of the trans isomer were established rapidly, and these were the equilibrium proportions measured in the previous chapter (section 6.4). The two cis forms then adjusted more slowly to their equilibrium proportions (section 6.4).

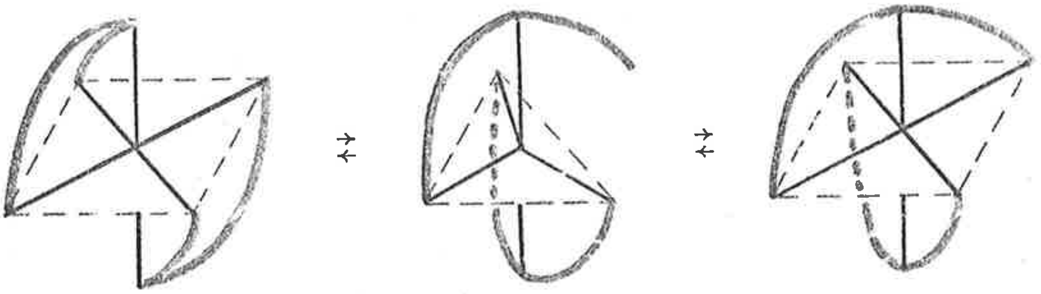
(v) Activated charcoal markedly catalysed the isomerisations.

(vi) Where data is available for comparisons, the same isomeric distribution was obtained with and without activated charcoal, but otherwise under the same experimental conditions.

Isomerisation Mechanisms for [Co $dien_2$]$^{3+}$.

The two general mechanistic types, intermolecular and intramolecular (section 7.1), can be considered for the present system. The intermolecular isomerisation process (in which one dien ligand would be totally dissociated from the coordination sphere) could lead to all possible interconversions as rearrangement of the coordinated ligand could occur before resubstitution of the fully dissociated ligand. Such total ligand exchange could be absolutely proved by the use of a labelled ligand, but this was not undertaken in the present work. Such labelling experiments in the racemisation of Λ[Co en_3]$^{3+}$ have shown[59a] that this process is intramolecular, as the rate of ligand exchange is slower than the rate of racemisation. The likelihood of simultaneous removal of the three donor atoms of one dien ligand (compared with two donor atoms for en) seems remote, so that this mechanism will not be considered further.

The intramolecular processes, dissociative and non-dissociative (twist), must therefore account for observed isomerisation in this system. s-cis and trans[Co $dien_2$]$^{3+}$ have the $>N^2$ - H groups at opposite sides of the metal atom whereas in the u-cis form they are adjacent (Figure 3). A bond rupture (one-ended dissociative) process can therefore lead only to the conversion s-cis $\rightleftarrows$ trans via a trigonal-bipyramid intermediate (Figure 26), unless a major rearrangement occurs whereby secondary nitrogen atoms move their relative positions, and no instance has been reported yet where this type of gross rearrangement is required. For example, a sec-N displacement, involving two coupled rings, was considered most unlikely for the $\alpha \rightleftarrows \beta$ isomerisation of $[\mathrm{Co\ trien(H_2O)_2}]^{3+}$.[76]



s-cis

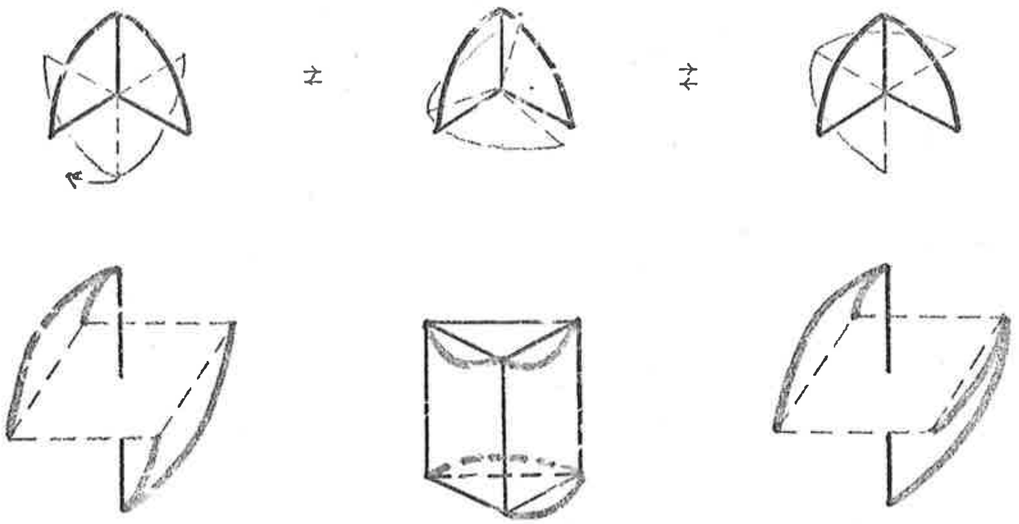
proposed trigonal-bipyramid intermediate

trans

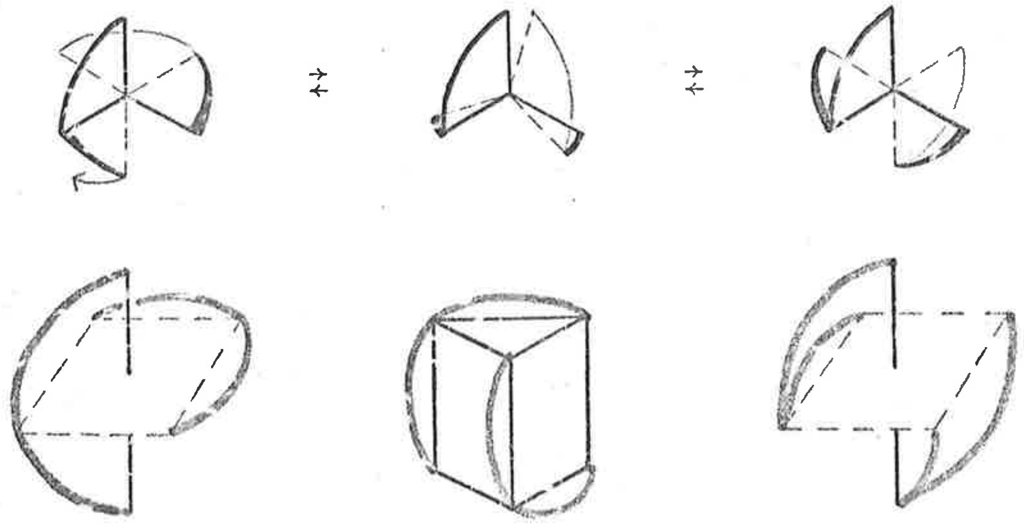
Figure 26. - The dissociative intramolecular mechanism for the isomerisation s-cis $\rightleftarrows$ trans.

The two basic intramolecular twist mechanisms (section 7.1) allow the interconversion of all three isomers, as they allow separately the isomerisations s-cis $\rightleftarrows$ u-cis and trans $\rightleftarrows$ u-cis, but not s-cis $\rightleftarrows$ trans directly. The two isomerisations are shown in Figure 27 where, for conceptual simplicity, they are viewed as trigonal twists about two different sets of octahedral faces.

The experimental results show that all three isomers were involved in the isomerisations so that a dissociative process alone cannot account



(a) s-cis intermediate u-cis



(b) trans intermediate u-cis

Figure 27. - The two possible intramolecular twist mechanisms for isomerisation in the [Co dien$_2$]$^{3+}$ system, viewed through alternative trigonal-prismatic intermediates.

for these results. This may be taken as good evidence for the involvement (at least in part), of the twist processes. It was hoped however that some indication of a stereochemical preference for one pathway might be obtained in the isomerisation reactions by analysis of the isomeric composition at various times. For example, *s-cis*$[\mathrm{Co\ dien_2}]^{3+}$ could isomerise by two separate processes,

$$\underline{\text{s-cis}} \overset{\text{twist}}{\rightleftarrows} \underline{\text{u-cis}} \overset{\text{twist}}{\rightleftarrows} \underline{\text{trans}}$$

or

$$\underline{\text{s-cis}} \overset{\text{dissociative}}{\rightleftarrows} \underline{\text{trans}} \overset{\text{twist}}{\rightleftarrows} \underline{\text{u-cis}}$$

or by two simultaneous processes,

$$\begin{tikzcd} & \underline{\text{u-cis}} \\ \underline{\text{s-cis}} \arrow[ur, leftrightarrow, "\text{twist}"] \arrow[dr, leftrightarrow, "\text{dissociative}"'] & \\ & \underline{\text{trans}} \end{tikzcd}$$

Depending on the relative rates of attainment of these individual equilibria, with the simultaneous processes alone the *u-cis* and *trans* should remain in constant ratio at all times. With consecutive processes however, the *u-cis*/*trans* proportions should (in general) change with time. The present results are not sufficiently comprehensive or accurate to allow a detailed analysis of the product ratios with time. From the limited studies reported in the Tables, it does appear that the product ratio was variable with time, and this would be more consistent with consecutive rather than with concurrent pathways.

pH Dependence of Isomerisations.

Twist mechanisms involve shifting but not breaking of Co-N bonds and the rates are therefore expected to be essentially independent of acid concentration. However, a dissociative process will be affected by pH if a change in acidity stabilises the dissociated donor, or promotes easier solvent or anion substitution into the coordination sphere. For example, the racemisation of $[\text{Fe bipy}_3]^{2+}$ [59n] has been shown to proceed by both intramolecular dissociative and twist mechanisms. While the twist process in this instance is virtually unaffected by increasing acidity, the dissociative pathway is inhibited as the lifetime of the intermediate (with one ring open) is decreased because of protonation.

Although the observed pH dependence of the isomerisation of $[\text{Co dien}_2]^{3+}$ would thus indicate a dissociative process, it has already been indicated that such a mechanism alone cannot account for the observed interconversion of all three isomers. It would seem possible therefore that the isomerisation was base-catalysed (or at least in part). It is proposed that in neutral and basic solution some deprotonation of the coordinated amine groups occurs, facilitating steric change in the same way as proposed by Poon and Tobe for $[\text{Co(cyclam)(OH)(H}_2\text{O)}]^{2+}$,[158] so that it is the deprotonated $[\text{Co dien}_2]^{3+}$ isomers which isomerise. The same mechanistic possibilities pertain to these deprotonated forms as to the $[\text{Co dien}_2]^{3+}$ species themselves, so that both intramolecular dissociative (Figure 26) and twist (Figure 27) processes are possible. On the basis of the proposal that isomerisations occur through deprotonated forms, the observed rates should be dependent on the deprotonation step itself, so that the overall process would be expected to show base catalysis of the type $k_{obs} = k[OH^-]$ over the pH range in which the isomerisation was observed (pH 6-9). However, no runs have been undertaken so far to enable the dependence of the observed rate on pH to be determined. However at 25° the occurrence of isomerisation in dien/H_2O at pH ca. 10 (runs 15 and 16), while no isomerisation was detectable in water and collidine/HCl buffer (pH 8) is consistent with base catalysis.

Alternative mechanistic proposals involve a reactive intermediate consisting either of a molecule with five coordination positions occupied by two dien ligands (one one-ended dissociation) and the sixth position by the solvent, or alternatively a seven-coordinate intermediate involving the solvent H_2O. In electron exchange studies[159] a rapid pentacoordinate-hexacoordinate equilibrium has been proposed for the $[Co(EDTA)]^-$ system, so that such an equilibrium in the present system might provide the necessary reactive intermediate for the isomerisation process. The seven-coordinate intermediate has been proposed by Cooke, Im, and Busch[591,160] to account for the racemisation of $[Co(EDTA)]^-$ (by a trigonal twist mechanism). If H_2O (rather than OH^-) were involved in these two alternatives, the isomerisation of the isomers of $[Co\ dien_2]^{3+}$ should not be base catalysed over a limited pH range. At this stage these processes cannot be eliminated as the isomerisation mechanisms, or as pathways concurrent with the base-catalysed deprotonation process. Rate studies as a function of pH in the range 6-9 would thus seem to be a valuable exercise, although similar studies using the methylated complex should more immediately establish whether deprotonation at the sec-N is involved (see later).

Appearance of Decomposition Products.

A red-violet product was detected in most reactions where isomerisation occurred (Tables). This product had an R_F value in the Sephadex separation intermediate between those of s-cis and u-cis, so that it would appear to be a Co(III) species with a 3+ charge. (Any conceivable Co(II) species should have charges 2+ or 1+.) If any dissociative process is occurring, this "decomposition product" may be a species in which water occupies one (or more) coordination positions, and suggests the possibility of this as the intermediate involved in the isomerisation. No "decomposition products" were observed in solutions where no isomerisation had occurred (runs 1-14, 26-28, 33).

Nature of the Proposed Deprotonated [Co $dien_2$]$^{3+}$ Species.

In the following chapter, it will be shown that the rate of hydrogen exchange in aqueous media for the $>N^2$ - H bonds of trans[Co $dien_2$]$^{3+}$ is about three times faster than the same process in the cis isomers. The $>N^2$ - H exchange is also expected to be ca. 10^3 times faster than the $-NH_2$ exchange process on the basis of rate measurements on the sym[Co(trenen)N_3]$^{2+}$ system.[10] If it is assumed that the re-protonation rates for all the deprotonated amines in the [Co $dien_2$]$^{3+}$ isomers are similar (they will all be extremely rapid, even perhaps diffusion controlled), then the acidity of the amine protons in these isomers will be related to their exchange rates. The *trans* molecule would thus deprotonate the most rapidly, and at the $>N^2-H$ position, and in aqueous solution the *trans* was observed to isomerise faster than the two *cis* forms (compare runs 31 (*trans*), 29 (*s-cis*) and 30 (*u-cis*)). Moreover, it was observed in the isomerisation reactions that there was a rapid establishment of the final equilibrium proportions of the *trans* isomer with a slower readjustment of the two *cis* proportions (runs 20-24, 29-31). As the deprotonated *trans* form would be the most rapidly formed (and therefore the deprotonated isomer in greatest concentration), then the *trans* $\rightleftarrows$ *u-cis* (twist) and *trans* $\rightleftarrows$ *s-cis* (dissociative) isomerisations should be expected to be established more rapidly than the *s-cis* $\rightleftarrows$ *u-cis* equilibrium. The slower *s-cis* $\rightleftarrows$ *u-cis* process could occur directly by a twist process (Figure 27a) or by the consecutive sequence of dissociative *s-cis* $\rightleftarrows$ *trans* and twist *trans* $\rightleftarrows$ *u-cis* mechanisms. In both cases however, a twist process would be involved.

Suggested Further Isomerisation Studies.

The study of the isomerisation reactions of the isomers of $[\mathrm{Co\ dien_2}]^{3+}$ presented here was preliminary in nature, but does provide evidence for twist processes. Further useful studies on this aspect now become evident. For example, the confirmation of base-catalysis of the isomerisations in the pH range 6 to 9 (by comparative rate studies) would provide evidence for the proposed deprotonation mechanism.

The twist mechanisms shown in Figure 27 involve no inversion at the $>N^2 - H$ centres, and thus for the *u-cis* $\rightleftharpoons$ *trans* process (Figure 27b) the use of optically active starting materials should (in principle) lead to a mutarotation and not a racemisation. If the isomerisation occurred by a series of equilibria *u-cis* $\rightleftharpoons$ *s-cis* $\rightleftharpoons$ *trans* then a racemisation would be observed since the intermediate *s-cis* isomer is not dissymmetric. Thus some differentiation between the mechanistic paths could in principle be realised. However, the conditions found necessary to bring about the isomerisation reactions of $[Co\ dien_2]^{3+}$ would lead to the racemisation of the *trans* molecule, so that this approach is not realistic, and was not tried. The use of the $[Co(4\text{-}Medien)_2]^{3+}$ system, in which the *trans* form is optically stable, should allow such a mutarotation to be observed. If however the deprotonation of the secondary amine in $[Co\ dien_2]^{3+}$ is important in the isomerisation (as proposed above), then the use of the 4-Medien ligand should lead to inhibition of isomerisation since the proposed deprotonation is not possible. The three geometric isomers of the $[Co(4\text{-}Medien)_2]^{3+}$ system have been separated and characterised (Chapter 10), and isomerisation studies using this system should be very profitable.

The use of unsymmetric tridentate ligands would also allow more information to be obtained on the distinction of dissociative and twist processes. However coordination of ligands such as 2,3-tri or a C-substituted dien could cause the *sec*-N atoms to become asymmetric, in which case there would be six geometric possibilities for $[Co\ L_2]^{3+}$, all of which would be dissymmetric, so that such isomerisation studies would be very complicated.

The $[Co(lin\text{-}penten)]^{3+}$ system is closely analogous to $[Co\ dien_2]^{3+}$ in that the lin-penten can be regarded as two dien ligands linked (through end primary groups) by an ethylene bridge. It has a limited number of geometric isomers (four, all dissymmetric) and the additional central ethylene bridge should impose some stereochemical restriction on the pathways possible for isomerisation. This restriction should be to advantage in deducing mechanistic paths, so that the present isomerisation studies will usefully be extended to the $[Co(lin\text{-}penten)]^{3+}$ system.[4]

Charcoal Catalysis of Isomerisation.

Activated charcoal catalysed the isomerisations, as expected by analogy with its effect on the racemisation of $\Lambda[Co\ en_3]^{3+}$.[61] An interesting feature of the present results however is that the same final (equilibrium) isomer proportions were obtained with or without charcoal (but the same experimental conditions otherwise). Thus charcoal does promote rapid attainment of a true equilibrium, but the present results do not allow any new information concerning the mechanism by which it catalyses the process (section 3.1). It cannot be firmly stated at this stage whether the isomerisation of the $[Co\ dien_2]^{3+}$ species on charcoal is identical to the mechanism without charcoal (discussed above), since the complete role of charcoal is unknown, even in the $[Co\ en_3]^{3+}$

racemisation.[58] If some electron exchange does occur (as in [Co en_3]$^{3+}$), the mechanism by which [Co^{II}dien$_2$]$^{2+}$ isomerises could be intermolecular, or may be intramolecular as in the [Co dien$_2$]$^{3+}$ species.

CHAPTER 8

KINETICS OF RACEMISATION AND HYDROGEN EXCHANGE IN trans[Co dien$_2$]$^{3+}$

8.1 INTRODUCTION

Donor Atom Asymmetry - The Historical Development.

Optical resolutions about the tetrahedrally coordinated atoms Si, Sn, N, P, As, and S are not extensive or numerous.[161] In particular, nitrogen in organic compounds is tervalent and usually has a lone electron pair and is consequently configurationally unstable because of rapid inversion. Nevertheless, optical separation of molecules about a nitrogen centre has been achieved in some circumstances: when inversion can be prohibited structurally (e.g. Troger's base),[161] in some quaternary ammonium salts (e.g. $(CH_2{=}CH.CH_2)(CH_2.C_6H_5)(C_6H_5)(CH_3)N^+$),[161] and in metal complexes where a nitrogen donor atom has become asymmetric on developing the fourth, coordinate, bond to the metal (donor atom asymmetry). The last of these types is particularly interesting as it is a general phenomenon; because of the properties of the resultant complexes, mechanistic studies of the process of inversion about the nitrogen centre can be made.

Keubler and Bailar[162] first demonstrated the phenomenon of donor atom asymmetry unequivocally (about a nitrogen donor atom) by resolution of the dinitro(N-methyl-N-ethylglycinato)platinate(II) ion (Figure 28) where the nitrogen atom was tertiary in the free amino acid ligand.

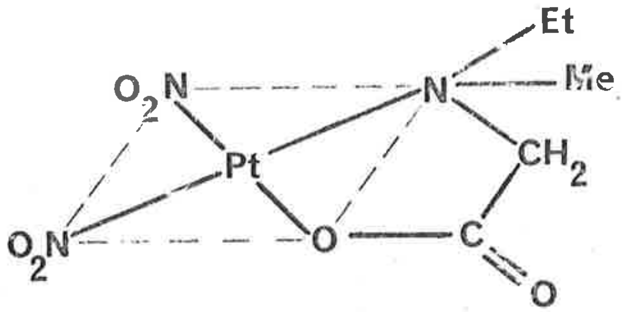


Figure 28. - The $[Pt(N\text{-}Me\text{-}N\text{-}Etgly)(NO_2)_2]^-$ ion.

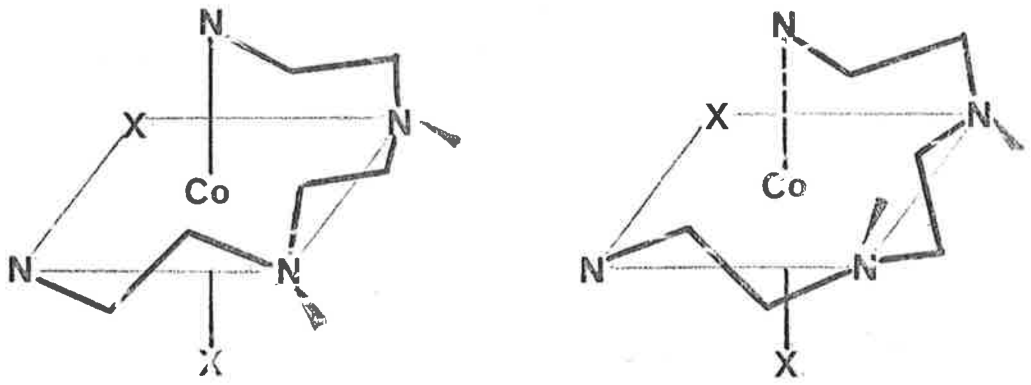
Since quaternary ammonium salts $R_1R_2R_3NH^+$ were optically unstable, these authors predicted that resolution of complexes of unsymmetric secondary amines R_1R_2NH would not be possible. The N-H exchange was expected (as in the quaternary ammonium salts) to be quite rapid, implying inversion and consequent racemisation. However it had been demonstrated that when one of the alkyl groups R was a metal ion such as Co(III), the rate of N-H exchange with solvent water was drastically reduced, so that for $[Co(NH_3)_6]^{3+}$ the half-life for exchange in 1M D^+ was ca. 10^6 minutes, although under neutral or basic conditions the exchange was rapid.[163,164] The proton exchange rate in cobalt(III) complexes of secondary amines might thus be sufficiently slow at suitably low pH to restrict inversion at the nitrogen centre of an unsymmetrically substituted secondary amine coordinated to a metal ion, so that optical resolution of the resulting complex should be feasible.

Using this fact, Halpern, Sargeson and Turnbull[24] first resolved a complex, $[Co(NH_3)_4sarc]^{2+}$, whose sole source of optical activity was a coordinated secondary nitrogen atom. Since that time several examples of resolutions, geometric isomerism and stereospecificity arising from the stability of coordinated secondary amines have been reported.

Most of this work has been carried out by Sargeson and Buckingham and co-workers. In the system [Co trienX_2]$^{+}$ [2] the inertness of the two secondary nitrogen centres under acid conditions allowed the separation of the two possible cisβ geometric forms shown in Figure 29 (X_2 = $(H_2O)_2$, amino acid), and of the two optical forms of the trans dichloro isomer (Figure 13). Stereospecific effects were observed for the [Co en_2sarc]$^{2+}$ ion,[118] the Λ-R/Δ-S ions being considerably more stable than Δ-R/Λ-S. These authors also employed several Co(III), Pt(II), and Pt(IV) systems containing asymmetric coordinated secondary amines in studies of the mechanism of the base catalysed optical inversion about the N atom. These complexes, [Co$(NH_3)_4$sarc]$^{2+}$,[24] [Co$(NH_3)_4$(N-Meen)]$^{3+}$,[101] trans, trans[Co$(N\text{-}Meen)_2Cl_2$]$^{+}$,[120,165] sym[Co trenenX]$^{2+}$,[10] [Pt(N-Meen)(en)]$^{2+}$ and [Pt(N-Meen)(en)Cl_2]$^{2+}$,[166] will be discussed subsequently in relation to the inversion mechanism.

The active Pt(II) complexes but in their racemic forms, [Pt(N-Meen)Cl_2], [Pt(N-Meen)$(NH_3)_2$]$^{2+}$ and [Pt(N-Meen)(phen)]$^{2+}$,[167] and [Pt(N,N'-Me_2en)$(NH_3)_2$]$^{2+}$ and [Pt(N,N'-Me_2en)(bipy)]$^{2+}$ [168] have also been studied by PMR methods in attempts to elucidate the mechanism of the ring conformational inversion process.

In the same way as for the [Co trienX_2]$^{+}$ system, trans[Co(2,3,2-tet)Cl_2]$^{+}$ has been resolved into its two optical forms,[169] and complexes of the tetradentate EDDA have also been shown to possess



β-RS β-RR

Figure 29. - The two conformational isomers of the cisβ[Co trienX_2]$^+$ ion.

configurational stability about the coordinated secondary amine groups under acidic conditions.[54,170] Stereospecificity has also been observed in complexes of N-substituted amino acids such as N-methyl-S-alanine[171,172] as mentioned earlier for sarcosine (N-methylglycine) systems.[24,118] Busch and co-workers[173] have employed macrocyclic ligands coordinated to Ni(II) and Co(III) to demonstrate both optical and geometric isomerism due to the restricted inversion about coordinated secondary nitrogen atoms.

In an analogous way to the present [Co dien$_2$]$^{3+}$ system, the configurational stability of coordinated nitrogen atoms has led to the isolation of four isomers of [Co(dien)(en)Cl]$^{2+}$,[8,9] two of which (I and II in Figure 5, section 1.3) differ only in the orientation of the $>N^2$ - H bonds in a meridionally coordinated dien ligand.

Inversion at the Secondary Nitrogen Centre in trans[Co dien$_2$]$^{3+}$.

Dien is a symmetrically substituted secondary amine so that *trans*[Co dien$_2$]$^{3+}$ does not contain an asymmetric donor atom. However racemisation will result if one of the N^2-H bonds adopts the alternative disposition (Figure 4). This process is equivalent to inversion of configuration at the asymmetric nitrogen centre in the situation Co-NHR$_1$R$_2$, and the term "inversion" is used henceforth to describe the analogous configurational change about a secondary nitrogen centre in *trans*[Co dien$_2$]$^{3+}$ despite the absence of asymmetry at that centre. This configurational change must involve N-H dissociation and will be accompanied by conformational inversion in each of the adjacent chelate rings.

These phenomena provided an unequivocal method for establishing the geometric configurations of the two dissymmetric forms of $[\text{Co dien}_2]^{3+}$, since the optical rotatory powers derive from different chiral sources in the u-cis and trans isomers. The u-cis form, whose optical activity arises essentially from a configurational effect, should be optically stable in base. The optical activity of the trans form arises essentially from the bond-pair chirality described earlier (section 3.4) which is typified and uniquely described by the two $>N^2 - H$ bonds. The racemisation of the trans isomer should therefore be OH^- catalysed. It was thus necessary to establish the OH^- dependence of the racemisation of the trans isomer, and this prompted the study of the kinetics of both racemisation and hydrogen exchange under a variety of conditions in the hope of further elucidating the mechanistic steps involved in the racemisation.

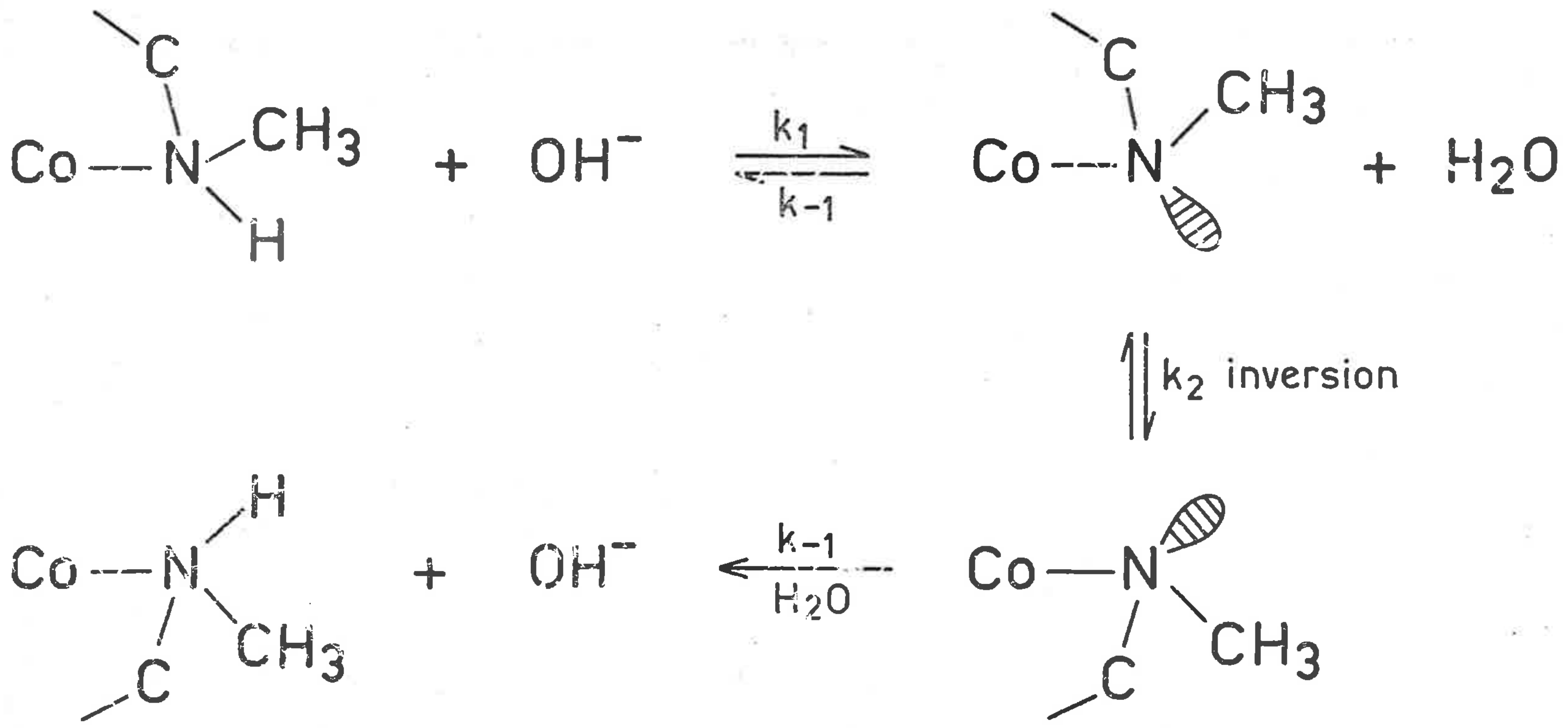
8.2 MECHANISTIC CONSIDERATIONS FOR RACEMISATION AND HYDROGEN EXCHANGE ABOUT AN ASYMMETRIC COORDINATED NITROGEN CENTRE

Recently the kinetics of racemisation and deuteration have been studied by Buckingham and Sargeson and co-workers for several cobalt(III) complexes where the sole source of asymmetry resides in a coordinated secondary amine N atom. For the three complexes $[\text{Co(NH}_3)_4\text{sarc}]^{2+}$,[24] $[\text{Co(NH}_3)_4\text{(N-Meen)}]^{3+}$ [101] and trans, trans$[\text{Co(N-Meen)}_2(\text{NO}_2)_2]^{+}$ [120] the rates of proton exchange were several orders of magnitude faster than the respective rates of racemisation, and both measured processes were described by rate laws of similar form,

$$R = k[\text{complex}][\text{OH}^-].$$

The two mechanisms which have been proposed by the above authors[101,120] to account for all these results are shown in Figure 30, where the part chelate ring indicated may be either N-Meen or sarc. The preferred scheme A involves abstraction of the N-proton with OH^- (k_1). The alternative mechanism B proposes formation of an ion-pair with OD^- (k_3) and ion-solvent dissociation (k_4). The two mechanisms are equivalent for the racemisation step as given by inversion of the deprotonated intermediate k_2. In mechanism B ion-solvent pair separation is required for racemisation for which k_4 could thus be the rate-determining step, but this step is not required for exchange to occur with retention of configuration k_{-3}. The absence of a substantial isotope effect $k_{\text{deuteration}}/k_{\text{protonation}}$ (k_D/k_H) for the exchanges, as would be expected for the step k_4,[120] gave support for the former mechanism, and circumstantial evidence also supporting mechanism A has been expounded.[101,120] Results of measurements of retention ratio $k_{\text{protonation}}/k_{\text{racemisation}}$ during exchange in non-aqueous solutions have also been interpreted on the basis of mechanism A.[165]

Erickson[174] has noted that the value of k_2 for these complexes in solution is relatively small compared with inversion rates for amines in the gas phase, and suggests the deprotonated intermediate is stabilised with respect to inversion in solution by hydrogen bonding to a solvent



Mechanism A

Figure 30A. - Proposed mechanism for hydrogen exchange and racemisation at an asymmetric nitrogen centre involving abstraction of the proton by OH^-.[101,120]

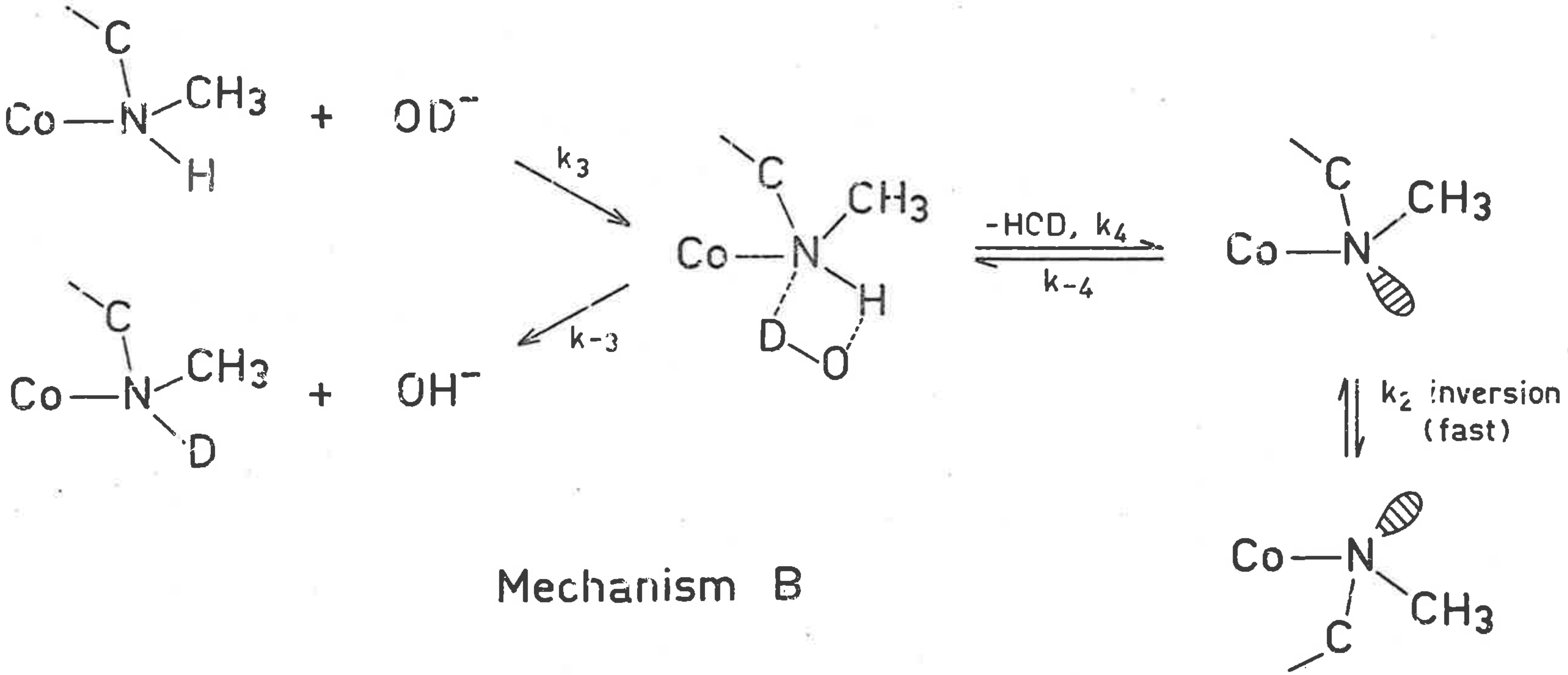


Figure 30B. - Proposed mechanism for hydrogen exchange and racemisation at an asymmetric nitrogen centre involving an ion-solvent pair.[101,120]

molecule. This intermediate then should probably be drawn with the water molecule attached to the lone pair, so that the equilibrium shown in Figure 30A might be written:

$$N - H + OH^- \rightleftharpoons N\!:^- H - O \diagdown H \quad .$$

The deprotonated intermediate in Figure 30B would be stabilised in a similar way, although these refinements are superficial to the basic issue at present.

The previous studies cited above are confined to complexes involving an asymmetric donor nitrogen centre in the bidentate ligands N-Meen or sarc. The chelate ring in the sarcosine complex is essentially planar[122] so that a ring conformational change is not involved. Mechanisms A and B as drawn in Figure 30 do not specifically consider inversion of the single chelate ring conformation in the N-Meen complexes, and k_2 in Figure 30 refers only to the nitrogen inversion which is the essential step for racemisation. The ring conformation must invert however if the methyl substituent is to remain in the preferred equatorial disposition with respect to the overall plane of the ring in the N-Meen complexes.[101,120] The increase in $\Delta H^{\dagger}$ and in retention ratio for the N-Meen complexes compared to the sarc complex was attributed to the additional energy required to invert the N-Meen ring conformation as well as the N centre.[101,120] In the studies mentioned, no decision could be made as to the time relationship between conformational interchange and inversion at the nitrogen atom during the observed racemisation, and Figure 30 is non-commital on whether the ring inversion precedes, postcedes, or is synchronous with k_2.[101,120]

A subsequent study of hydrogen exchange and racemisation of (+)-sym[Co(trenen)N_3]$^{2+}$ attempted to clarify the issue of the interaction between conformational interchange and nitrogen inversion.[10] This complex has coupled ring conformations (Figure 6, X = azido) and it was felt that the conformations of the two rings abreast of the asymmetric nitrogen (conformations designated δ and λ[6] in the Figure) would invert synchronously with configurational inversion at the asymmetric centre. The close correspondence between observed activation energies for racemisation of this system and of $(+)_{480}$-[Co$(NH_3)_4$(N-Meen)]$^{3+}$ was then taken to imply that inversion at the N centre and conformational interchange might coincide for puckered ring systems generally. However the trenen complex has multiple ring coupling at the tertiary nitrogen atom also, and this should confer some restriction on the conformational interchange in question (about the sec-N atom). The portion of the trenen ligand comprising the interlocked rings (δ and λ) about the asymmetric nitrogen in sym[Co(trenen)N_3]$^{2+}$ should be closely similar stereochemically to each dien ligand in trans[Co dien$_2$]$^{3+}$ (compare Figures 4 and 6). This latter complex is free of the restriction mentioned however, and is also a better basis for comparison with [Co$(NH_3)_4$(N-Meen)]$^{3+}$ on account of similar cation charge and the absence of the electronegative azido substituent. The comparison of the kinetic patterns for the dien and trenen complexes may be expected to give some further information on the effects of cation charge and azido substituent however.

8.3 EXPERIMENTAL

(+)-trans[Co dien$_2$](NO$_3$)$_3$.H$_2$O. - The racemic chloride was resolved with Ag(+)-[Co enmal$_2$].2H$_2$O as described earlier (section 3.2). The active bromide thus obtained was converted to the nitrate by passage of a solution in 0.01M HNO$_3$ through an exchange resin in the nitrate form. The elute was concentrated on a rotary evaporator, and crystallisation was completed by the addition of ethanol.

Anal. Calcd. for (+)-*trans*[Co(C$_4$H$_{13}$N$_3$)$_2$](NO$_3$)$_3$.H$_2$O: C, 20.5; H, 6.0; N, 26.8. Found: C, 20.6; H, 5.7; N, 26.5.

Deuterated (±)-trans[Co(dien-d$_5$)$_2$]Cl$_3$.xD$_2$O. - A sample of racemic chloride 2.5 hydrate was dissolved in D$_2$O (99.8%), and after standing at 80° for 1 hour the D$_2$O/H$_2$O was evaporated off under vacuum. The process was repeated with fresh D$_2$O, and the PMR spectrum showed that deuteration was essentially complete.

Buffer Solutions. - The buffer solution for each pH was made up using 2,4,6-collidine (freshly distilled) and the appropriate amount of HNO$_3$,[175] and sufficient solid NaNO$_3$ was added to adjust the ionic strength of this solution to μ = 1.9M. The solid complex, when added for each racemisation run, contributed a further 0.1M to the ionic strength.

Racemisation Kinetics. - (+)-trans[Co dien$_2$](NO$_3$)$_3$.H$_2$O (0.075 g) was dissolved in collidine-HNO$_3$ buffers (10 ml) giving solutions 0.016M in complex, with ionic strength adjusted to 2.0M with NaNO$_3$. Racemisation was conveniently followed at the Hg line 546.1 nm which is coincident with the first peak of the ORD curve (section 5.4). Rotations were measured on a Perkin-Elmer 141 MC polarimeter in a 1 dm cell jacketed to ±0.1°C from a water bath. Initial rotations were about $\alpha_{546} = +0.14^{\circ}$, and individual measurements were accurate to ±0.002°. In the slower runs light was excluded between readings and each run was followed to at least two half-lives.

The pH of each solution was obtained with a Radiometer model 22 pH meter (±0.005 pH unit) by measurement of the kinetic solution at the run temperature after each run was completed (the collidine buffer is temperature dependent). Rates were reproducible to ±5% with the accuracy limited by the pH determination.

Hydrogen Exchange Kinetics. - The deuteration runs were carried out on racemic trans[Co dien$_2$]Cl$_3$.2.5H$_2$O in D$_2$SO$_4$/D$_2$O, and the corresponding deuterated compound was used for the protonation studies in H$_2$SO$_4$ solutions. The stock acid solutions were titrated potentiometrically against sodium tetraborate. PMR spectra were measured using a Varian T60 NMR spectrometer with sodium trimethylsilylpropanesulphonate as the external reference standard. All solutions were 0.33M in complex whence $\mu = 2.0$M. The NMR tubes were kept in the probe of the spectrometer throughout the runs at 34.9°C, and in a constant temperature water bath for the higher temperatures. In these latter runs the tubes were withdrawn from the bath at suitable times, cooled quickly to 35°, and the N-H region of the spectrum was recorded immediately.

It was not possible to assess peak areas using the instrument integrator due to its instability over the broad N-H peak and with time. Relative peak areas were obtained by making three tracings of the peak recorded at each time (smoothing out noise) on to paper of uniform thickness, sketching in the baseline, and cutting out. The triplicate paper pieces were weighed together (weights corresponding to maximum peak areas were about 0.25 g). This procedure averaged out variations caused by subjective judgements in making the tracings.

This tedious technique differed from that used by the previous workers. With the complexes of N-Meen and sarc, the peak heights of the methyl singlets (methyl doublets collapse on deuteration) were taken as proportional to the concentrations of the N-deuterated species.

Ideally, the exchange and racemisation rates should be measured at similar complex concentrations. However this would necessitate the use of a much shorter pathlength cell (0.5 cm) for the racemisation runs, and consequently either a smaller volume of solution (ca. 1 ml) or use of a considerably larger amount of the active complex. The accuracy of the racemisation rates k_R is limited by the determination of pH, and it was felt that the larger errors in pH measurement associated with the use of very much smaller volumes and more concentrated solutions did not warrant the use of these conditions. Furthermore there is some uncertainty in any case in the variation of K_w with complex concentration [Co] and ionic strength μ (see next section). The variation of k_R with [Co] and μ was not large and formed only a minor part of the investigation. The techniques and conditions used are essentially similar to those used previously on the other Co(III) systems,[10,24,101,120] where exchange and racemisation were measured under differing conditions of [Co].

8.4 RESULTS

Hydrogen Isotope Exchange. - The PMR spectrum of trans[Co dien$_2$]Cl$_3$.2.5H$_2$O in D^+/D_2O is given in Figure 31. The band assignments follow from the peak area ratios NH:NH$_2$:CH$_2$ = 1:4:8 as determined previously (section 4.3.3). The >NH peak is also shown at the higher amplitude at which the deuteration runs were followed, and it is evident (Figure 31C) that after ~10 half-lives exchange was essentially complete. The exchange was followed in both directions, by measurement of peak area of the >NH signal at appropriate times. Plots of $\log[(\text{peak area})_t - (\text{peak area})_\infty]$ versus t were linear (within the errors) over at least two half-lives for the deuteration runs in D_2SO_4/D_2O. Protonation runs of the deuterated sample in aqueous H_2SO_4 solutions were more difficult to measure due to the large HOD peak lying close to the >NH signal under these conditions. The HOD background tail under the NH had to be extrapolated subjectively for each recording, and the experimental points in the plot of $\log[(\text{peak area})_\infty - (\text{peak area})_t]$ versus t (peaks background corrected)

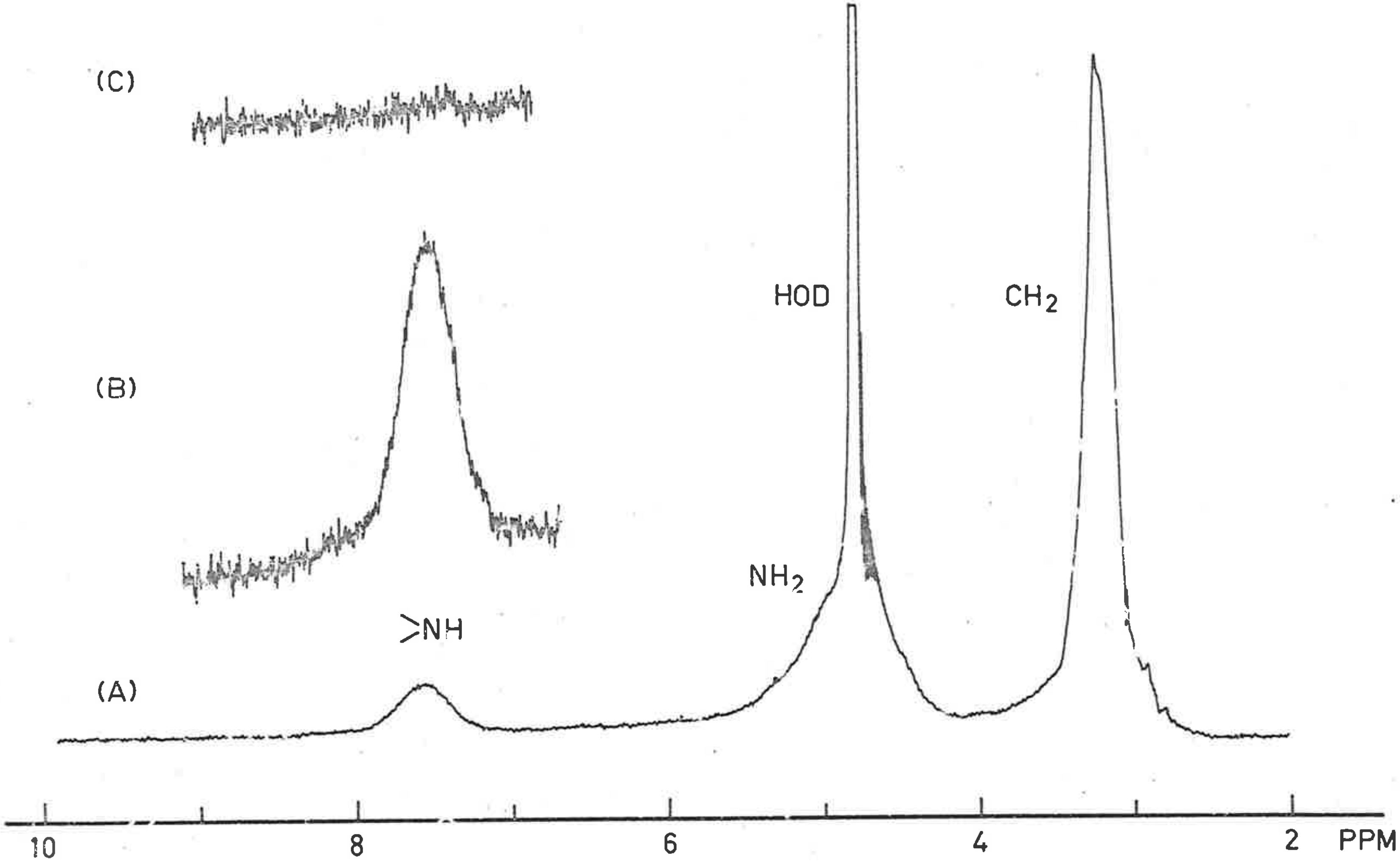


Figure 31. - PMR spectrum of <u>trans</u>[Co dien$_2$]$^{3+}$ in D$^+$/D$_2$0.

(A) Complete spectrum.

(B) NH peak at amplitude increased 8 times, initially, and

(C) after deuteration was complete (10 half-lives).

were more scattered. All rate constants were computed by least-squares analysis of the experimental points up to 2 half-lives for each run. The number of points used in the computation was at least eight, but was usually about twelve. Rate constants for the exchanges are listed in Tables 11 and 12. k_D and k_H were obtained by

$$k_D = k_{obs}/[OD^-] = k_{obs}[D^+]/K_{D_2O} \quad \text{and} \quad k_H = k_{obs}[H^+]/K_w.$$

The constants used were $K_w = 2.11 \times 10^{-14}$ for 2M KCl at 34.9°[176] and values of K_w for the other temperatures were also calculated for 2M KCl using data from the same source.[176] K_{D_2O} was taken as 0.195 K_w for zero ionic strength.[177] The assumption has been made that the ratio 0.195 does not change significantly with ionic strength or temperature, as zero ionic strength is the only condition for which strictly comparable values of K_{D_2O} and K_w have been determined.[178] The constancy of k_D over 9 runs with D^+ concentration varied over the range 10^{-1} to 10^{-3}M at constant temperature (runs 1-9; average value $1.04 \times 10^8 M^{-1}$ sec^{-1} with spread ±0.05 at 34.9°) establishes the rate law to be the same as that for the previously studied bidentate complexes,

$$R = k_D[\text{complex}][OD^-].$$

The average value of k_H under the same conditions is $0.35 \times 10^8 M^{-1}$ sec^{-1} at 34.9° (runs 22, 23) giving the isotope effect as $k_D/k_H = 3.0$. The data indicate that rate constants for the deuterations were generally reproducible to within 10%, all replicate values being within 5% of the mean. Data for a typical deuteration run are plotted in Figure 32. The

TABLE 11

Rate Constants for Deuteration in D_2SO_4/D_2O of *sec* N-H in *trans*[Co dien$_2$]Cl$_3$.2.5H$_2$O[a]

Run No.	$[D^+]$ molar	Temp. ^oC	$k_{obs} \times 10^5$ sec^{-1}	$k_D \times 10^{-8}$ M^{-1} sec^{-1}
1	0.100	34.9	0.444	1.08
2	0.100	34.9	0.408	0.99
3	0.0300	34.9	1.51	1.09
4	0.0100	34.9	4.18	1.01
5	0.0100	34.9	4.06	0.99
6	0.00300	34.9	14.1	1.03
7	0.00300	34.9	13.8	1.01
8	0.00100	34.9	45.0	1.09
9	0.00100	34.9	44.3	1.07
10-12	0.0100	34.9	2.45	0.60[b]
13-15	0.0100	34.9	6.79	1.68[c]
16	0.0300	40.0	2.95	1.51
17	0.0300	40.0	2.66	1.36
18	0.0300	45.0	5.81	2.23
19	0.0300	45.0	5.83	2.23
20	0.0300	50.0	10.0	2.7
21	0.0300	50.0	12.6	3.3

[a] [Co] = 0.33M; μ = 2.0M (no supporting electrolyte added).

[b] [Co] = 0.167M; μ = 2.0M; [KCl] = 1.0M. Rates are means of triplicate runs.

[c] [Co] = 0.167M; μ = 1.0M (no supporting electrolyte added). Rates are means of triplicates.

TABLE 12

Rate Constants for Protonation in H_2SO_4 of *sec* N-D in Deuterated *trans*[Co(dien-d_5)$_2$]$Cl_3 \cdot xD_2O$[a]

Run No.	$[H^+]$ molar	Temp. ^oC	$k_{obs} \times 10^5$ sec^{-1}	$k_{H} \times 10^{-8}$ M^{-1} sec^{-1}
22	0.00976	34.9	7.23	0.335
23	0.00976	34.9	8.06	0.373
24	0.0976	40.0	2.16	0.702
25	0.0976	40.0	2.20	0.715
26	0.0976	45.0	3.27	0.797
27	0.0976	50.0	6.11	1.04
28	0.0976	50.0	6.85	1.16

[a] [Co] = 0.33M; μ = 2.0M (no supporting electrolyte added).

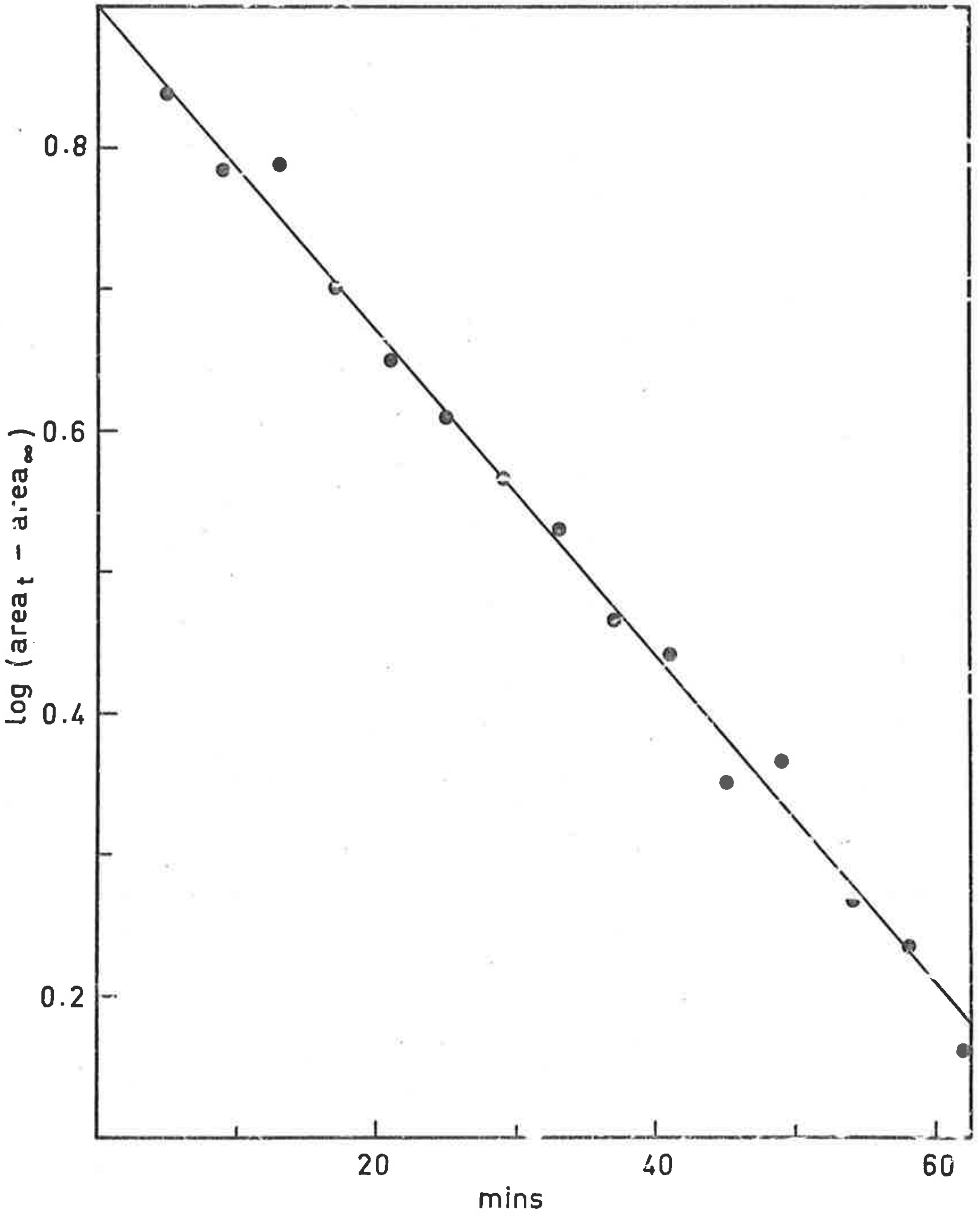


Figure 32. - Rate plot for a typical deuteration run (Run 9; $[D^+]$ = 10^{-3}M, T = 34.9°, k_{obs} = 4.43×10^{-4} sec^{-1}).

accuracy and precision were less than this however for protonation (within 7% of the mean).

Racemisation. - The rates of racemisation were measured in buffer solutions at constant ionic strength ($\mu = 2.0M$) over almost the complete pH range 7.08-8.27 of the collidine-HNO_3 buffer system at various temperatures, Table 13. Pseudo-first order plots of log $\alpha_{546}{}^{o}$ versus t were linear to at least three half-lives, and lines of best fit were drawn visually through the large number of points for each run. Several runs were followed to zero rotation over the visible range ($>10\ t_{1/2}$), and the constancy of the visible spectrum indicated that in the reaction times any hydrolysis or isomerisation was insignificant. Chromatographic analysis on SP C-25 Sephadex (section 2.4) of a solution which had completely racemised failed to detect any other species. $k_R = k_{obs}/[OH^-]$ was calculated using values of K_w as mentioned above. The constancy of k_R over the pH range 7.20 to 8.12 (runs 32-36; average value with standard deviation $2.36 \pm 0.09 \times 10^2 M^{-1}\ sec^{-1}$ at 35^o) confirmed that only the one reaction was being observed and that the rate law was as previously,

$$R = k_R[\text{complex}][OH^-].$$

Activation Parameters. - Activation energies E_a for the three processes were computed by least-squares analysis of the Arrhenius plots of k_R, k_D and k_H, where these rate constants from the individual runs have been

TABLE 13

Rate Constants for Racemisation of

(+)-trans[Co dien$_2$](NO$_3$)$_3$.H$_2$O in Collidine-HNO$_3$ Buffers[a]

Run No.	Temp. °C	pH	$k_{obs} \times 10^4$ sec^{-1}	$k_R \times 10^{-2}$ M^{-1} sec^{-1}
29	25	8.27	1.30	0.687
30	30	7.51	0.586	1.23
31	30	7.92	1.25	1.29
32	35	7.20	0.769	2.28
33	35	7.42	1.24	2.27
34	35	7.46	1.51	2.46
35	35	7.75	2.76	2.32
36	35	8.12	6.89	2.48
37	35	7.67	1.81	1.86[b]
38	35	7.62	2.85	3.29[c]
39	35	7.76	4.94	4.10[c]
40	35	7.68	2.84	2.86[d]
41	35	6.42	0.086	1.54[e]
42	40	7.31	2.89	4.71
43	40	7.55	4.87	4.58
44	40	6.44	0.297	3.59[e]
45	45	7.08	4.17	8.66
46	45	7.15	4.75	8.39
47	45	6.45	0.865	7.66[e]

[a] [Co] = 0.016M; μ = 2.0M (supporting electrolyte NaNO$_3$).

[b] [Co] = 0.008M; μ = 2.0M (NaNO$_3$)

[c] [Co] = 0.016M; μ = 1.0M (NaNO$_3$)

[d] [Co] = 0.008M; μ = 1.0M (NaNO$_3$)

[e] Phosphate buffer HPO$_4^{2-}$, H$_2$PO$_4^-$. [Co] = 0.016M; μ = 2.0M (NaNO$_3$)

calculated allowing for the temperature variation of K_w or K_{D_2O}. Figure 33 shows the Arrhenius plots for the deuteration and racemisation. The activation parameters calculated for the three processes ($\Delta H^{\dagger} = E_a - 0.60$ kcal $mole^{-1}$) are given in Table 14. Errors listed were obtained from the standard errors in the least-squares analyses.

8.5 DISCUSSION

The kinetic results obtained for the hydrogen exchanges and racemisation of trans[Co $dien_2]^{3+}$ follow the general pattern previously observed for the asymmetric nitrogen centre complexes, each reaction following the same form of rate law,

$$R = k_{R,D, \text{ or } H}[\text{complex}][OH^-]$$

$$= k_{obs}[\text{complex}] \text{ at constant pH.}$$

The close similarity in activation parameters for the same reaction between the dien, N-Meen and trenen complexes, as compared in Table 14, strongly indicates a common mechanism. It would thus appear that the coupling of two puckered chelate rings across the sec-N atom in Co-dien confers no additional constraint on the nitrogen "inversion" over that in the single ring case of Co-N-Meen. It may be inferred also that the additional ring coupling around the tertiary-N in the sym$[Co(trenen)N_3]^{2+}$ complex (Figure 6) places no additional restriction on inversion at the sec-N centre.

The present results do not allow a firm decision to be made as to whether nitrogen inversion and conformational interchange are synchronous

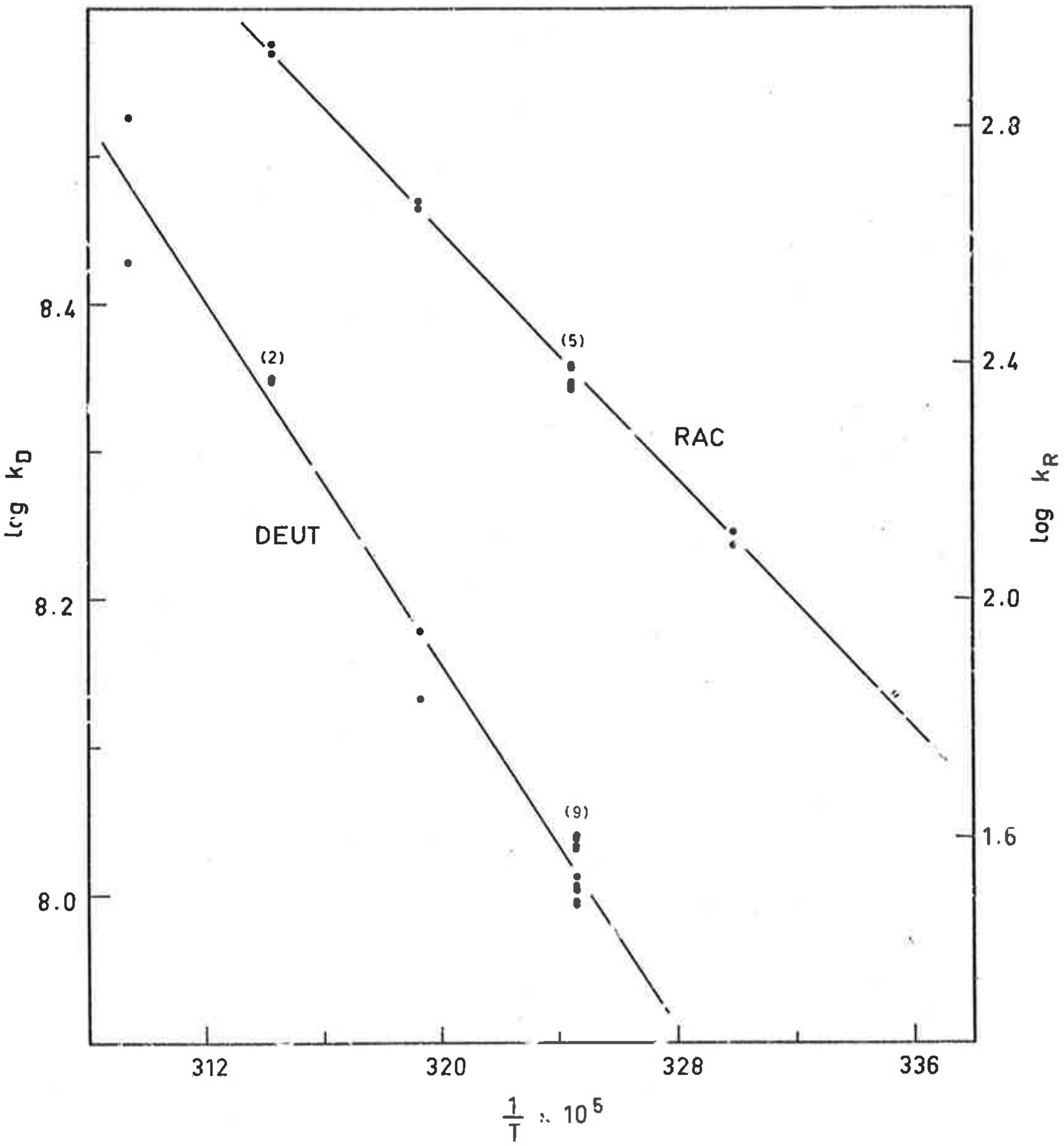


Figure 33. - Arrhenius plots for deuteration and racemisation of *trans*[Co dien$_2$]$^{3+}$. The figures in brackets are the numbers of points at each temperature.

TABLE 14

Rate Constants and Activation Parameters for *sec* N-H Hydrogen Exchange and Racemisation

Reaction	Medium	Temp. °C	$k_{D,H}$, or R M^{-1} sec^{-1}	$\Delta H^{\dagger}$ kcal $mole^{-1}$	$\Delta S^{\dagger}$ e.u.
trans$[Co\ dien_2]^{3+}$					
Deuteration	D_2SO_4	34.9	1.0×10^8	13.5 ± 1	22 ± 3
Protonation	H_2SO_4	34.9	0.35×10^8	13.4 ± 2	20 ± 7
Racemisation	collidine-HNO_3	35.0	2.4×10^2	23.5 ± 0.4	29 ± 2
$[Co(NH_3)_4(N\text{-}Meen)]^{3+}$					
Deuteration	DCl	34.3	3.0×10^7	13.8	21
Protonation	HCl	34.3	1.0×10^7	15.4	24
Racemisation	collidine-HCl	34.3	2.5×10^2	24.3	31
	acetate buffer	34.3	2.4×10^2	23.8	30
sym$[Co(trenen)Cl]^{2+}$					
Deuteration	DCl	34	5.6×10^9	13.7[a]	31
sym$[Co(trenen)N_3]^{2+}$					
Deuteration	DCl	34	1.3×10^9	-	-
Racemisation	tris-$HClO_4$ buffer	34	5.7×10^2	22.7	28

[a] Reference 10 states that $\Delta H^{\dagger}$ for deuteration of the chloro and "activation energy" for racemisation of the azido complexes are 28 and 36 kcal $mole^{-1}$ respectively. It appears from the context that these values are both $E_{a,obs}$ and the $\Delta H^{\dagger}$ and $\Delta S^{\dagger}$ parameters in the above table have been calculated accordingly.

processes or not. Certainly in the Co-N-Meen case inversion and ring interchange are not required to be synchronous,[101] and conformational change or distortion could occur subsequent to deprotonation but prior to nitrogen inversion. In the present system, as in <u>sym</u>[Co(trenen)N_3]$^{2+}$,[10] Dreiding models imply that it is difficult to invert at the N centre without inverting at least one of the ethylenediamine (en) rings, but even this is not required by the results. However recent X-ray studies on coupled en ring systems[124,127,179,180] reveal departures from the idealised structures implied by Dreiding models (with fixed Co, C and N bond angles) so that caution must be exercised in the use of such models for mechanistic predictions.

It might be argued that if synchronous conformational interchange does not occur in Co-N-Meen, the similarity in $\Delta H^{\dagger}$ (racemisation) for these three systems suggests inversion of only one ring in each of the dien and trenen complexes during the nitrogen inversions, equivalent to configurational interchange only of the methyl and hydrogen substituents in Co-N-Meen (without conformational change). If ring conformational change does occur synchronously in the Co-N-Meen system, then on this basis both rings would have to invert synchronously in Co-dien. While it seems likely therefore that one ring in Co-dien inverts synchronously with the nitrogen inversion, the same uncertainties remain for the second ring as in the previous comments[101] on the [Co$(NH_3)_4$(N-Meen)]$^{3+}$ results.

The concurrent inversion of both chelate rings in one dien ligand of <u>trans</u>[Co $dien_2$]$^{3+}$ would produce a deprotonated intermediate having substantial eclipsing of these chelate rings.[10] From the known energy barriers between the staggered and eclipsed conformers of ethane and methylamine,[181] the energy barrier to formation of the eclipsed deprotonated intermediate for the dien complex may be assessed as ca. 14 kcal mole^{-1}. On this basis alone this symmetrical intermediate seems unlikely, and such an intermediate has been discounted also in the base hydrolysis of sym$[Co(trenen)Cl]^{2+}$ where the product retains optical activity,[10] and in the racemisation of $[Pt(N\text{-}Meen)(en)]^{2+}$ [166] where the high retention ratio k_D/k_R dictated against a symmetrical π-bonded intermediate.[168] It is proposed therefore that in the conformational interchanges associated with the nitrogen inversion in trans$[Co\ dien_2]^{3+}$, the two coupled rings will not invert simultaneously. This consideration is distinct from whether or not the inversion of one of the rings is synchronous with nitrogen inversion.

In comparing racemisation and exchange rates for the various complexes, account has to be taken of the number of active centres in each molecule, and the relationship between inversion at each centre and the observed racemisation. The significant comparison should be between inversion rates related to a single centre, k_1.

Trans, trans$[Co(N\text{-}Meen)_2(NO_2)_2]^+$, with two reactive centres, requires inversion of one centre in each molecule to form the inactive meso form, so that $k_R = k_1$. However, with both trans$[Co\ dien_2]^{3+}$ (two reactive centres) and $[Co(NH_3)_4(N\text{-}Meen)]^{3+}$ (one asymmetric centre) only one centre per two molecules need invert to form racemate, so that $k_R = 2k_1$. The inversion rates k_i are thus essentially similar for these latter ions of identical charge (allowing for the [Co] and μ differences), while that for sym[Co(trenen)N_3]$^{2+}$ (k_R = $2k_i$) may be slightly higher (Table 14).

Statistical factors do not enter into the H-exchange rate measurements so that the deuteration rates for the two 3+ complexes differ 3-fold (Table 14) as do the retention ratios k_D/k_i, 2.5×10^5 for [Co$(NH_3)_4$(N-Meen)]$^{3+}$ and 8×10^5 for trans[Co dien$_2$]$^{3+}$. These ratios for the 3+ complexes are considerably less than for sym[Co(trenen)N_3]$^{2+}$, $k_D/k_i = 4.6 \times 10^6$. This factor can not be correlated with the charge difference (a more positive overall complex charge would be expected to enhance the H^+-dissociative process) and it is difficult to associate with some restriction on conformational interchange in the trenen complex since the k_i rates are similar, so that it is probably to be ascribed to the electronegative azido substituent. Although the two highly electronegative groups did not appear to increase the retention ratio in trans, trans[Co(N-Meen)$_2$$(NO_2)_2$]$^+$,[120] ($k_D/k_i = 9 \times 10^4$) the nitro groups are cis to the asymmetric centres in this instance. It seems likely that the azido group is exerting a trans effect in sym-[Co(trenen)N_3]$^{2+}$, enhancing k_D and k_D/k_i. This may not be a general effect however, since estimates of N-H exchange rates at both "angular" and "planar" secondary nitrogen donor sites in α[Co(trien)NH_3Cl]$^{2+}$ [131] and the various configurations of β[Co(trien)(gly)]$^{2+}$ [182] indicate that both detailed ring geometry and position of electronegative substituent affect these rates, but so far few generalisations have emerged.

Other features found common with previous observations are a similar isotope effect for exchange to that in $[Co(NH_3)_4(N\text{-}Meen)]^{3+}$ ($k_D/k_H \sim 3$),[101] and a decrease of racemisation rate in phosphate buffers (runs 41, 44, 47, Table 13) associated with ion-pairing.

A feature not observed previously[24,120] however is a small dependence of all rates on complex concentration (compare runs 4-5 and 10-12 at μ = 2.0M Table 11, runs 32-36 and 37 at μ = 2.0M, runs 38-39 and 40 at μ = 1.0M Table 13), and the effect of ionic strength on all rates is larger than previously noted[24] (compare runs 10-12 and runs 13-15 Table 11, runs 32-36 and 38-39, 37 and 40 Table 13). These features may be rationalised on the basis of ion-pairing. Ion-association of Cl^- (or NO_3^-) may restrict access of the catalysing base to the exchangeable proton or reduce the effective positive charge on the complex moiety, so that the ion-pair would be less reactive towards exchange (on both mechanisms A and B) and the racemisation rate would be consequently diminished also. Slower rates would thus result from increasing μ, or by adding KCl to maintain μ constant when [complex] is reduced. Such interactions may be rather specific[90,91,183] so that the smaller effects noted by the previous workers need not be surprising, despite the larger specific effect of phosphate on the $[Co(NH_3)_4sarc]^{2+}$ system.[24]

The parallel effects of varying [complex] and μ on both the exchange and racemisation rates are more consistent with mechanism A involving a common intermediate for both processes, than with mechanism

B (Figure 30), so that the present conclusions concur with the remarks of the previous authors. The conceptual difference between the alternative mechanisms A and B is small however.

8.6 HYDROGEN EXCHANGE RATES FOR DIFFERENT AMINO GROUPS IN THE $[Co\ dien_2]^{3+}$ ISOMERS

The rate of deuteration (k_D) of the $>N^2 - H$ protons in the s-cis$[Co\ dien_2]^{3+}$ isomer, determined in the same way as for the trans isomer, was found to be $4(\pm1) \times 10^7 M^{-1} sec^{-1}$ (at 35°). This is about three times slower than the $>N^2 - H$ exchange rate for the trans form, where $k_D = 1.0 \times 10^8 M^{-1} sec^{-1}$ at 35°.

In the PMR spectra of the $[Co\ dien_2]^{3+}$ isomers, the $-NH_2$ resonances were directly beneath the HOD peak in solutions of the acid strength used for the deuteration studies (Figure 31A). The measurement of the $-NH_2$ hydrogen exchange rates could nevertheless be made as the $-NH_2$ and HOD resonances were shifted differentially by the addition of small amounts of Co(II) (as $CoCl_2$). However, no such determination of these rates was undertaken.

The kinetic studies on the system sym$[Co\ trenenCl]^{2+}$ [10] (Figure 6, X = Cl) showed that for the deuteration process, $k_{obs} < 10^{-6} sec^{-1}$ at 34° for all $-NH_2$ protons, compared with $k_{obs} = 1.2 \times 10^{-4} sec^{-1}$ in a comparable run for the $>N^2 - H$ proton. Thus the primary amino protons exchanged 10^2-10^3 times slower than the secondary amino proton in this molecule. Due to the stereochemical analogy between these protons in sym[Co trenenCl]$^{2+}$ (Figure 6) and [Co dien$_2$]$^{3+}$ (Figure 4), it would seem reasonable to assume that a similar relationship would hold for the hydrogen exchange rates of -NH$_2$ and $>N^2$ - H protons in [Co dien$_2$]$^{3+}$. Moreover, it would be expected that the rates of $>N^2$ - H exchange in the two cis isomers were similar, and it is predicted that in the isomers of [Co dien$_2$]$^{3+}$, the relative rates of the hydrogen exchanges (k_D) would be:

$>N^2$ - H (trans) > $>N^2$ - H (s-cis and u-cis) >> -NH$_2$ (all isomers).

In their studies of the effect of chelation and of alkyl substitution on the rate of hydrogen exchange in cobalt(III) amines, Basolo, Palmer and Pearson[38] measured the exchange rate for [Co dien$_2$]$^{3+}$ using IR methods and found only one rate experimentally, whence they concluded that "all the hydrogens exchange at the same rate". However, from the present results, it appears that their measured rate ($1.4 \times 10^7 M^{-1}$ sec^{-1} at 25°) was the fastest of the exchange rates ($>N^2$ - H for the trans isomer), and that the much slower -NH$_2$ exchange process was not observed, consistent with the order of exchange rates proposed above. Furthermore, it would also appear from the preparative studies reported earlier (section 3.3) that their [Co dien$_2$]$^{3+}$ product was predominantly trans (equilibrium substitution preparation and isolation in the low yield of 44%), so that the $>N^2$ - H exchange rates for the cis isomers were not observed.

CHAPTER 9

CRYSTAL STRUCTURE STUDY OF (-)-trans[Co $dien_2$]$Br_2(ClO_4).2H_2O$

9.1 INTRODUCTION

As discussed previously (section 5.4), the absolute configuration of active trans[Co $dien_2$]$^{3+}$ cannot be assigned by optical methods so an absolute X-ray crystal structure analysis was attempted. The analysis would also determine the ring conformations, which are important in considering the origins of optical activity in this molecule (section 5.4). Further, the structure analysis would allow the comparison with energy minimisation calculations,[142] as discussed in Chapter 6.

Unfortunately, the analysis was not successful because of crystal disorder. Some conclusions were reached concerning the structure however, and the following description illustrates the difficulties encountered.

9.2 EXPERIMENTAL

Attempts were made to find an anion which gave suitable crystals. [Al ox_3]$^{3-}$ was tried initially as it matches the charge of the cation, and all atoms contained in it are of low atomic weight. Difficulties were incumbent in its use however as it is labile and consequently unstable in the acid conditions necessary for the (-)-trans[Co $dien_2$]$^{3+}$ cation to retain its optical activity during a crystallisation from aqueous solution. Crystallisation of this ion combination therefore had to be rapid and from neutral solutions using solute diffusion[184] between solutions of K_3[Al ox_3]$.3H_2O$ and (-)-trans[Co $dien_2$]$Br_3.H_2O$, but no crystals could be obtained. Br^- (+)-tart^{2-} (in combination) offered a particular advantage as the tartrate ion would have constituted an internal reference for the absolute configuration of the cation. A solution of (−)-*trans*[Co $dien_2$]Br(+)-tart was formed by shaking together in solution (acidified with acetic acid) equimolar amounts of (−)-*trans*[Co $dien_2$]$Br_3.H_2O$ and Ag (+)-tart, filtering off the AgBr and attempting crystallisation of the product from the filtrate by interfacial growth[185] at an n-butanol layer. Again no crystals were obtained. An attempt was also made to crystallise the thiocyanate salt $\underline{(SCN^-)}_3$ by the diffusion technique[184] using solutions of NH_4SCN and the complex bromide (acidified with HBr). In this instance very small crystals were formed but these were not useful for the crystal structure work. The bromide salt $\underline{(Br^-)}_3$ of the complex could be grown to good-sized crystals by slow recrystallisation from a warm concentrated solution in dilute HBr (0.1M). From examination by the polarising microscope these crystals were found to be monoclinic. The crystals contained imperfections however which eliminated the use of this derivative also.

The salt used in the determination was $\underline{Br_2(ClO_4)^{3-}}$, prepared by dissolving (−)-*trans*[Co $dien_2$]$Br_3.H_2O$ in warm $HClO_4$ (1M) and slowly cooling. The orange crystals formed were filtered off, washed with ice-cold $HClO_4$ (1M), ethanol, and air-dried. These crystals were considered satisfactory for the structure determination, although not ideal because of the large scattering power of the anion atoms.

Anal. Calcd. for (-)-trans[Co $dien_2]Br_2(ClO_4).2H_2O$, $CoH_{30}N_6C_8ClO_6Br_2$: C, 17.14; H, 5.39; N, 14.99; Br, 28.5. Found: C, 17.04; H, 5.19; N, 15.08; Br, 27.9.

9.3 SPACE GROUP AND UNIT CELL DATA

From the extinction directions under crossed polars, and from the symmetry and systematic absences of the reciprocal lattice on non-integrated precession photographs, the system was established as orthorhombic of space group $P_{2_12_12_1}$. The cell dimensions were determined as a = 8.53 (±0.02) Å, b = 17.41 (±0.05) Å, and c = 13.67 (±0.04) Å whence V = 1984 $Å^3$. The formula weight is 560.64 and ρ_{obs} = 1.87 (±0.01) g cm^{-3} (determined by flotation in 1,3-dibromopropane/carbon tetrachloride), giving Z = 4 and ρ_{calc} = 1.876 g cm^{-3}.

9.4 INTENSITY DATA COLLECTION

For the collection of the intensity data a crystal of dimensions 0.75 mm x 0.15 mm x 0.10 mm was selected and mounted on a glass fibre along the a axis. Zirconium-filtered MoK_α radiation (λ = 0.7107 Å) was used, and the reflection intensities integrated over one square millimetre of film.

Using a Buerger integrating precession camera, reciprocal lattice layers h0l-$h\bar{6}l$ were collected by precession of the -b axis about the X-ray beam. By precession about the c axis, the layers hk0 and hkl were also collected. Three exposures were taken of each layer, with the ratio of exposure times being (in most cases) 1:3:8.

Integrated Weissenberg photographs of the layers 0kl-5kl were collected using the equi-inclination technique. Three films, interleaved with brass foil, were used for each exposure.

The relative intensities of the reflections were measured on a Nonius II densitometer, the values being recorded on paper tape using a Facit 4070 tape punch. As the Laue symmetry for an orthorhombic unit cell is mmm, then $I_{hkl} \equiv I_{\bar{h}kl} \equiv I_{h\bar{k}l} \equiv I_{hk\bar{l}} \equiv I_{\bar{h}\bar{k}l} \equiv I_{\bar{h}k\bar{l}} \equiv I_{h\bar{k}\bar{l}} \equiv I_{\bar{h}\bar{k}\bar{l}}$, so that only one octant need be measured. Accordingly in any one layer, only one quadrant was actually measured, but the correct indices were nevertheless recorded for use as anomalous data in the final determination of the absolute configuration. The total number of unique reflections thus measured was 1640, of which 472 were considered to be below the detection capabilities of the instrument. These reflections represent 7% of those accessible to MoK_α radiation or 77% of those within the CuK_α limiting sphere.

9.5 DATA REDUCTION

The reflection data was punched on cards from paper tape.[186a] Using least-squares methods, the inter-film scale factors of each reciprocal lattice layer were determined,[186b] and the reflections were corrected for Lorentz and polarisation effects, but not for absorption. By successive approximations, a weighting scheme was determined for the precession data. The weighted mean intensities $\bar{I}_{hkl}$ and standard deviations from the mean were calculated for each reflection.

Equivalence of the octants was assumed at this stage, and the signs of the hkl indices ignored. By comparison of the same reflections on different layer photographs, the inter-layer scale factors were determined by least-squares methods,[186c] so that the weighted mean intensities of all unique reflections were set on the same scale.

9.6 STRUCTURE DETERMINATION

The unit cell of space group $P_{2_1 2_1 2_1}$[187] has its origin half-way between three pairs of non-intersecting screw axes. There are four equivalent general positions in the unit cell, and as Z = 4, each asymmetric unit contains one formula unit.

A three dimensional Patterson synthesis was computed[186d] and from the Harker sections ($u = \frac{1}{2}$) four peaks were obtained, none of which appeared significantly stronger than the others. It was believed at this stage that the crystal was actually (-)-trans[Co dien$_2$](ClO$_4$)$_3$ and consequently the heaviest of the peaks was assigned as Co (although not significantly heavier than the other three). A Fourier map[186d] based on this atom revealed three other relatively heavy atoms which all satisfied the Patterson peaks. All these four Fourier peaks were very close to $y = 0, \frac{1}{4}$ or $\frac{1}{2}$ so that considerable overlapping would be expected in the Patterson map. These four atomic positions are shown in Figure 34 numbered 1 to 4. Peak number 1 is that assigned to Co at this stage. Peak 2 (6 Å from Co) was found to be split. Atoms 3 and 4 (Figure 34) were each less than 5 Å from peak 1 (Co), but this distance was less than that expected for a Co-ClO_4 approach.[133]

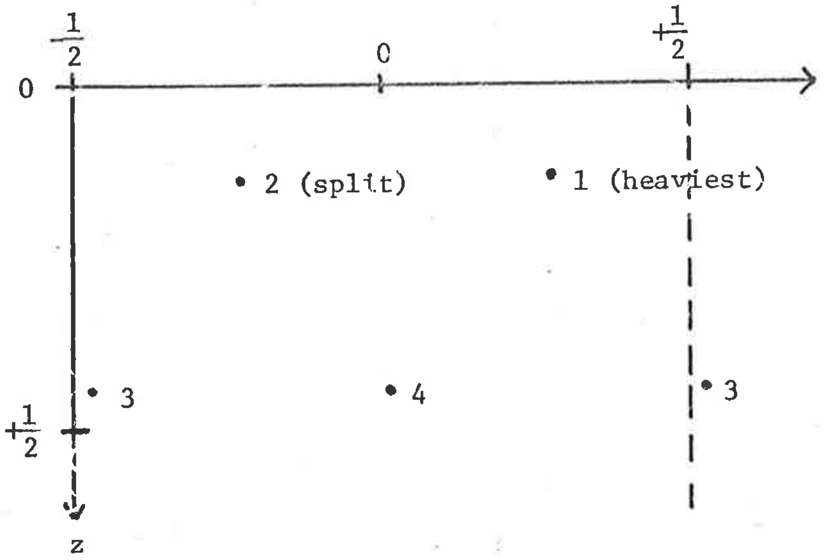


Figure 34. - yz projection of the asymmetric unit for (-)-trans[Co $dien_2$]$Br_2(ClO_4).2H_2O$, being one quarter of the $P_{2_1 2_1 2_1}$ unit cell. Fractional coordinates are indicated.

Subsequent structure factor calculations[186e] and Fourier maps[186d] phased on these four heavy atoms did not readily yield the nitrogen octahedron and the carbon atoms about Co, but by refining[186e] the positions of the heavy atoms, and their isotropic temperature factors, the nitrogen octahedron and a possible carbon set was located. These atoms were found by computing the radii of spheres 2 Å and 3 Å from Co, and drawing the resultant circle on each section of the Fourier map, as it is known that the Co-N coordination distance is about 2 Å,[21] and from Dreiding models it appeared that all carbon atoms would be between 2.8 and 2.9 Å distant from Co in this molecule. There was also much diffuse electron density in the map. A combination of Fourier and difference[186d] maps led to the positions of some perchlorate oxygen atoms, but in subsequent difference maps large discrepancies in the positioning of many atoms were obvious. Such disagreement led to re-examination of the atom assignments.

It was realised at this stage that the crystals used contained bromide, and analysis showed that the compound was in fact (-)-trans-[Co dien_2]$Br_2(ClO_4).2H_2O$, which has a formula weight almost identical to the triperchlorate.

Re-examination of the Patterson map yielded little further information because of the overlapping of the peaks. A guide to the atom assignments was sought by assigning each of the four heavy atoms an atomic weight and scattering power corresponding to Co (i.e. intermediate values) in the structure factor calculations, and refining the multipliers. This procedure confirmed that atom 1 (Figure 34) was the heaviest atom, so it was assigned as Br. Atom 3 was chosen as Co, atom 4 as Cl and the split peak 2 was assumed to be Br, and the Fourier and difference maps were then recalculated on this basis.

Both the Fourier and difference maps showed there was considerable electron density, with concentrations or peaks, surrounding both atoms 3 and 4. The electron density was particularly diffuse around atom 4 and was difficult to interpret. The peaks surrounding atom 3 (assigned as Co) could be interpreted as a clearly defined octahedron of nitrogen atoms at distances ca. 2.0 Å, with a satisfactory carbon skeleton further out. However there were also peaks at ca. 1.5 Å, and these were not consistent with atom 3 being Co since the nearest atoms should be nitrogen atoms at 2 Å. In a similar manner, peaks surrounding atom 4 (assigned as Cl) were at ca. 1.5 Å, consistent with a tetrahedron of perchlorate oxygen atoms, but there were also quite diffuse peaks at 2-3 Å which are not consistent with the assignment of 4 as Cl. These peaks at 2 Å could roughly fit an octahedron of N atoms, although the actual positions were not easily defined.

The difference map also indicated that the Co and Cl assignments for atom positions 3 and 4 (respectively) should be interchanged, since a lower electron density was indicated for position 3 than that assigned from Co, and a higher electron density was indicated at position 4 than from Cl.

When positions 3 and 4 were reassigned as Cl and Co respectively (interchanged from the above) a similar general pattern was evident from the new difference map. Again electron density peaks were observed at ca. 1.5, 2.0 and 2.9 Å surrounding each position 3 and 4, and again interchange of the assigned Cl and Co was indicated.

There thus appeared to be disorder in the unit cell. The best model obtained for this system was a partial occupancy of positions 3 and

4 by Co and Cl, and consequent partial occupancy of the N and C sites around each of these positions 3 and 4. Position 2 was also considered split, with a single Br ion being shared between two close sites centred at this general position. Assuming an occupancy factor of 0.5 for the above model, structure factor calculations gave a residual index of R = 0.278. The structure determination was abandoned at this stage when it had become clear that the above-mentioned difficulties would not permit the absolute configuration to be obtained.

Interpretation of the Patterson map was difficult because of overlapping due to the particular positions of the heavy atoms. The partial occupancy and splitting adds to the diffuseness and similar magnitudes of peaks in the vector map. The proposed disorder explains the presence of electron density within the 2 Å radius sphere of each atom 3 and 4 on the Fourier maps as being due to the perchlorate O atoms. The diffuse nature of these oxygen peaks need not be surprising since the perchlorate ion tends to be thermally disordered,[133,188,189] an effect which would itself lower the precision of the determination.[188] An unusual feature of the partial occupancy is that atom 3 has a clearly defined N octahedron and C chain, whereas the corresponding regions are very diffuse about the interchangeable position 4.

Partial occupancy by Co and Cl of these two positions 3 and 4 would obviate to some extent the electrostatic repulsion between the Br^- and ClO_4^- anions that would exist if either atom, Co or Cl, solely occupied one position, leaving three negative ions in close contact. The split nature of the Br in position 2 may correspond to its alternate sites depending on the occupancy by Co or Cl of the positions 3 and 4 in a particular unit cell. The Br in position 1 was not split in the same way however. Some electron density was evident surrounding position 1 (hence the initial location of a N octahedron and C skeleton when 1 was initially assigned as Co) so that the disorder may extend to involve position 1 to some degree also.

Further evidence for CoN_6-ClO_4 disorder was that the electron densities of the atoms at positions 3 and 4 were similar and intermediate between those of Co and Cl. Similarly the nitrogen octahedron about either site did not give a satisfactory difference map when inserted in the synthesis at full weight for either position.

9.7 CONCLUSIONS

Because of the partial occupancy of two positions in the unit cell (positions 3 and 4 in Figure 34), determination of the structure and absolute configuration of (-)-trans[Co $dien_2$]$Br_2(ClO_4).2H_2O$ was not possible. The structural information required for comparison with an energy minimised calculated structure,[142] and to clarify some of the problems associated with optical activity in this molecule, should be provided by the X-ray structural analysis of the racemic form of the complex, (±)-trans[Co $dien_2$]$Br_3.H_2O$, which is in progress.[36] However, the determination of absolute configuration of the active ion relies on an absolute X-ray structural analysis. Because of the unusual symmetry properties of this ion, and the uncertainty of the source of its optical activity, it is hoped that such an analysis can be made using another suitably crystallised derivative.

CHAPTER 10

THE $[Co(4\text{-Medien})_2]^{3+}$ SYSTEM, AND EXTENSION OF THE PRESENT STUDIES

10.1 PREPARATION AND SPECTRAL PROPERTIES OF THE ISOMERS OF THE $[Co(4\text{-Medien})_2]^{3+}$ SYSTEM

It has already been suggested that the analogous complex system of the 4-Medien ligand (methylation at the sec-N atom of dien) should afford considerable further information to clarify some of the partly answered problems discussed earlier in this thesis. These aspects are briefly summarised subsequently (section 10.1.2).

The 4-Medien ligand and the resultant complex system have been prepared and the isomers separated and characterised, with a view to extending the studies on certain stereochemical aspects. It is hoped that these particular studies can be undertaken in the future.

The 4-Medien ligand was prepared by a method based on the synthesis by Mann of the same compound.[190] In the present work, the two primary amino groups of dien were protected by their inclusion in phthalimido rings, and the free secondary amino group was then directly methylated. Subsequent acid hydrolysis of the phthalimido groups gave the required ligand as the hydrochloride salt. The present synthesis differs from Mann's[190] in the first of these three stages. The diphthalimido derivative of dien was formed by direct reaction of dien with phthalic anhydride, whereas Mann reacted 2,2'-dichlorodiethylamine ($Cl-CH_2-CH_2-NH-CH_2-CH_2-Cl$) with potassium phthalimide to give the same compound.[190] It is noted that other workers have reported failure in attempts to form the diphthalimido derivative of dien by direct reaction.[191] The two subsequent steps were essentially the same as used by Mann. The reaction scheme used in this work is shown in Figure 35.

The complex was prepared, and the isomers separated, using methods similar to those previously described for [Co $dien_2]^{3+}$ (sections 3.3 and 2.4).

10.1.1 EXPERIMENTAL

Diethylenetriamine, from either Fluka (puriss) or Union Carbide Australia Ltd., was used without further purification. Phthalic anhydride of laboratory reagent grade (Unilab), was purified as described in the synthesis (below). The charcoal was freshly ground BDH "granulated charcoal for gas absorption". The solvents (chloroform and acetone) were of commercial quality. $[Co(NH_3)_5Cl]Cl_2$ was prepared using literature methods,[71] iodomethane (Unilab) was freshly distilled before use (b.p. 42°), and all other chemicals used were analytical grade reagents.

The electronic, IR and PMR spectra were recorded in the same way as those of the [Co $dien_2]^{3+}$ isomers (section 4.2).

Preparation of 2,2'-diphthalimidodiethylamine. - Phthalic anhydride (185 g, 1.25 mole) was dissolved in hot chloroform (ca. 1 l) and the hot solution was filtered to remove some phthalic acid. The solution was transferred to a large evaporating basin, cooled to ca. 30°, and dien

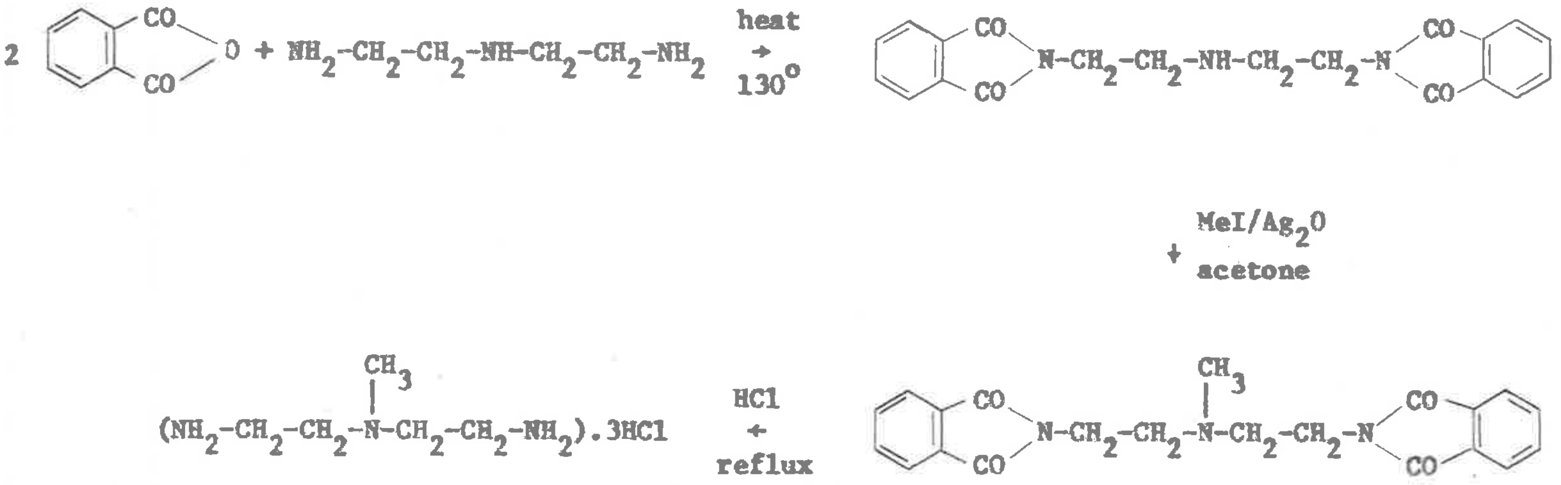


Figure 35. - Reaction scheme for the synthesis of 4-Medien.3HCl.

(52 g, 0.50 mole) dissolved in chloroform (ca. 250 ml) was added cautiously with stirring. A quite vigorous exothermic reaction occurred and a sticky white solid separated. The chloroform was removed by heating on a steam bath, and the resultant yellow sticky mass was then heated in an oven at 130° for 45 minutes. After cooling, the yellow brittle solid product was ground to a powder and washed in turn with water, 0.5M sodium carbonate solution (to remove unreacted phthalic anhydride, phthalic acid, and partially reacted open-ring material), water, and cold ethanol until the washings were colourless. The product was recrystallised by dissolution in a minimum quantity of chloroform (ca. 400 ml), filtering, and precipitating by cooling and adding ethanol (ca. 600 ml). The recrystallised material was filtered off, washed with ethanol and air-dried. Yield 95 g, 52% of theoretical. M.p. 180° (literature 178-180° [190]). The product could also be recrystallised by continuous extraction (Soxhlet) with hot ethanol or acetone but these methods were not particularly efficacious.

Anal. Calcd. for $C_{20}H_{16}N_3O_2$: C, 66.1; H, 4.72; N, 11.6. Found: C, 66.0; H, 4.74; N, 11.4.

Preparation of 2,2'-diphthalimidodiethylmethylamine. - The 2,2'-diphthalimidodiethylamine (36.3 g, 0.10 mole) was refluxed for 4 hours in acetone (ca. 3 l) with freshly distilled iodomethane (20 g, 0.15 mole) and freshly precipitated silver oxide (ca. 16 g, 0.075 mole) in the dark. After this time the brown Ag_2O had turned yellow (AgI) indicating that the reaction had occurred. The solution was filtered (by Buchner and then under gravity) and the acetone evaporated off. The product was recrystallised by Soxhlet extraction with hot ethanol, filtered off, washed with ethanol, and air-dried. Yield of recrystallised material 29.0 g (77%), m.p. 120° (literature 124-126°[190]).

The analysis of this product was unsatisfactory. From the correspondence with the literature melting point it was decided however to use this product for the third reaction stage, and to purify that subsequent product.

Preparation of 2,2'-diaminodiethylmethylamine trihydrochloride (4-Medien.3HCl). - This hydrolysis can be performed on any scale, and with either HCl or HBr. It is quoted here on a 0.10 mole scale.

The recrystallised 2,2'-diphthalimidodiethylmethylamine (38 g, 0.10 mole) was refluxed for 2 hours with conc. HCl/water (250 ml/90 ml) and the solution was cooled and filtered. The collected phthalic acid precipitate was then extracted again by refluxing with more of the acid mixture, and this was also cooled and filtered. The combined filtrates were evaporated to dryness on the steam bath. After cooling, the resultant solid was extracted with a small quantity (ca. 20 ml) of conc. HCl, the mixture filtered, and the phthalic acid collected washed with a little more conc. HCl (ca. 5 ml). The filtrate was then precipitated by adding ethanol, with cooling and scratching, until precipitation just occurred. Under these conditions any dien.3HCl or by-products of the methylation reaction remain in solution. The product was recrystallised from conc. HCl/ethanol, as above. Yield 12.0 g (55%), m.p. 236° with decomposition (literature 239°(d)[190]).

<u>Anal.</u> Calcd. for $C_5H_{18}N_3Cl_3$: C, 26.5; H, 8.01; N, 18.5. Found: C, 26.3; H, 8.01; N, 18.5.

The overall yield of 4-Medien.3HCl, based on dien, was 22%.

<u>Preparation of $[Co(4\text{-}Medien)_2]^{3+}$, separation of the isomers, and their isolation as the bromide salts</u>. - To a slurry in water of $[Co(NH_3)_5Cl]Cl_2$ (10.0 g, 0.04 mole) and activated charcoal (ca. 5 g) was added 4-Medien.3HCl (18.2 g, 0.08 mole) and sodium hydroxide (9.6 g, 0.24 mole), and the solution was heated on a steam bath for 4 hours with occasional stirring. The solution was filtered hot and the filtrate cooled.

The complex was not isolated from this solution, but separated into its three geometric forms, designated as A, B, C, by chromatography on Sephadex columns. The solution was diluted to 4 litres with water (so that $[Na^+] < 0.1M$), and 1 litre of this solution was applied to a column (70 x 4.5 cm) of SP-Sephadex C-25 cation exchanger, and the complex eluted with 0.3M Na_2 (+)-tart solution. Three clearly separated hexamine complex bands were obtained, the fastest moving (A) being yellow, while the predominant band (B) and the minor, slowest moving band (C), were orange. A considerable number of minor red and purple bands were also observed, and these probably corresponded to the various $[Co(4\text{-}Medien)(H_2O)_xCl_{3-x}]^{x+}$

species. (The use of 0.5M $NaClO_4$ solution as eluent gave two hexamine bands, and a different elution order, namely C fastest followed by a mixture of A and B.) The eluant bands were collected, and the separation process was repeated with further 1 litre samples of the solution until all the complex sample had been separated. The combined eluants for each bands were separately passed through a column of ion-exchange resin (Bio-Rad AG 50W-X4, 200-400 mesh), and the +3 absorbed cation was washed with 1M HBr to remove 1+ and 2+ cations. The +3 complex isomers were then eluted by 3M HBr, and these solutions were evaporated almost to dryness on a rotary evaporator (60°), and the complex bromides precipitated by the addition of ethanol (A and B) or iso-propanol (C). This second ion-exchange procedure effectively combined the removal of the tartrate ion and the concentration of the solution into one step, and as well insured the elimination of trace amounts of purple species. Yield:

Isomer A - 1.1 g (5% of theoretical yield, based on the bromide salt being anhydrous).

Isomer B - 12.7 g (57%, bromide salt is monohydrate).

Isomer C - ca. 0.2 g, hygroscopic (1%, assuming bromide salt is monohydrate).

The overall yield of the complex was thus 63% of the theoretical.

Isomers A and B were each recrystallised from hot water. Isomer A analysed as the anhydrous salt, and B as the monohydrate. C could not be analysed as the bromide salt, due to its hygroscopicity.

Anal. Calcd. for (A) $[Co(C_5H_{15}N_3)_2]Br_3$: H, 5.68; N, 15.8; Br, 45.0; Co, 11.06. Found: H, 5.67; N, 15.5; Br, 44.7; Co, 11.07.

Calcd. for (B) $[Co(C_5H_{15}N_3)_2]Br_3.H_2O$: C, 21.8; H, 5.85; N, 15.3. Found: C, 22.0; H, 5.63; N, 15.0.

Despite considerable effort, the carbon analyses for samples of A (ca. 20.4%) were always significantly less than those calculated (22.5%). However, from the Co, N and Br analyses it seems certain that the compound is anhydrous and that particular difficulties were inherent with this compound in releasing all the carbon during analytical procedures.

10.1.2 RESULTS AND DISCUSSION

The 4-Medien ligand was prepared and the resulting Co(III) system, $[Co(4\text{-}Medien)_2]^{3+}$ isolated as the three possible geometric isomers. These isomers A (yellow), B (orange), C (orange) were formed (under equilibrium conditions at 82°) in the ratios A:B:C = 8:90:2. This complex was isolated in lower yield (63%) than the $[Co\ dien_2]^{3+}$ system (94%), which is consistent with the reduced coordinating tendency of tertiary amines (4-Medien) compared with secondary amines (dien).

Electronic Spectra.

The visible spectra of the isomers in aqueous solution are given in Figure 36, and the extinction coefficients in Table 15.

The form of the spectrum of isomer C is considerably different to the other two isomers (Band 2 is presumably beneath the large charge-transfer peak).

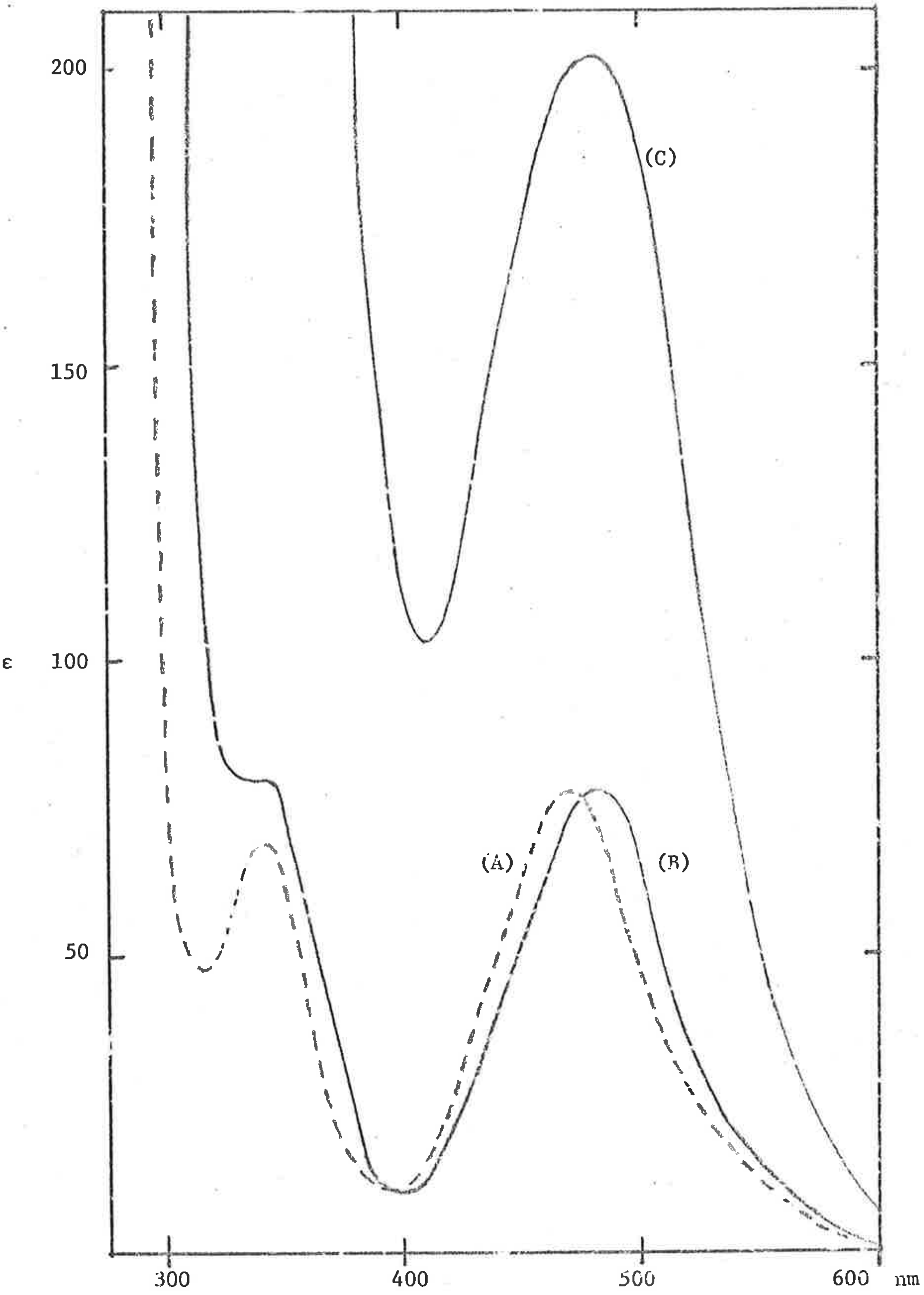


Figure 36. - Electronic spectra of the isomers of the $[Co(4\text{-}Medien)_2]^{3+}$ system.

TABLE 15

Molar Extinction Coefficients at Absorption Maxima in the Visible Spectra of the $[Co(4\text{-Medien})_2]^{3+}$ Isomers

	Band 2	Band 1
Isomer A	$\varepsilon_{341} = 67.3$	$\varepsilon_{471} = 77.4$
Isomer B	$\varepsilon_{342} = 77.0$	$\varepsilon_{482} = 77.3$
Isomer C	-	$\varepsilon_{481} = 212$

Infrared Spectra.

It was proposed earlier (section 4.3.2) that three regions of the IR spectra would be useful for the assignment of the configuration of coordinated dien and dien derivatives in their metal complexes. These regions were

(i) 2900–2800 cm^{-1}, where the ν_{CH_2} region for trans isomers was observed to be more intense than for cis isomers;

(ii) ca. 1250 cm^{-1}, where there was a sharp ω_{N-H} absorption for trans isomers (absent, or a broader absorption for cis); and

(iii) 950–800 cm^{-1}, where trans isomers showed a quartet, compared with (three or fewer) bands for cis isomers.

The criterion (ii) is not applicable to the $[Co(4\text{-Medien})_2]^{3+}$ system. (i) and (iii) should be applicable, although their application would require some caution in the present instance due to the extra $>N - C$ and $-CH_3$ bonds present, whose IR spectral modes would be anticipated to contribute to the observed spectra in these two regions. Study of the IR spectra in these regions (Figure 37) indicates that isomer A has a relatively more intense ν_{CH_2} region (2900-2800 cm^{-1}) than the other isomers and shows the quartet in the 950-800 cm^{-1} region. Accordingly it would appear to be the trans isomer. The further assignment of B and C was not obvious.

PMR Spectra.

PMR spectra allowed unequivocal assignment of the geometric isomers of $[Co\ dien_2]^{3+}$, and it was hoped that it would also allow assignment in the $[Co(4\text{-}Medien)_2]^{3+}$ system, since the corresponding isomers in the two systems are symmetrically analogous.

In the u-cis and s-cis isomers of $[Co\ dien_2]^{3+}$, the PMR spectra in both neutral and acid solutions were consistent with rapid conformational inversion. The substitution of the methyl group at the central nitrogen atom to give $[Co(4\text{-}Medien)_2]^{3+}$ should not prohibit the conformational inversion process in the cis isomers of this system, so that the corresponding $-NH_2$ and $>CH_2$ regions in the PMR spectra of these isomers in these two complexes should be closely comparable. Trans$[Co(4\text{-}Medien)_2]^{3+}$ on the other hand should be rendered conformationally and configurationally inert by the tertiary amino group (even under neutral or basic conditions), contrasting with trans$[Co\ dien_2]^{3+}$ where $>N^2 - H$ dissociation facilitates

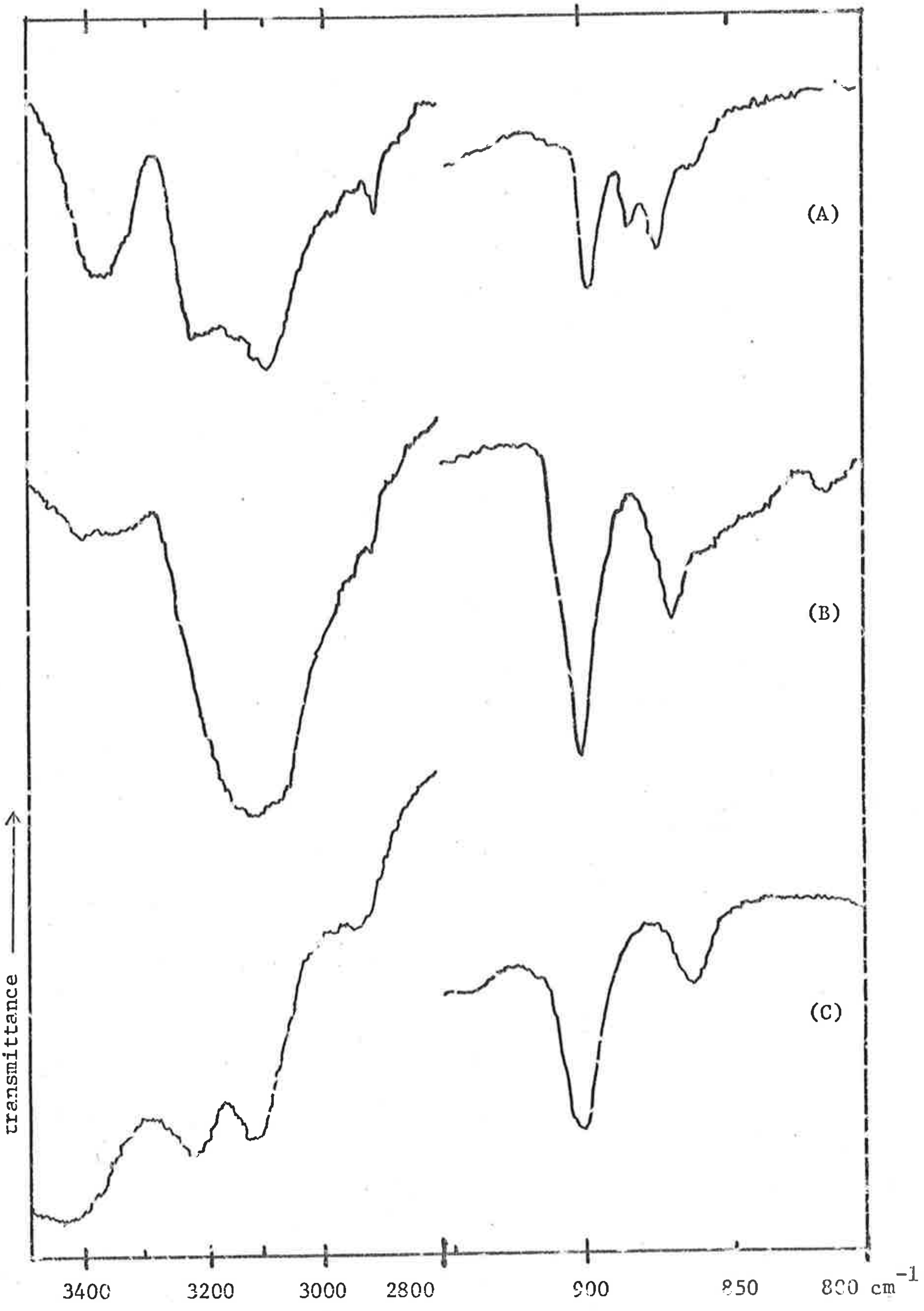


Figure 37. - IR spectral regions 3500-2800 cm^{-1} and 950-800 cm^{-1} for the isomers of the [Co(4-Medien)$_2$]$^{3+}$ system.

conformational inversion. Thus while the $-NH_2$ and $>CH_2$ resonances should be comparable in acid conditions (no conformational inversion in trans[Co dien$_2$]$^{3+}$), the $>CH_2$ resonance for the dien complex should be simpler under neutral conditions because of conformational averaging.

The 100 MHz PMR spectra of the three isomers of [Co(4-Medien)$_2$]$^{3+}$ in neutral and acid solutions of D_2O are given in Figure 38. Comparison with the 100 MHz spectra of the [Co dien$_2$]$^{3+}$ isomers in acidic D_2O (Figure 9a) reveals a close correspondence between the $-NH_2$ resonances of trans[Co dien$_2$]$^{3+}$ and isomer B of the 4-Medien system, and similarly between s-cis[Co dien$_2$]$^{3+}$ and isomer A of the present system.

From a study of Dreiding models, there appears to be very considerable steric crowding between the two $-CH_3$ groups in u-cis[Co(4-Medien)$_2$]$^{3+}$. To accommodate such an interaction the molecule would have to distort. No such gross distortions would be required for the other two isomers, from Dreiding models. The appearance of a methyl doublet in the PMR spectrum of C is consistent with distortion occurring in the u-cis structure such that the molecular C_2 axis of the dien case is destroyed, and the two $-CH_3$ groups being rendered non-equivalent. On this basis C is therefore taken to be the u-cis geometric isomer.

These tentative isomeric assignments from the IR spectra (A = trans ?) and PMR spectra (B = trans ?, A = s-cis ?) are thus in conflict, although they are both consistent with C being assigned as u-cis. In this latter case, there is also consistency with the electronic spectra, where the spectrum of C differing greatly from the other two may be correlated with

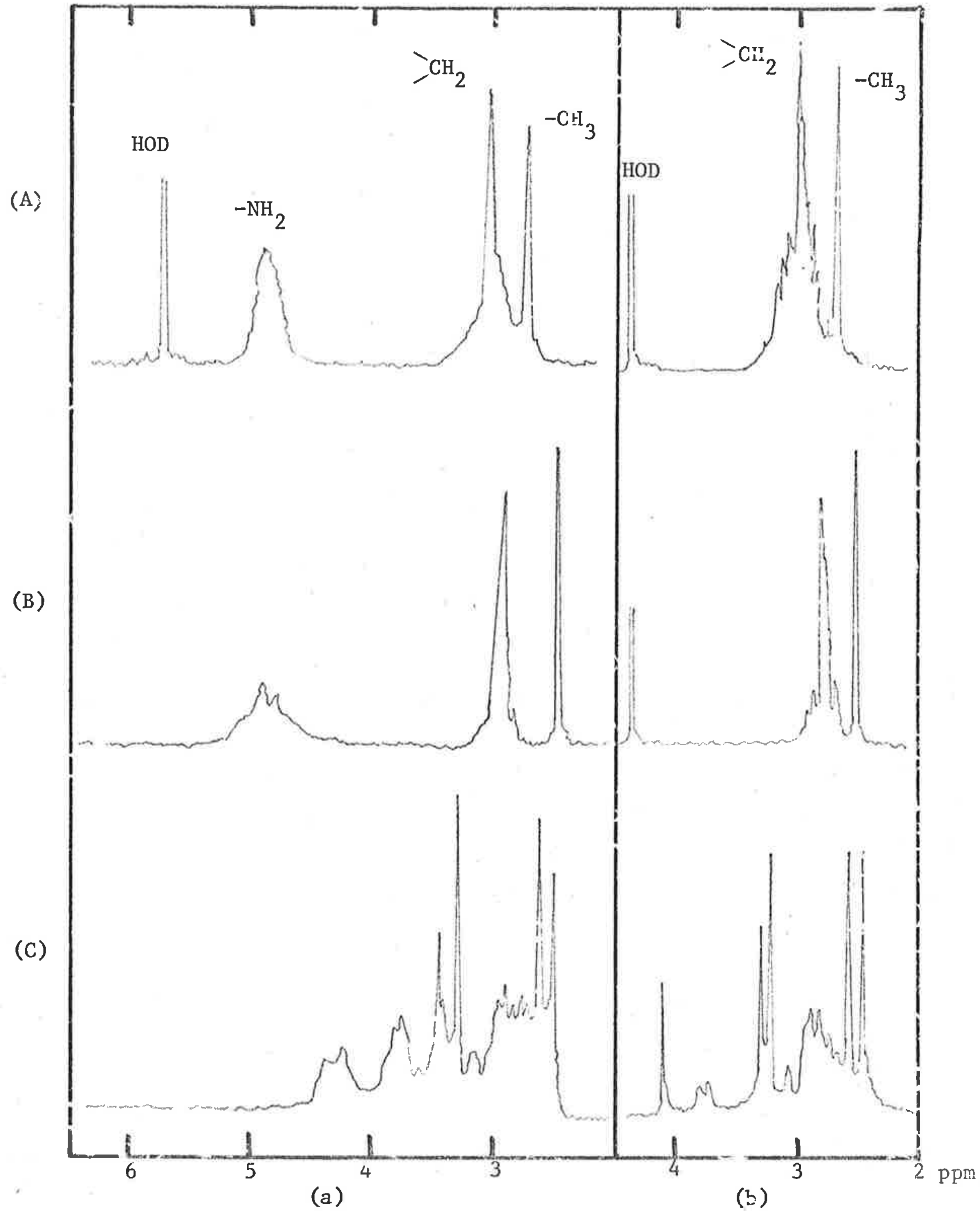


Figure 38. - 100 MHz PMR spectra of the isomers of $[Co(4\text{-Medien})_2]^{3+}$ in (a) D_2O/D_2SO_4, and (b) D_2O.

the reduced symmetry of the u-cis isomer. It is possible that the presence of extra $>N-CH_3$ bonds has led to erroneous conclusions with the IR technique.

Future Optical Rotatory Power Studies.

The unequivocal isomer assignment is dependent on the optical resolutions and the rotatory properties. As in the $[Co\ dien_2]^{3+}$ system, the optical resolutions of the u-cis and trans isomers will allow unequivocal assignment of the s-cis structure which is not dissymmetric. The active trans isomer in the $[Co(4\text{-}Medien)_2]^{3+}$ instance will be optically stable in base, since $>N^2$ - H exchange (as in the dien case) cannot occur thus preventing racemisation.

The trans isomer, as in trans$[Co\ dien_2]^{3+}$, is optically active only because of the bond-pair chirality, in this instance typified and described by the relative dispositions of the two $>N-CH_3$ bonds. As with trans$[Co\ dien_2]^{3+}$ (section 5.4), no CD would be expected in the charge transfer spectral region, whereas the u-cis isomer should show a CD response in this region because its activity arises primarily from a configurational effect.

Resolution of isomer B (suspected as trans) has been attempted with the resolving agents AsO(+)-tart, SbO(+)-tart, α-bromocamphorsulphonate, and $(-)\text{-}[As\ cat_3]^-$,[75] but in all these instances the least soluble diastereoisomers obtained contained only the inactive cation.

Isomer Proportions.

Assuming the assignment of the isomers of $[Co(4\text{-Medien})_2]^{3+}$ from PMR, the proportions of s-cis:u-cis:trans = 8:2:90 are compared with the isomeric ratio 12:41:47 for $[Co\ dien_2]^{3+}$ under comparable conditions. Due to the crowding of the $-CH_3$ groups expected in u-cis$[Co(4\text{-Medien})_2]^{3+}$, it would be anticipated that the relative proportion of this isomer would decrease compared with the situation in the $[Co\ dien_2]^{3+}$ system. However, the reason for the increase in the trans/s-cis ratio ($^{90}/_8$ compared with $^{47}/_{12}$ for $[Co\ dien_2]^{3+}$) is less apparent, and energy minimisation calculations may be required to rationalise this observation.

The specific ion-pair proposed between s-cis$[Co\ dien_2]^{3+}$ and PO_4^{3-} (section 6.4.3) should not form to such an extent between $[Co(4\text{-Medien})_2]^{3+}$ and the anion because one of the three N-H bonds involved in such hydrogen bonding in the former system has been replaced by a methyl group (Figure 17). Comparable equilibrium preparations at 18°, in the absence of PO_4^{3-}, and with excess of that anion present (1.2M, cf. [Co] = 0.02M), showed that the anion increased the s-cis/trans ratio from $^{16}/_{84}$ to $^{35}/_{65}$, consistent with lower association than in the $[Co\ dien_2]^{3+}$ system where the s-cis/trans ratio changed from $^{7}/_{65}$ to $^{59}/_{12}$ under the same conditions. No u-cis$[Co(4\text{-Medien})_2]^{3+}$ was detected in these runs at 18°.

It is also noteworthy that the proportion of s-cis isomer decreased on increasing the temperature (16% at 18°, 8% at 80°) whereas with the $[Co\ dien_2]^{3+}$ system, the s-cis isomer increases in proportion (7% at 18°, 12% at 80°). Such studies might usefully be extended to allow assessment of the energy differences between these forms.

10.2 FURTHER STUDIES IN BIS(TRIDENTATE) SYSTEMS

It has been mentioned in the course of this thesis that several aspects of the study of $[Co\ dien_2]^{3+}$ have not been completed. For example, the more accurate assessment of the effect of temperature variation on the equilibrium isomer proportions would lead to determination of the individual contributions of ΔH^o and ΔS^o to the free energy differences (and hence the equilibrium constant K) by environmental parameters (Chapter 6). Also, the extension of the isomerisation studies reported in Chapter 7 to include confirmation or otherwise of base catalysis may afford useful information on the proposed isomerisation mechanisms, as outlined in that chapter. The use of the 4-Medien and lin-penten systems in these mechanistic studies has also been mentioned previously.

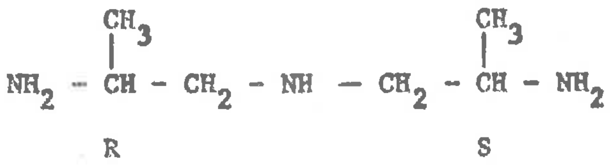
There are several other systems on which such stereochemical studies could be carried out. For example, the isomer proportion studies (with concurrent energy minimisation calculations) could be extended to consider the effect of metal size ($[Cr\ dien_2]^{3+}$) or of ring size ($[Co\ ditn]^{3+}$).

A preliminary study of $[Cr\ dien_2]^{3+}$ has been undertaken.[4b] The product was prepared by a non-equilibrium method, but was found to readily undergo hydrolysis so that chromatography was not possible in aqueous solvents. So far the isomeric content of this material is unknown, although it is suspected (from comparison of the X-ray powder photograph with those of the three [Co $dien_2]^{3+}$ isomers) that it is at least predominantly trans. No optical resolution has been achieved, and this work is being pursued.

Similarly, the [Co $ditn_2]^{3+}$ system, which has the same gross geometric properties as [Co $dien_2]^{3+}$, has been prepared but no isomeric forms have been separated. As less is known about the conformations of six-membered rings in general, a proportion study of the isomers (once separated) may be valuable. Further, the energetics associated with the base-catalysed racemisation of the trans isomer of this system may be rewarding (compare Chapter 8) because the inversion process should involve the conformational interchange of interlocked six-membered chelate rings.

In the studies of optical rotatory power (Chapter 5), the demonstration of the existence of the "bond chiral effect" leads to the consideration of other systems where these effects might be demonstrated. The systems $[Co(dien)(IDA)]^+$,[31] $[Co(dien)(MIDA)]^+$ [31] and $[Co(IDA)_2]^-$ [136] have all been prepared and the geometric isomers separated, but the resolution of their trans isomers and measurement of their CD spectra would further demonstrate this new effect. Similarly, the effect on the optical rotatory power of alkyl substitution in trans$[Co(4\text{-}Medien)_2]^{3+}$ will be of interest since there are few metal complexes where this has been possible to date.

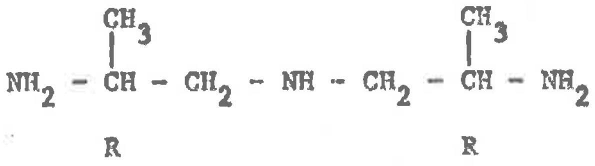
The absolute configuration of these complexes cannot be assigned by spectroscopic means however. The present author proposes to undertake an absolute X-ray structure analysis of a suitable anion derivative of either optically active trans[Co $dien_2]^{3+}$ or trans$[Co(4\text{-}Medien)_2]^{3+}$. This seems to be the only method to enable the absolute configuration problem to be settled, since contemplation of the employment of an optically active analogue of dien which would coordinate stereospecifically, such as $NH_2CH(CH_3)CH_2NHCH_2CH_2NH_2$, would not resolve the problem and would introduce the complication of a vicinal effect in the trans, as well as further cis isomers. The meso ligand RS-dipn



$$NH_2-\underset{R}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-NH-CH_2-\underset{S}{\overset{\overset{CH_3}{|}}{CH}}-NH_2$$

(λ chelate rings) (δ chelate rings)

would coordinate, but still give two "bond chiral" trans optical isomers, whereas the active ligand RR-dipn



$$NH_2-\underset{R}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-NH-CH_2-\underset{R}{\overset{\overset{CH_3}{|}}{CH}}-NH_2$$

(λ chelate rings) (λ chelate rings)

should not give a trans isomer, due to the requirement of coordinated R-pn rings to adopt the λ conformation[80] (compare Figure 4).

The use of other unsymmetric tridentate ligands such as 2,3-tri[192] or C-substituted diens could also provide more stereochemical information in the proportions and isomerisation studies since they add a further reference point within the complex molecules. Because the sec-N atom is asymmetric in these instances there will be 6 geometric possibilities (all dissymmetric) so that such systems would be very complicated and difficult experimentally. The syntheses of ligands such as these is not straightforward and is also an area of current research. Synthetic methods for 4-Medien, 4-Etdien, 4,7-diMetrien,[193] and lin-penten[4b] have been devised in these laboratories.

A number of problems have been clarified in this thesis, but the work itself posed further interesting questions. It is believed that this thesis clearly indicates that there is considerable scope for useful extension of this work.

REFERENCES

1. A.M. Sargeson and G.H. Searle, Inorg. Chem., 6, 787 (1967).
2. D.A. Buckingham, P.A. Marzilli, and A.M. Sargeson, Inorg. Chem., 6, 1032 (1967).
3. D.A. Buckingham, A.M. Sargeson, et al., Australian National University, unpublished work.
4. (a) K. Yamasaki et al., Nagoya University, unpublished work.
   (b) F.R. Keene, G.H. Searle, and D.C. Vozzo, University of Adelaide, unpublished work.
   (c) G.H. Searle, work in progress.
5. R.S. Cahn, C. Ingold, and V. Prelog, Angew. Chem. (Intl. Edtn.), 5, 385 (1966).
6. Inorg. Chem., 9, 1 (1970).
7. J.I. Legg, Inorg. Chem., 10, 2370 (1971).
8. A.R. Gainsford and D.A. House, Proc. XII ICCC, Sydney, 1969, p. 100.
9. A.R. Gainsford and D.A. House, Inorg. Chim. Acta, 3, 369 (1969).
10. D.A. Buckingham, P.A. Marzilli, and A.M. Sargeson, Inorg. Chem., 8, 1595 (1969).
11. F.G. Mann, J. Chem. Soc., 466 (1934).
12. J. Brigando, Bull. Soc. Chimie, 211 (1957).
13. (a) R.G. Wilkins and M.J.G. Williams in "Modern Coordination Chemistry", J. Lewis and R.G. Wilkins, eds., Interscience, London, 1960, p. 183.

13 (b) T.D. O'Brien in "The Chemistry of Coordination Compounds", J.C. Bailar Jr., ed., Reingold, New York, 1956, p. 288.

14. F.P. Dwyer, Aust. J. Science, 24, 97 (1961).

15. P.H. Crayton and J.A. Mattern, J. Inorg. Nucl. Chem., 13, 248 (1960).

16. H. Sueda, Bull. Chem. Soc. Japan, 13, 450 (1938).

17. V.O. Kling and H.L. Schlafer, Z. Anorg. Allg. Chem., 313, 187 (1961).

18. W.H. Baddley, F. Basolo, and H.B. Gray, Inorg. Chem., 2, 921 (1963).

19. G.W. Watt and D.S. Klett, Spectrochim. Acta, 20, 1053 (1964).

20. W.F. Marzluff, Inorg. Chem., 3, 395 (1964).

21. Y. Kushi, K. Watanabe, and H. Kuroya, Bull. Chem. Soc. Japan, 40, 2985 (1967).

22. F.S. Stephens, J. Chem. Soc. A, 883 (1969).

23. F.S. Stephens, J. Chem. Soc. A, 2233 (1969).

24. B. Halpern, A.M. Sargeson, and K.R. Turnbull, J. Amer. Chem. Soc., 88, 4630 (1966).

25. H.H. Schmidtke, Z. Anorg. Allg. Chem., 339, 103 (1965).

26. H.H. Schmidtke and D. Garthoff, Inorg. Chim. Acta, 2, 357 (1968).

27. D.A. House, Inorg. Nucl. Chem. Lett., 3, 67 (1967).

28. D.A. House and C.S. Garner, Inorg. Chem., 5, 840 (1966).

29. A.D. Fowlie, D.A. House, W.T. Robinson, and S.S. Rumball, J. Chem. Soc. A, 803 (1970).

30. S.H. Caldwell and D.A. House, J. Inorg. Nucl. Chem., 31, 811 (1969).

31. J.I. Legg and D.W. Cooke, Inorg. Chem., 5, 594 (1966).

32. K. Yamasaki and Y. Yoshikawa, Proc. XII ICCC, Sydney, 1969, p. 98.

33. Y. Yoshikawa and K. Yamasaki, Inorg. Nucl. Chem. Lett., 4, 697 (1968).

34. Y. Yoshikawa and K. Yamasaki, Inorg. Nucl. Chem. Lett., 6, 523 (1970).

35. F.R. Keene, G.H. Searle, Y. Yoshikawa, A. Imai, and K. Yamasaki, Chem. Commun., 784 (1970).

36. Y. Saito, University of Tokyo, private communication through K. Yamasaki, 1970. X-ray crystal structure analyses of the compounds *s-cis*[Co dien$_2$]Br$_3$, (+)-*trans*[Co dien$_2$]Br$_3$.H$_2$O, and (+)-*u-cis*[Co dien$_2$][Co(CN)$_6$] are in progress.

37. G.A. Barclay and A.K. Barnard, J. Chem. Soc., 2540 (1958).

38. F. Basolo, J.W. Palmer, and R.G. Pearson, J. Amer. Chem. Soc., 82, 1073 (1960).

39. H. Yoneda and Y. Morimoto, Bull. Chem. Soc. Japan, 39, 2180 (1966).

40. H. Yoneda, Bull. Chem. Soc. Japan, 40, 2442 (1967).

41. G. Stefanovic and T. Janjic, Anal. Chim. Acta, 11, 550 (1954).

42. G. Stefanovic and T. Janjic, Anal. Chim. Acta, 19, 488 (1958).

43. E.L. King and R.R. Walters, J. Amer. Chem. Soc., 74, 4471 (1952).

44. R. Burwell, R.G. Pearson, G. Haller, P. Tjok, and S. Chock, Inorg. Chem., 4, 1123 (1965).

45. L.F. Druding and R.B. Hagel, Anal. Chem., 38, 478 (1966).

46. B. Bosnich, J. Amer. Chem. Soc., 89, 6143 (1967).

47. L.F. Druding and G.B. Kauffman, Coord. Chem. Rev., 3, 409 (1968); and references therein.

48. F.P. Dwyer, A.M. Sargeson, and L.B. James, J. Amer. Chem. Soc., 86, 590 (1964).

49. F.P. Dwyer, T.E. MacDermott, and A.M. Sargeson, J. Amer. Chem. Soc., 85, 2913 (1963).

50. D.A. Buckingham, F.P. Dwyer, and A.M. Sargeson, Aust. J. Chem., 16, 921 (1963).

51. F.R. Keene and G.H. Searle, to be published.

52. G.R. Brubaker, J.I. Legg, and B.E. Douglas, J. Amer. Chem. Soc., 88, 3446 (1966).

53. L.T. Taylor and D.H. Busch, J. Amer. Chem. Soc., 89, 5372 (1967).

54. J.I. Legg and B.E. Douglas, Inorg. Chem., 7, 1452 (1968).

55. P. Proletti, S. Biagini, and M. Cannas, Chem. Commun., 513 (1969).

56. K. Randerath, "Thin-Layer Chromatography", Verlag Chemie, Weinheim, 1963, p. 21.

57. E. Stahl, "Thin-Layer Chromatography", Springler Verlag, Berlin, 1962, p. 6.

58. F.P. Dwyer in "Advances in the Chemistry of Coordination Compounds" (Proc. VI ICCC, Detroit, 1961), Macmillan, New York, 1961, p. 21; and references therein.

59. F. Basolo and R.G. Pearson, "Mechanisms of Inorganic Reactions", 2nd edition, Wiley, New York, 1967; and references therein.
(a) 330-332, (b) 256, (c) 37, (d) 275, (e) 277,
(f) 283, (g) 311, (h) 282, (i) 317, (j) 320,
(k) 285, (l) 321, (m) 286, (n) 316.

60. J.C. Bailar and J.B. Work, J. Amer. Chem. Soc., 67, 176 (1945).

61. B.E. Douglas, J. Amer. Chem. Soc., 76, 1020 (1954).

62. J. Bjerrum and S.E. Rasmussen, Acta Chem. Scand., 6, 1265 (1952).

63. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase, Copenhagen, 1941, p. 235.

64. F.P. Dwyer and A.M. Sargeson, Nature, 187, 1022 (1960).

65. F.P. Dwyer, F.L. Garvan, and A. Schulman, J. Amer. Chem. Soc., 81, 290 (1959).

66. M. Mori, Bull. Chem. Soc. Japan, 29, 883 (1956).

67. H.F. Bauer and W.C. Drinkard, J. Amer. Chem. Soc., 82, 5031 (1960).

68. H.F. Holtzclaw Jr., ed., Inorg. Synth., 8, 202 (1966).

69. M.S. Al-Obadie, A.M. Qureshi, and A.G. Sharpe, J. Inorg. Nucl. Chem., 30, 3357 (1968).

70. H. Diehl, H. Clark, and H.H. Willard, eds., Inorg. Synth., 1, 186 (1939).

71. G.G. Schlessinger, ed., Inorg. Synth., 9, 160 (1967).

72. J. Kleinberg, ed., Inorg. Synth., 7, 207 (1963).

73. P. Wilairat and C.S. Garner, J. Inorg. Nucl. Chem., 32, 2293 (1970).

74. D. Mettrick and D.R. Stranks, University of Adelaide, unpublished results.

75. G.E. Ryschkewitsch and J.M. Garrett, J. Amer. Chem. Soc., 90, 7234 (1968).

76. A.M. Sargeson and G.H. Searle, manuscript in preparation.

77. D.A. House, University of Canterbury, N.Z., private communication, 1971.

78. F. Basolo, H.B. Gray, and R.G. Pearson, J. Amer. Chem. Soc., 82, 4200 (1960).

79. D.B. Powell and N. Sheppard, Spectrochim. Acta, 17, 68 (1961).

80. E.J. Corey and J.C. Bailar, J. Amer. Chem. Soc., 81, 2620 (1959).

81. K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, Bull. Chem. Soc. Japan, 30, 795 (1957).

82. K.N. Raymond, P.W.R. Corfield, and J.A. Ibers, Inorg. Chem., 7, 842 (1968).

83. K.N. Raymond, P.W.R. Corfield, and J.A. Ibers, Inorg. Chem., 7, 1362 (1968).

84. K.N. Raymond and J.A. Ibers, Inorg. Chem., 7, 2333 (1968).

85. J.K. Beattie, Acc. Chem. Res., 4, 253 (1971); and references therein.

86. J.L. Sudmeier and G.L. Blackmer, Inorg. Chem., 10, 2010 (1971).

87. C.J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley, New York, 1971; and references therein.
(a) 167-176, (b) 210-226, (c) 176-199, (d) 200-209,
(e) 206.

88. A.J. McCaffery, S.F. Mason, R.E. Ballard, and B.J. Norman, Mol. Phys., 6, 359 (1963); J. Chem. Soc., 2883 (1965); Chem. Commun., 661 (1966).

89. R. Dingle, Chem. Commun., 304 (1965).
R.G. Denning, Chem. Commun., 120 (1967).

90. S.F. Mason and B.J. Norman, Chem. Commun., 73 (1965).

91. S.F. Mason and B.J. Norman, Proc. Chem. Soc., 339 (1964).

92. H.L. Smith and B.E. Douglas, J. Amer. Chem. Soc., 86, 3885 (1964).

93. S.F. Mason and B.J. Peart, Inorg. Nucl. Chem. Lett., 5, 491 (1969).

94. B.E. Douglas, Inorg. Chem., 4, 1813 (1965).

95. A.J. McCaffery, S.F. Mason, B.J. Norman, and A.M. Sargeson, J. Chem. Soc. A, 1304 (1968).

96. R. Larsson, G.H. Searle, S.F. Mason, and A.M. Sargeson, J. Chem. Soc. A, 1310 (1968).

97. K. Ogino, K. Murano, and J. Fujita, Inorg. Nucl. Chem. Lett., 4, 351 (1968).

98. J.I. Legg and B.E. Douglas, J. Amer. Chem. Soc., 88, 2697 (1966).

99. J.I. Legg and B.E. Douglas, J. Amer. Chem. Soc., 89, 6854 (1967).

100. A. Muto, F. Marumo, and Y. Saito, Inorg. Nucl. Chem. Lett., 5, 85 (1969).

101. D.A. Buckingham, L.G. Marzilli, and A.M. Sargeson, J. Amer. Chem. Soc., 89, 825 (1967).

102. F.M. Jaeger and H.B. Blumendal, Z. Anorg. Allg. Chem., 75, 161 (1928).

103. L.T. Tschugaeff and W. Sokoloff, Ber., 42, 55 (1909).

104. A.P. Smirnoff, Helv. Chim. Acta, 3, 177 (1920).

105. W. Theilacker, Z. Anorg. Allg. Chem., 234, 161 (1937).

106. J.P. Mathieu, Ann. Phys., 19, 335 (1944).

107. J.V. Quagliano and S. Mizushima, J. Amer. Chem. Soc., 75, 6084 (1953).

108. D.B. Powell and N. Sheppard, J. Chem. Soc., 791 (1959).

109. E.A. Mason and M.M. Kreevoy, J. Amer. Chem. Soc., 77, 5808 (1955).

110. P.F. Crossing and M.R. Snow, University of Adelaide, unpublished results.

111. A.J. McCaffery, S.F. Mason, and B.J. Norman, Chem. Commun., 49 (1965).

112. A.M. Sargeson in "Transition Metal Chemistry", 3, R.L. Carlin, ed., Arnold, London, 1966, p. 303.

113. P.J. Garnett, D.W. Watts, and J.I. Legg, Inorg. Chem., 8, 2534 (1969).

114. E.L. Eliel, N.L. Allinger, S.J. Angyal, and G.A. Morrison, "Conformational Analysis", Wiley, New York, 1965, Chapter 7.

115. T.L. Hill, J. Phys. Chem., 16, 399 (1948).

116. J.B. Hendrickson, J. Amer. Chem. Soc., 83, 4537 (1961).

117. J.R. Gollogly and C.J. Hawkins, Aust. J. Chem., 20, 2395 (1967).

118. D.A. Buckingham, S.F. Mason, A.M. Sargeson, and K.R. Turnbull, Inorg. Chem., 5, 1649 (1966).

J.F. Blount, H.C. Freeman, A.M. Sargeson, and K.R. Turnbull, Chem. Commun., 324 (1967).

119. L.G. Marzilli and D.A. Buckingham, Inorg. Chem., 6, 1042 (1967).

120. D.A. Buckingham, L.G. Marzilli, and A.M. Sargeson, J. Amer. Chem. Soc., 89, 3428 (1967).

121. D.A. Buckingham, H.C. Freeman, L.G. Marzilli, I.E. Maxwell, and A.M. Sargeson, Proc. XII ICCC, Sydney, 1969, p. 157.

122. D.A. Buckingham, L.G. Marzilli, I.E. Maxwell, A.M. Sargeson, and H.C. Freeman, Chem. Commun., 583 (1969).

H.C. Freeman and I.E. Maxwell, Inorg. Chem., 9, 649 (1970).

123. R.H. Boyd, J. Chem. Phys., 49, 2574 (1968).

124. M.R. Snow, J. Amer. Chem. Soc., 92, 3610 (1970).

125. M.R. Snow, Proc. XII ICCC, Sydney, 1969, p. 92.

126. D.A. Buckingham, I.E. Maxwell, A.M. Sargeson, and M.R. Snow, J. Amer. Chem. Soc., 92, 3617 (1970).

127. D.A. Buckingham, I.E. Maxwell, A.M. Sargeson, and H.C. Freeman, Inorg. Chem., 9, 1921 (1970).

128. D.A. Buckingham, I.E. Maxwell, and A.M. Sargeson, Inorg. Chem., 9, 2663 (1970).

129. J.R. Gollogly and C.J. Hawkins, Inorg. Chem., 8, 1168 (1969).

130. J.R. Gollogly and C.J. Hawkins, Inorg. Chem., 9, 576 (1970).

131. M. Dwyer, Ph.D. Thesis, Australian National University, 1971.

132. K.R. Butler, R.J. Geue, and M.R. Snow, Proc. IV National Convention, R.A.C.I., Canberra, 1970, p. 12.

133. R.J. Geue and M.R. Snow, submitted for publication, 1971; private communication.

134. L.R. Froebe and B.E. Douglas, Inorg. Chem., 9, 1513 (1970).

135. S.F. Mason and B.J. Norman, J. Chem. Soc. A, 307 (1966).

136. D.W. Cooke, Inorg. Chem., 5, 1141 (1966).

137. D.A. House and C.S. Garner, J. Amer. Chem. Soc., 88, 2156 (1966).
C.Y. Hsu and C.S. Garner, Inorg. Chim. Acta, 1, 17 (1967).

138. J.I. Legg, Chem. Commun., 675 (1967).
L.N. Schoenberg, D.W. Cooke, and C.F. Liu, Inorg. Chem., 7, 2386 (1968).
P.F. Coleman, J.I. Legg, and J. Steele, Inorg. Chem., 9, 937 (1970).

139. J.H. Worrell and D.H. Busch, Inorg. Chem., 8, 1563 (1969).

140. R.S. Asperger and C.F. Liu, Inorg. Chem., 4, 1395 (1965).
A.T. Phillip, Aust. J. Chem., 21, 2797 (1968).
M. Goto, M. Saburi, T. Sakihara, and S. Yoshikawa, Inorg. Chem., 6, 169 (1967); 8, 358 (1969).

141. M. Goto, A. Okubo, T. Sawai, and S. Yoshikawa, Inorg. Chem., 9, 1488 (1970).

142. M. Dwyer and M.R. Snow, University of Adelaide, work in progress.

143. M.R. Snow, University of Adelaide, unpublished work.

144. E.W. Gillow and G.M. Harris, Inorg. Chem., 7, 394 (1968).

145. E.N. Duesler and K.N. Raymond, Inorg. Chem., 10, 1486 (1971).

146. S.F. Lincoln and D.R. Stranks, Aust. J. Chem., 21, 1745 (1968).

147. R.J. Dellaca, V. Janson, W.T. Robinson, D.A. Buckingham, L.G. Marzilli, I.E. Maxwell, K.R. Turnbull, and A.M. Sargeson, Chem. Commun., submitted for publication, 1971.

148. M.E. Farago, B.A. Page, and C.F.V. Mason, Inorg. Chem., 8, 2270 (1969).

149. P. Ray and N.K. Dutt, J. Indian Chem. Soc., 20, 81 (1943).

150. W.G. Gehman, Ph.D. Thesis, Pennsylvania State University, 1954.

151. L. Seiden, Ph.D. Thesis, Northwestern University, 1957.

152. J.C. Bailar, J. Inorg. Nucl. Chem., 8, 165 (1958).

153. C.S. Springer and R.E. Sievers, Inorg. Chem., 6, 852 (1967).

154. E.L. Muetterties, J. Amer. Chem. Soc., 90, 5097 (1968).

155. N. Serpone and R.C. Fay, Inorg. Chem., 6, 1835 (1967).

156. J.E. Brady, Inorg. Chem., 8, 1208 (1969).

157. G.W. Watt, P.W. Alexander, and B.S. Manhas, J. Amer. Chem. Soc., 89, 6483 (1967).

158. C.K. Poon and M.L. Tobe, Inorg. Chem., 7, 2398 (1968).

159. W.C.E. Higginson, J. Chem. Soc., 1998 (1960).

W.H. Jolley and D.R. Stranks, University of Adelaide, unpublished work.

160. D.W. Cooke, Y.A. Im, and D.H. Busch, Inorg. Chem., 1, 13 (1962).

161. I.L. Finar, "Organic Chemistry Vol. 2", 4th edition, Longmans, London, 1968, pps. 192-229.

162. J.R. Keubler and J.C. Bailar, J. Amer. Chem. Soc., 74, 3525 (1952).

163. J.S. Anderson, H.V.A. Briscoe, and N.L. Spoor, J. Chem. Soc., 361 (1943).

164. J.W. Palmer and F. Basolo, J. Amer. Chem. Soc., 64, 778 (1960).

165. D.A. Buckingham, L.G. Marzilli, and A.M. Sargeson, J. Amer. Chem. Soc., 90, 6028 (1968).

166. D.A. Buckingham, L.G. Marzilli, and A.M. Sargeson, J. Amer. Chem. Soc., 91, 5227 (1969).

167. J.B. Goddard and F. Basolo, Inorg. Chem., 8, 2223 (1969).

168. P. Haake and P.C. Turley, J. Amer. Chem. Soc., 90, 2293 (1968).

169. H.G. Hamilton and M.D. Alexander, J. Amer. Chem. Soc., 89, 5065 (1967).

170. J.I. Legg, D.W. Cooke, and B.E. Douglas, Inorg. Chem., 6, 700 (1967).

171. M. Saburi and S. Yoshikawa, Inorg. Chem., 7, 1890 (1968).

172. M. Saburi, M. Homma, and S. Yoshikawa, Inorg. Chem., 8, 367 (1969).

173. L.G. Warner, N.J. Rose, and D.H. Busch, J. Amer. Chem. Soc., 89, 703 (1967); 91, 4092 (1969).
E. Ochiai and D.H. Busch, Inorg. Chem., 8, 1474 (1969); 8, 1798 (1969).

174. L.E. Erickson, J. Amer. Chem. Soc., 91, 6284 (1969).

175. R.M.C. Dawson, D.C. Elliott, W.H. Elliott, and K.M. Jones, "Data for Biochemical Research", 2nd edition, Oxford, 1969, p. 491.

176. H.S. Harned and W.J. Hamer, J. Amer. Chem. Soc., 55, 2194 (1933).

177. W.F.K. Wynne-Jones, Trans. Faraday Soc., 32, 1397 (1936).

178. Chemical Society London, Special Publications No. 17, "Stability Constants", p. 39.

179. D.A. Buckingham, P.A. Marzilli, I.E. Maxwell, A.M. Sargeson, and H.C. Freeman, Chem. Commun., 473 (1969).

180. M. Dwyer and I.E. Maxwell, Inorg. Chem., 9, 1459 (1970).

181. D.J. Millen in "Progress in Stereochemistry", 3, P.B.D. de la Mare and W. Klyne, eds., Butterworths, London, 1962, p. 138.

182. D.A. Buckingham, M. Dwyer, L.G. Marzilli, A.M. Sargeson, and K.R. Turnbull, unpublished results.

183. I.R. Lantzke and D.W. Watts, Aust. J. Chem., 19, 969 (1966); 20, 2623 (1967).

184. G.H. Stout and L.H. Jensen, "X-ray Structure Determination", Macmillan, London, 1968, p. 65.

185. C.W. Bunn, "Chemical Crystallography", 2nd edition, Oxford, 1961, p. 24.

186. (a) DATA and AUFIN, by R.J. Geue and M.R. Snow, University of Adelaide, 1970.

(b) AUFAC, and (c) AULAC, modifications of SUFFAC (G.L. Paul, University of Sydney, 1961) by M.R. Snow.

(d) FORDAPB, modifications of a Fourier and utility program (A. Zalkin) by M.R. Snow.

(e) FUORFLS, modifications of ORFLS (W.R. Busing and H.A. Levy) by M.R. Taylor.

187. "International Tables for X-ray Crystallography", 2nd edition, Kynoch, Birmingham, 1965, No. 19, p. 105.

188. H.C. Freeman and I.E. Maxwell, Inorg. Chem., 8, 1293 (1969).

189. J.W. Turley, F.P. Boer, and F. Van Remootere, Chem. Commun., 720 (1970).

190. F.G. Mann, J. Chem. Soc., 461 (1934).

191. W. Gauss, P. Moser, and G. Schwarzenbach, Helv. Chim. Acta, 35, 2359 (1952).

192. A.R. Gainsford and D.A. House, J. Inorg. Nucl. Chem., 32, 688 (1970).

193. G.H. Searle, F.R. Keene, and M. Petkovic, Aust. J. Chem., submitted for publication, 1972.