COMPOUNDS OF
6,13-DIAMINO-6,13-DIMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECANE

ASOKAMALI SIRIWARDENA

A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN CHEMISTRY
AT VICTORIA UNIVERSITY OF WELLINGTON,
NEW ZEALAND.

JANUARY 1988

ABSTRACT

The reaction of *bis*-(diaminoethane)nickel(II) chloride, $[\text{Ni}(\text{en})_2]\text{Cl}_2$ in methanol with formaldehyde and nitroethane in the presence of triethylamine proceeds readily to produce (6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane)nickel(II) chloride, $[\text{Ni}(\text{dini})]\text{Cl}_2$. Reduction of the nitro groups of this compound by catalytic hydrogenation yields three isomers of the pendant arm macrocyclic complex (6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) chloride, designated a-, b- and c- $[\text{Ni}(\text{diam})]\text{Cl}_2$. These were separated by fractional crystallization. The a-isomer was observed to isomerize slowly in solution to the b-form. A parallel dissociation reaction of the a-isomer was also observed.

The demetallation of a- and b- isomers of the diam complex of nickel by reaction with cyanide or concentrated acid at 140°C produces the macrocycle *meso*-(6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane), diam.

A variety of hexamine, pentamine and tetramine complexes of diam with nickel(II), copper(II), cobalt(II) and (III), chromium(III), palladium(II), rhodium(III), zinc(II) and cadmium(II) were prepared. Hexamine and tetramine forms of labile metal complexes could be rapidly and reversibly interconverted by altering the pH. The hexamine cobalt(III) cation, $[\text{Co}(\text{diam})]^{3+}$ was by far the most inert of the prepared cobalt(III) complexes, remaining unaffected in hot acidic solutions. In contrast, a single pendant arm of the hexamine $[\text{Cr}(\text{diam})]^{3+}$ cation could be dissociated in acid. (Two possibly triamine complexes of lead were also prepared). These compounds were characterized by elemental analysis, magnetic

measurements, electronic, infrared, ^1H and ^{13}C nuclear magnetic resonance spectra.

The pendant arm protonation constants ($\log K$) of diam and selected complexes of nickel, copper and palladium were calculated from potentiometric titration measurements at 25°C . The $\log K$ values for diam at 25°C ($I = 0.1 \text{ M NaClO}_4$) were 11.15, 9.7, 6.2 and 5.3.

Kinetics of the parallel isomerization and dissociation of $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ in HCl/NaCl solutions were monitored spectrophotometrically at 50°C . The rate of reaction in acidic solutions showed a non-linear dependency on acid concentration. The observed first order rate constant (k_{obs}) for disappearance of $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ (by isomerization and dissociation) in 2.0 M HCl , 0.1 M NaOH and 2.0 M NaCl were 3.05×10^{-4} , $2.0(3) \times 10^{-2}$ and $5.0 \times 10^{-5} \text{ s}^{-1}$ respectively. The rate of the dissociation component of the reaction of $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ in 2.0 M HCl at 50°C was $1.82 \times 10^{-7} \text{ s}^{-1}$.

Acid hydrolysis kinetics of $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ in hydrochloric acid and perchloric acid at 50 and 70°C were studied spectrophotometrically. The reactions were slow and the observed first order rate constants were to a first approximation independent of the particular acid or its concentration. The observed first order rate constants were 1×10^{-9} and $8 \times 10^{-9} \text{ s}^{-1}$ at 50 and 70°C respectively. Questions about the nature of the reaction being followed have been raised.

ACKNOWLEDGEMENTS

I would like to thank:

my supervisor, Professor Neil F. Curtis, for his guidance, invaluable advice, encouragement and patience over the years; Dr. David C. Weatherburn, for his advice and help; the other members of the Chemistry Department who have contributed with discussions and technical assistance, including Dr. Burns, Dr. Pearce, Ian, Douglas, David, Romany, Sheila, Rhyl, Eddie and also Cliff from Earth Sciences; Professor A.D. Campbell of the University of Otago for the microanalyses; Dr. G. Gainsford of DSIR for the crystal structures; University Grants Committee and William Georgetti Scholarship Board for the financial assistance; My husband, Kosala, for his love, constant support, patience (and for making life easier); My parents, Mr. and Mrs. A. Mettananda for their love, encouragement and for always having confidence in me; My sister, Indumathie, for all her help and friendship; The rest of my family, especially my grandfather, Mr. L.H. Wijetunga and my parents-in-law, Dr. and Mrs. Siriwardena for their constant support; and last but not least, my friends Joanne, Chris, Raj, Dugald, Victor, Robyn, Anna and Murray...

LIST OF CONTENTS

	<u>page</u>
Title page	i
Abstract	ii
Acknowledgements	iv
List of Contents	v
List of figures	viii
List of Tables	x

CHAPTER 1: INTRODUCTION**1.1 GENERAL INTRODUCTION**

-Definition of a macrocyclic ligand	1
-History	1
-Terminology	3
-Abbreviations for macrocyclic compounds	4
-Synthesis of macrocyclic complexes	5
-Structural Aspects of Tetraazamacrocyclic compounds	15

**1.2 AZAMACROCYCLIC COMPLEXES CONTAINING PENDANT ARMS
WITH ADDITIONAL LIGATING GROUPS**

-Introduction	27
-Categories of Pendant Arm Macrocycles	30
-Equilibria in Solution	35
-Kinetic Aspects	37

CHAPTER 2: EXPERIMENTAL

2.1 INSTRUMENTATION	40
----------------------------	-----------

2.2 SYNTHESSES**page**

-General Introduction	42
-Condensation Reaction	43
-Reduction of $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	43
-Separation of Reduction Reaction Products	44
-The Relative Yields of a-, b- and c- Isomers	45
-Isolation of the Ligand	47
-Nickel(II) Compounds	50
-Copper(II) Compounds	58
-Cobalt(III) Compounds	61
-Cobalt(II) Compounds	68
-Chromium(III) Compounds	70
-Palladium(II) Compounds	72
-Zinc(II) Compounds	74
-Rhodium(III) Compounds	75
-Cadmium(II) Compounds	76
-Lead(II) Compounds	77
- $[\text{Ni}(\text{en})_3]\text{Cl}_2$	78
-Raney Nickel Catalyst	78
2.3 ELEMENTAL ANALYSES	79
2.4 INFRARED SPECTRA	88
2.5 ELECTRONIC SPECTRA	99
2.6 MAGNETIC DATA	104
2.7 ^1H and ^{13}C NUCLEAR MAGNETIC RESONANCE DATA	106
2.8 PROTONATION CONSTANTS	115

	<u>Page</u>
2.9.1 KINETICS OF ISOMERIZATION AND DISSOCIATION OF THE α - ISOMER OF THE NICKEL COMPLEX OF DIAM	117
2.9.2 ACID DISSOCIATION KINETICS OF $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$	122
 CHAPTER 3: DISCUSSION	
-Diam	124
-Nickel(II)	129
-Copper(II)	147
-Cobalt(II) and (III)	155
-Chromium(III)	170
-Palladium(II)	174
-Rhodium(III)	176
-Zinc(II)	178
-Cadmium(II) and Lead(II)	179
-Protonation Constants	181
-Kinetics	186
 CONCLUSION	 195
 APPENDIX A: Abbreviations and Trivial Names	 196
 REFERENCES	 197

LIST OF FIGURES

	<u>page</u>
Figure 1: Cyclam	1
Figure 2: Reaction of $[\text{Ni}(\text{en})_3]^{2+}$ with acetone	2
Figure 3: Diam	7
Figure 4: Template reactions	10
Figure 5: Configurations of coordinated cyclam	15
Figure 6: Relationship between strain energy, U , and ideal M-N bond length, r° , for <i>trans</i> -I [12]aneN ₄ and <i>trans</i> -III cyclam complexes	19
Figure 7: Structures of <i>trans</i> -I and <i>trans</i> -III 1, 4, 8, 11-tetra- <i>N</i> -methylcyclam	23
Figure 8: Structure of $[\text{Ni}(\text{diam})\text{Cl}_2]$ showing some bond angles	25
Figure 9: Analytically useful pendant arm macrocycles	28
Figure 10: N-functionalized derivatives of [9]aneN ₃	31
Figure 11: Tetraazacycloalkanes with four N-functiona- lized pendant arms	31
Figure 12: Synthesis and coordination modes of taec	32
Figure 13: A disubstituted N-functionalized pendant arm macrocycle	32

	<u>page</u>
Figure 14: C-functionalized macrocycles	33
Figure 15: A C-functionalized phenol pendant macrocycle	34
Figure 16: A bis-macrocycle	34
Figure 17: N, N', N'', N'''-tetraacetate complexes of tetraazamacrocycles	35
Figure 18: Equilibrium between the open and apically coordinated forms of a pendant arm macrocyclic complex	36
Figure 19: Pendant arm macrocycles that exhibit pH dependent high spin-low spin equilibria	37
Figure 20: Atom designation for ^1H and ^{13}C NMR spectra	107
Figure 21: The relationship between K_{Obs} and $[\text{H}^+]$ for the disappearance of $\text{a-}[\text{Ni}(\text{diamH}_2)](\text{ClO}_4)_4$	120
Figure 22: Structure of $\text{b-}[\text{Ni}(\text{diam})](\text{ClO}_4)_2$	142
Figure 23: $[\text{Co}(\text{sar})]^{3+}$	166

LIST OF TABLES

	<u>page</u>
Table 1: Elemental Analysis	80
Table 2: Infrared Spectral Data of Compounds of Diam	89
Table 3: Infrared Spectral Bands of (diam). $3\frac{1}{2}\text{H}_2\text{O}$	95
Table 4: The Main Infrared Bands of "c- Ligand"	95
Table 5: A Comparison of the Fingerprint Regions of a-/b-(diamH ₆)Cl ₆ . 2H ₂ O and "c- ligand"	96
Table 6: A Complete List of Infrared Spectral bands of a-, b-, and c-[Ni(diam)(NCS) ₂]	97
Table 7: Electronic Spectra of Metal Complexes of Diam	99
Table 8: Magnetic Data for Selected Diam Complexes	104
Table 9: ¹ H NMR data for Selected Compounds of Diam	108
Table 10: ¹³ C NMR Data for Selected Compounds of Diam	112
Table 11: Diam Compounds for which Protonation Constants were Determined and the Salts Used	115
Table 12(i): Protonation Constants and Standard Deviations for Diam	116

	<u>page</u>
Table 12(ii): Protonation Constants and Standard Deviations for Selected Nickel, Copper and Palladium Complexes of Diam	116
Table 13: The Observed First Order Rate Constants for the Disappearance of $a\text{-[Ni(diamH}_2\text{)](ClO}_4\text{)}_4$ in Hydrochloric Acid	119
Table 14: Temperatures and Acid Concentrations Used for Acid Dissociation Kinetics of $[\text{Cu(diamH}_2\text{)]-(ClO}_4\text{)}_4$	122
Table 15: Observed First Order Rate Constants for the Acid Dissociation Kinetics of $[\text{Cu(diamH}_2\text{)]-(ClO}_4\text{)}_4$	123
Table 16: $\nu(\text{NH})$ of Cyclam Type Ligands	126
Table 17: ^1H and ^{13}C Spectra of Diam and Cyclam	127
Table 18: Relative Strain Energies for Square Planar and <i>trans</i> -Octahedral Diaquo Nickel(II) Complexes of Cyclam	136
Table 19: Electronic Spectra of Selected Nickel(II) Complexes	139
Table 20: Magnetic Moments of Selected Nickel Complexes	139
Table 21: The Average Equatorial and Axial Ni-N Lengths of Some b- Nickel Complexes of Diam	141

	<u>page</u>
Table 22: Electronic Spectral Data of Thiocyanate and Perchlorate Compounds of a-, b- and c- isomers	145
Table 23: The Frequencies of $\nu(\text{NH})$ and $\delta(\text{NH})$ of a-, b- and c-[Ni(diamH ₂)] ⁴⁺	146
Table 24: The Electronic Spectra of Copper(II) Complexes	151
Table 25: Electronic Spectral Data of Selected Cu-Diam Complexes in Water	152
Table 26: Electronic Spectra of [Cu(diamH ₂)](ClO ₄) ₄ in Various Media	152
Table 27: Infrared Spectra of Selected Copper Complexes	153
Table 28: Electronic Spectra of Cobalt(III) Complexes of Selected Ligands	163
Table 29: Infrared Bands in the 800-910 cm ⁻¹ Region for the Cobalt Complexes of Diam	164
Table 30(a): ¹ H and ¹³ C Data for [Co(diam)]X ₃	165
Table 30(b): ¹³ C Data for Selected Sar Complexes	166
Table 31: ¹ H and ¹³ C Spectra of Cobalt Complexes of Diam	168
Table 32: Electronic Spectra of Selected Chromium(III) Complexes	172

	<u>page</u>
Table 33: Electronic Spectra of Selected Palladium(II)- Diam Complexes	174
Table 34: Electronic Spectra of Selected Rhodium(III) Complexes	176
Table 35: Protonation Constants of Selected Cyclic and Linear Amines	182
Table 36: The Protonation Constants of Perchlorate and Thiocyanate Salts of b- and c- salts of [Ni(diamH ₂)] ⁴⁺	183

CHAPTER 1: INTRODUCTION

SECTION 1.1: GENERAL INTRODUCTION

Definition of a Macrocyclic Ligand

A macrocyclic ligand is a cyclic compound with nine or more members (including all hetero atoms) of which three or more are donor (ligating) atoms [1].

History

Macrocyclic compounds have been studied since the beginning of this century. Early investigations include complexes of porphyrins and later of corrins because of their relationship to important natural products such as heme, chlorophyll, cytochromes and vitamin B12. In the 1930's, metallophthalocyanines were investigated because of their potential as dyes and pigments.

Until the 1960s, the range of macrocyclic compounds was limited with occasional reports of "synthetic macrocycles", for example the work of Linstead, Elvidge and co-workers in the 1950s [2-5]. The synthesis of 1,4,8,11-tetraazacyclotetradecane, which has the trivial name cyclam (figure 1), was first reported in 1936 [6].

Figure 1: Cyclam

The cobalt and nickel complexes of this ligand were not

ethers or "crown" compounds. The ability of these oxygen donor ligands to form complexes with alkali metal and alkaline earth ions led to further expansion of the field of macrocyclic chemistry.

In 1969, Lehn and co-workers reported the first oxygen donor macropolycyclic ligands or cryptands [19]. These compounds can accommodate a metal ion of an appropriate size to form an inclusion complex. The first cryptands reported were bicyclic; however, tri- and tetracyclic species have since been reported [20].

In 1977, Sargeson and co-workers reported the first nitrogen analogues of the polyether cryptates, (*S*)-[(1, 3, 6, 8, 10, 13, 16, 19-octaazabicyclo[6.6.6]eicosane)-cobalt(III)]³⁺ by reaction of the *tris*(diaminoethane) cobalt(III) cation with formaldehyde and ammonia [21]. In keeping with the cryptate nomenclature, this was given the trivial name [Co(sepulchrates)]³⁺, (or [Co(sep)]³⁺). The cobalt(II) compound was also reported. This work which has been extended to include other inert (Rh(III), Ir(III) and Pt(IV)) and labile (Cu(II) and Ni(II)) complexes [22] will be discussed further in **Condensation Reactions Between Amine Complexes and Aliphatic Carbonyl Groups** (page 8).

Terminology

The developments in the field of macrocyclic coordination compounds has led to the introduction of new terminology.

The term "template effect" was introduced by Busch [13, 15, 23] to describe the controlling influence of a metal ion in a particular macrocyclic ligand synthesis. Two types of template effects have been observed. In the kinetic template effect, the steric course of the reaction is controlled by the directive influence of the metal ion. In the equilibrium or thermodynamic template effect, the

metal ion perturbs an existing equilibrium in an organic system to produce the required macrocyclic complex, often in high yield. These effects have been utilized in *in situ* syntheses of macrocyclic ligands.

"Macrocyclic effect", a term introduced by Cabbiness and Margerum [24] describes the greater thermodynamic stability of macrocyclic complexes when compared with complexes containing linear ligands of similar structure. An extension of the macrocyclic effect is the "cryptate effect" for cage complexes [25].

The phrase "multiple juxtapositional fixedness" was introduced by Busch and co-workers [26] to explain the increased stability of macrocyclic complexes in terms of inertness towards substitution, even for labile metal ions, in the presence of strong acids. A macrocycle can not dissociate from the metal ion by stepwise replacement or substitution analogous to that observed with noncyclic ligands since the ring structure does not contain an "end" at which the removal process can be started.

Abbreviations for Macrocyclic Compounds

Since the early days, the authors in the field of macrocyclic coordination chemistry have sought simple abbreviations to use in place of lengthy and cumbersome systematic names of macrocycles. Originally, trivial or nonsystematic names were used; however, as the number and complexity of synthetic macrocycles increased, the need for a systematic abbreviation scheme became apparent. Curtis [11] introduced an abbreviation scheme based on the ring size and degree of unsaturation. Busch [27, 28] modified this scheme by using locants for the positions of unsaturated linkages, including the type and positions of donor atoms and substituents. Fully saturated macrocycles were also considered. The modified scheme of Busch has

been extended to include anionic macrocycles and those containing fused rings.

The usage of nonsystematic names has continued over the years with prevailing ambiguities, mainly because of the lack of rules for the systematic abbreviation of macrocycles. However, a comprehensive set of rules based on the extensions of Busch's modified scheme is now available [1]. These rules can be applied to the derivation of abbreviations for "two-dimensional" macrocycles with a variety of donor types. "Three-dimensional" cryptands are not included; though it is possible to extend these rules to cover at least some macropolycyclic compounds.

The derived abbreviation may be simplified further if no ambiguity exists, by excluding locants for substituents, unsaturation, donor atoms and the charge designation for anionic macrocycles. For example, 1,4,8,11-tetraazacyclotetradecane (cyclam), shown in figure 1, becomes [14]ane-1,4,8,11-N₄, which can be simplified further to [14]aneN₄.

Synthesis of Macrocyclic Complexes

In general, the synthesis procedures described in the literature [11, 15, 23, 26, 29-45, among many others] fall into main three categories. They are (a) syntheses involving complexation reactions of the preformed ligand, (b) *in situ* reactions and (c) syntheses involving modification of the macrocyclic ligand and/or the metal ion. The synthetic procedure of many compounds involve steps from more than one category.

(a) Synthesis by Complexation

This method involves complexation between the metal ion and the presynthesised macrocycle in solution.

Advantages and Disadvantages of Synthesis by Complexation

Advantages of this general method are numerous. Firstly, the ligand may be isolated, purified and characterized prior to complexation; the organic ligand is often more readily purified and characterized than the metal complex. Properties of the ligand such as volatility, diamagnetism and solubility in less polar solvents makes spectroscopic characterization (for example with nuclear magnetic resonance spectroscopy and mass spectrometry) simpler. Thus, after purification and characterization, the complexation procedure should be quite free of side reactions, leading to a relatively pure product. Another advantage of this method is that the ligand can be precisely designed (for example, the exact location of substituents can be controlled). Also, changes in the macrocycle arising from coordination can be detected easily since the uncoordinated ligand is available for comparison. In addition, information on metal to ligand bonding can be obtained.

A possible disadvantage of the complexation method is low yields of the desired product. This may be overcome by carrying out the final ring closure reaction of a step-wise procedure under highly dilute conditions. For example high yield of the sulphur analogue of cyclam [14]aneS₄ can be obtained by carrying out the condensation reaction between 1,3-dibromopropane and 1,4,8,11-tetrathioundecane under conditions of high dilution [46,47]. However, in certain reactions, dilution alone can not overcome poor yields. Until the 1970s, cyclam was prepared by the condensation of 1,3-dibromopropane with 1,4,8,11-tetraazaundecane in ethanolic potassium hydroxide. Though dilute conditions were used, the yield of cyclam was less than 5% [6,7]. The method of Richman and Atkins [48] using a tosylated derivative and the *in situ* method of

Barefield [49, 50] produce comparatively higher yields of cyclam.

Despite the possible problems of this method, it has been extensively used, particularly in the synthesis of tetraazamacrocyclic complexes, crowns and cryptands [1].

Most of the metal complexes discussed in this work were prepared by synthesis procedures involving complexation reactions between the isolated ligand, 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane, (diam) shown in figure 3, and various metal ions, in solution.

Figure 3: Diam

(b) In Situ Syntheses

In situ reactions involve the synthesis of a macrocycle in the presence of a metal ion. *In situ* methods have been used a great deal in the synthesis of "classical" macrocycles such as porphyrins, corrins and phthalocyanines. It has been shown that the presence of a metal ion in certain cyclization reactions greatly improves the yield of the cyclic product. The *in situ* synthesis of cyclam described by Barefield [49, 50] uses nickel(II) ions in a ring closure reaction between 1,9-diamino-3,7-diazanonane and glyoxal. The catalytic hydrogenation of the condensation product results in a high yield (>65%) of cyclam.

An important role is played by the metal ion due to template effects discussed earlier. Kinetic template effects are thought to be more important in most *in situ* reactions. However, it is not always possible to deduce the exact function of the metal ion or to determine which template effect plays the greater role. Some important factors that determine the course of a reaction include polarization effects, kinetic lability, thermodynamic stability and stereochemistry of the metal ion and reactants [1].

Condensation Reactions Between Amine Complexes and Aliphatic Carbonyl Groups

Many macrocycles are synthesized by *in situ* condensation reactions of metal-amine complexes with aliphatic carbonyl groups. The synthesis and characterization of a variety of complexes formed by condensation reactions have been discussed by Curtis [11]. Other earlier studies include those of Jäger [51-56], Bamfield [57] and Melson [58, 59].

These template reactions can be divided into several categories [60]. One of the most common methods is to react a bifunctional aldehyde or ketone with a metal complex of a multidentate amine, as shown in figure 4.1, or a simple diamine with a potentially multidentate aldehyde [23, 44]. A variety of complexes can be prepared from the reaction of ketones such as acetone with metal complexes of multidentate amines, as shown in figure 4.2. In these syntheses, the ketone reacts with the initially formed coordinated imine [11]. With dithiolates, reaction with dibromoalkanes is possible [61, 62]. Less frequently studied are the reaction of nickel(II) dimethylglyoxime with diphenylborinic acid aminoethyl ester (DPBE) [16] or boron trifluoride and the reaction between coordinated

dihydrazine and formaldehyde [63].

Metal-amine complexes also react with formaldehyde in basic solution; the $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ ion reacts in the presence of lithium carbonate to form 3,10-dioxocyclam, which has been characterized by a crystal structure analysis [64]. This type of synthesis has been extended to include reactions of *tris*(diamine) metal complexes, $[\text{M}(\text{en})_3]^{n+}$ with formaldehyde and ammonia, or the carbon acid nitromethane [21, 22(b), 65-67]. Metal ions studied were Co(III), Rh(III), Ir(III) and Pt(IV). The reactions with ammonia or nitromethane lead to the macrobicyclic complexes (1, 3, 6, 8, 10, 13, 16, 19-octaazabicyclo[6.6.6.]cicosane) M^{n+} and (1, 8-dinitro-3, 6, 10, 13, 16, 19-hexaazabicyclo-[6.6.6]cicosane) M^{n+} . These compounds are trivially known as $\text{M}(\text{sepulchrates})^{n+}$ or $\text{M}(\text{sep})^{n+}$ (figure 4.3) and $\text{M}(\text{dinitrosarcophagines})^{n+}$ or $\text{M}(\text{dinosars})^{n+}$ respectively (figure 4.4). The latter reaction is thought to proceed via imine formation and subsequent attack by $^-\text{CH}_2\text{NO}_2$ anion [68], as in figure 4.5, leading to the stepwise capping of the open faces of the octahedron. $\text{M}(\text{dinosar})^{n+}$ can be reduced with SnCl_2 in acid to yield (1, 8-diamino-3, 6, 10, 13, 16, 19-hexaazabicyclo[6.6.6]cicosane) M^{n+} , $\text{M}(\text{diaminosarcophagines})^{n+}$ or $\text{M}(\text{diamsars})^{n+}$. From related condensation reactions such as capping 5-methyl-5-(4-amino-2-azabutyl)-3, 7-diazanonane-1, 9-diamine) M^{n+} , (*sen*) with nitromethane and formaldehyde and subsequent reaction of the resultant product, $\text{M}(\text{nitromethylsarcophagines})^{n+}$ or $\text{M}(\text{menosars})^{n+}$ with reagents such as zinc/acid, nitrosyl chloride or hydrogen/platinum, a variety of substituted *sar* complexes can be prepared [22b, 65].

Efforts to bring about macrobicyclization about labile metal ions such as nickel(II), copper(II) and zinc(II) in protic solvents have not been entirely successful [60, 69]. Also, the inert $[\text{Cr}(\text{en})_3]^{3+}$ precursor could not

Figure 4: Template Reactions

Figure 4.1: Reaction of a bifunctional aldehyde or ketone with a complexed multidentate amine

Figure 4.2: Reaction of acetone with a complexed multidentate amine

Figure 4.3: Reaction of $[M(en)_3]^{n+}$ with formaldehyde and ammonia; synthesis of $[M(sep)]^{n+}$

Figure 4 continued

Figure 4.4: Reaction of $[M(en)_3]^{n+}$ with formaldehyde and nitromethane; synthesis of $[M(dinosar)]^{n+}$

Figure 4.5: Imine formation and attack by $^-CH_2NO_2$ anion during synthesis of $[M(dinosar)]^{n+}$

Figure 4.6: Reaction of $[M(en)_2]^{n+}$ with formaldehyde and nitroethane; synthesis of $[M(dini)]^{n+}$

4.6(a): $M = Cu(II)$; anion = ClO_4^-

4.6(b): $M = Ni(II)$; anion = Cl^-

be encapsulated because of rapid dissociation of the imine intermediate [69]. A similar reaction with $[\text{Ni}(\text{en})_3]^{2+}$ has produced a macrobicyclic complex in a very low yield [70]. Nevertheless, free macrobicyclic ligands can form complexes with a variety of labile metal ions [69,71].

Since copper(II) and nickel(II) form stable *bis* and *tris* diaminoethane complexes, it is likely that they may undergo condensation reactions similar to those of inert metal ions [60]. For example, the reaction between the *bis*(diaminoethane)copper(II) perchlorate, nitroethane and formaldehyde is found to produce the macrocyclic complex (6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane)copper(II) perchlorate, $[\text{Cu}(\text{dini})](\text{ClO}_4)_2$ (1), and other condensation products such as the intermediate tetramine complex (2), as shown in figure 4.6(a) [60]. (The conditions can be optimized to give the desired product). The zinc/acid reduction of $[\text{Cu}(\text{dini})](\text{ClO}_4)_2$ produces the protonated ligand, (6,13-diammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane) hexahydrochloride, $(\text{diamH}_6)\text{Cl}_6$ which can be used for complex formation with metal ions.

The reaction shown in figure 4.6(a) is of significance to this work since it produces the copper(II) analogue of the nickel complex, $[(\text{Ni}(\text{dini}))\text{Cl}_2]$, which is the starting material for nearly all the metal complexes described in Chapter 2 of this thesis. $[(\text{Ni}(\text{dini}))\text{Cl}_2]$ was prepared by reacting *bis*-(diaminoethane)nickel(II) chloride with formaldehyde and nitroethane in the presence of a non-coordinating base, triethylamine (figure 4.6(b)). $[(\text{Ni}(\text{dini}))\text{Cl}_2]$ was then reduced by catalytic hydrogenation and demetallated to yield the free ligand, 6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane, *diam*. This ligand was used for complex formation with nickel(II), copper(II), cobalt(II), cobalt(III), chromium(III), palla-

dium(II), rhodium(III), zinc(II), lead(II) and cadmium(II) ions. Recently, Lawrance and co-workers reported an unusual cleavage and macrocyclization reaction which also produced the complex $[\text{Cu}(\text{diam})](\text{ClO}_4)_2$ [72].

Advantages and Disadvantages of the *In Situ* Method

An advantage of *in situ* syntheses is that high yields of the macrocycle can be obtained, because of the elimination or considerable reduction of side reactions such as those producing polymers and non-macrocyclic products. Certain macrocycles can be synthesised only if a metal ion is present, since they are too unstable to be isolated as ligands. Another advantage of this method is the scope for selectivity; by choosing a metal ion with certain steric requirements or preferences, a given reaction and its products can be regulated, resulting in high yields of a desired macrocyclic product.

In some cases, the steric requirements of the metal ion can be a disadvantage; for instance by preventing the formation of the required macrocyclic complex. Another potential disadvantage of the *in situ* approach is that the macrocycle is almost always coordinated to the metal ion and its isolation from the metal ion may be difficult. An additional obstacle often encountered in *in situ* syntheses is the lack of control over the number and exact location of substituents. Thus *in situ* reactions can be metal ion specific and less general than syntheses involving complexation reactions. Contamination of the macrocyclic product by other metal complex impurities is also a possibility.

In spite of the potential disadvantages the *in situ* approach to synthesis is considered to be an effective way of preparing many macrocyclic complexes.

Often, the *in situ* and complexation methods are combined; the macrocycle is first prepared by an *in situ*

reaction and then the metal ion is removed by a displacement process. Complexation reactions between the free ligand and other metal ions can then be carried out in solution. This combination approach was used in the preparation of most of the metal complexes synthesized during the course of this research.

(c) The Modification of the Ligand and/or the Metal Ion

The third type of macrocyclic complex preparation involves the modification of either or both of the macrocycle and the metal ion. Some macrocycles can be chemically modified while remaining coordinated to a metal ion. Many macrocyclic complexes are kinetically inert to ligand substitution, and consequently the metal ion has an important role in these "coordinated-ligand" reactions.

A well studied example of ligand modification is oxidative dehydrogenation. Since Curtis [11] demonstrated the ease with which a series of complexes with different degrees of unsaturation interconverted, many oxidative dehydrogenations employing a variety of reagents have been reported [1,73]. Metal ion specific products are often obtained.

Other means of ligand modification include substitution and addition reactions, deacylation, protonation/deprotonation and hydrogenation. The secondary amines of cyclam can be deprotonated with potassium hydroxide in dimethylsulphoxide and the subsequent reaction with methyl iodide produces tetra-*N*-methylycyclam [74].

Ligand modification by catalytic hydrogenation of nitro groups to amino groups and protonation/deprotonation of primary and secondary amines by pH variation were employed as means of ligand modification during syntheses discussed in this work.

In addition to modification of the macrocyclic

system, reactions involving oxidation or reduction of the metal ion has been investigated [75-81]. Metal complexes with unusual oxidation states have been produced by both chemical and electrochemical methods. These include compounds of nickel(I) and (III), cobalt(I), copper(I), mercury(III), cadmium(III), silver(II) and (III), and ruthenium(II) [82-87].

Structural Aspects of Tetraazamacrocyclic Compounds

(a) Configurations and Conformations of Tetraazamacrocyclic Systems

In theory, coordinated cyclic tetramines can exist as five distinct configurations as a result of the chirality of the coordinated nitrogens in the macrocyclic ring. Bosnich, Poon and Tobe [7] assigned the Roman numerals I-V to these configurations of cyclam shown in figure 5. Alternatively, the R,S designation based on the

Figure 5: Configurations of coordinated cyclam; the + indicates that the NH group is above the plane of the macrocycle and the - indicates that it is below [1].

sequence rules of Cahn, Ingold and Prelog can be used to replace the +, - designation of Bosnich and co-workers, to indicate the direction of the axial amino protons [88]. The relative strain of the configurations has been determined qualitatively [7] and recently, Billo and co-workers reported final minimized strain energies of the square planar and *trans*-octahedral conformers of nickel(II) cyclam [89a].

The relative energies of the configurations depend on the conformations possible for the individual chelate rings of the macrocyclic complex. The conformations of the bidentate five and six membered chelate rings in linear or cyclic polyamines are related to those of cyclopentane and cyclohexane respectively [90]. The five membered chelate ring can assume a range of symmetric and asymmetric gauche conformations with similar strain energies. However, the strain energy is much greater if the chelate ring is forced in to an eclipsed conformation. Similarly, the six membered chelate ring can assume a range of chair conformations of similar strain energies, but if forced to twist or assume boat conformations, the strain energies are much greater.

The conformations adopted by the chelate rings in the coordinated polyamine depend on the configuration of the coordinated nitrogens. For planar coordination of a cyclam macrocycle, the optimum staggered (five-membered) and chair (six-membered) conformation of all four chelate rings are possible only for the configuration III. This configuration is present for noncoordinated cyclam, its diprotonated salt and many of its metal complexes, including those of nickel(II), copper(II), cobalt(II) and cobalt(III).

Until recently, only the *trans*-III configuration of $[\text{Ni}(\text{cyclam})]^{2+}$ had been observed in solution. In 1986,

Billo and co-workers reported the isolation of the kinetically unstable *trans*-V isomer, prepared *via* the folded *cis*-V $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$, and in 1987, they reported the observation of the *trans*-I isomer by ^1H nuclear magnetic resonance spectroscopy [89]. In aqueous solution, 15% *trans*-I isomer was found to be in equilibrium with the *trans*-III form at 25°C.

In folded coordination (one "fold-line" NMN angle is about 180°, the other about 90° for *cis* octahedral or about 120° for trigonal bipyramidal arrangements), the macrocycle is highly strained unless the fold-line NH groups are on the same side of the molecular plane. Only configuration V allows optimum chelate ring conformations for folded cyclam and is assumed by *cis*- $[\text{Co}(\text{cyclam})(\text{en})]\text{Cl}_3$, *cis*- $[\text{Co}(\text{cyclam})\text{Cl}_2]\text{Cl}$, $[\text{Ni}(\text{tet b})(\text{CH}_3\text{COO})](\text{ClO}_4)$ (tet b = *C-rac*-5, 5, 7, 12, 12, 14-hexamethylcyclam) and $[\{\text{Cu}(\text{tet b})\}_2\text{Cl}](\text{ClO}_4)_3$ among others [1].

(b) Metal-Nitrogen Distances

When a metal ion is incorporated into a cyclic amine, the nitrogen donors are compelled to occupy the coordination sites about the metal ion, with the lone-pair electrons facing the metal ion. The uncoordinated macrocycle can in theory adopt a variety of conformations, which under most circumstances are quite different from the *endo* conformation required for coplanar coordination. However, the azamacrocycle can generally adopt a relatively strain-free *endo* conformation with nitrogen donors approximately coplanar, and strain is introduced if the donor atoms are forced inwards or outwards from their preferred coordination sites.

An early study reported the calculated centre-nitrogen distances for the most strain-free conformation with approximately coplanar nitrogens for the tetraazamac-

rocycles [12]aneN₄, [13]aneN₄, cyclam, [15]aneN₄ and [16]aneN₄ as being 1.83, 1.92, 2.07, 2.22 and 2.38 Å respectively [91]. These values indicate that the ideal M-N distance increases by 0.10-0.15 Å for each ring member added. The calculated value for 14 membered rings agrees with that obtained by structural analysis of cyclam and its salt, which have centre-nitrogen values of 2.06 and 2.05 Å respectively [1]. However, the structural analyses of *trans*-MN₄X₂ type complexes of Ni(II), Zn(II) and Co(III) with cyclam, [15]aneN₄ and [16]aneN₄ have shown that the M-N distance increases by 0.04-0.06 Å for each added ring member, significantly less than those expected from calculations of strain energy minimizations for free macrocycles [92, 93]. For example, the reported M-N distances for *trans*-dichloro nickel(II) complexes of cyclam, [15]aneN₄, and [16]aneN₄ are 2.07, 2.11 and 2.17 Å respectively [92].

For folded coordination, no special macrocyclic constraints are present, and the M-N distances are similar to those observed with open chain ligands with similar donors. For example, average Co(III)-N distances of 1.96 and 2.0 Å have been observed for the folded compounds *cis*-[Co([12]aneN₄)(NO₂)₂]Cl and *cis*-[Co(cyclam)(en)]Cl₃ respectively [1].

For several square planar hexamethylcyclam compounds of singlet ground state Ni(II), the average Ni-N distance is 1.92 Å, similar to the values of nickel complexes of open chain amines [94, 95]. The Ni-N distance for a [13]aneN₄ complex of this ion is slightly less at 1.86 Å, indicating some strain in this system.

(c) Anomalous Metal Ion Selectivity of Tetraazamacrocycles

When a metal ion is in planar coordination with four nitrogens in a cyclic tetramine complex, it might be

expected that complexes of highest thermodynamic stability will be formed by metal ions and macrocycles with matching M-N bond length requirements, as found with crown ethers [1]. However, this is not the case [96]. For example, Zn^{2+} which has a preferred M-N length in the range 2.10-2.22 Å shows greatest stability with the small macrocycle [12]aneN₄, rather than with cyclam or [15]aneN₄, which should provide a better fit if planar coordination is adhered to [96]. Interestingly, the preference for [12]aneN₄ over larger macrocycles increases with increasing metal ion size for metal ions larger than Cu^{2+} . This is illustrated by $[\text{Hg}([12]\text{aneN}_4)]^{2+}$ which has a formation constant ($\log K_1$) two orders of magnitude higher than that of the corresponding cyclam complex [97]. For larger Cd^{2+} and Pb^{2+} , this preference for [12]aneN₄ is even greater.

This apparent paradox has been explained (in a simple way) by the relationship between strain energy, U , and the ideal M-N bond length, r^0 , as shown in figure 6 [97, 98].

Figure 6: Relationship between strain energy, U , and ideal M-N bond length, r^0 , for *trans*-1 [12]aneN₄ complex (A) and *trans*-111 cyclam complex (B). The arrows indicate the strain free bond lengths for Cu^{2+} , Zn^{2+} , Hg^{2+} and Pb^{2+} [97].

Hancock and co-workers have used molecular mechanics to show that the lowest strain energy conformer of [12]aneN₄ complexes was *trans*-I, and that for cyclam complexes with most metal ions was *trans*-III [98]. The minimum in the strain energy (U) vs M-N length (r°) for *trans*-I [12]aneN₄ occurs at 2.11 Å and that of *trans*-III cyclam occurs at 2.05 Å. Also, the shapes of the two curves in figure 6 are distinctly different; the curve for [12]aneN₄ complexes has a shallower minimum. This indicates that the *trans*-I [12]aneN₄ is more tolerant towards variation in metal ion size than the *trans*-III cyclam. This can be understood in terms of the nature of chelate rings in the two systems. The cyclam system has two six membered and two five membered rings with an optimal staggered arrangement of hydrogen atoms, giving rise to considerable resistance to macrocyclic ring expansion or contraction. On the other hand, the [12]aneN₄ system with four five membered rings can not achieve such an ideal arrangement of hydrogens, and this allows considerable expansion and contraction within the macrocycle [97].

The strain energy reasoning of Hancock and co-workers explains the preference of ions with a M-N length requirement less than about 2.12 Å (such as Cu(II)) for cyclam and the preference of larger ions for [12]aneN₄.

This work has been expanded to cover the behaviour of nickel ions with macrocyclic rings of various sizes [99]. Nickel(II) is a particularly interesting metal ion since it is in a sense two metal ions in one; namely the high spin and low spin forms with M-N lengths of ca. 2.1 and 1.9 Å respectively. A puzzling feature of the nickel complexes of 12-16 membered azamacrocycles is that the low spin nickel(II) complex of cyclam has a larger formation constant ($\log K_1$) than the analogous

trans-III [13]aneN₄ complex which has the (theoretically) best fit cavity size of 1.92 Å. Several explanations for this observation have been put forward, none of which are very convincing at this stage [99]. Possibly the most important of these explanations may be the distribution of strain in the low spin Ni(II) complexes of [13]aneN₄ and cyclam. The calculated strain energies for the two systems is similar (about 60 kJ mol⁻¹). However, the strain in the Ni-N bonds is much higher for nickel complexes of cyclam than [13]aneN₄ (23.0 and 6.7 kJ mol⁻¹ respectively) because of stretching of the bonds from the ideal length of 1.90 Å in the former [99]. Bonds are not distorted in the [13]aneN₄ complexes, but during orientation of the nitrogen orbitals to overlap with those of Ni(II), the hydrogens on the central ethane bridge of the ligand adopt a completely eclipsed conformation causing high strain in the ligand but having negligible effect on the Ni-N bonds. Thus [13]aneN₄ offers a best fit to low spin Ni(II) only as far as Ni-N lengths are concerned but since the overall strain in cyclam is lower, low spin [Ni(II)(cyclam)]²⁺ has a higher formation constant.

(d) Metal-Axial Substituent Distance

Ito and co-workers have carried out X-ray structural studies of *trans*-MX₂N₄ type complexes of cyclam, [15]aneN₄ [16]aneN₄ [92, 93]. The metal ions investigated were zinc(II), nickel(II) and cobalt(III) with chloride and thiocyanate as the axial ligands. This data showed that out-of-plane coordination bond length (M-X distance) decreases with increasing in-plane bond length (M-N distance). Also, the degree of correlation was found to be metal ion dependent; Zn²⁺ > Ni²⁺ > Co³⁺. This interrelationship has been associated with softness of the metals;

zinc(II) being the softest and Co(III) being the hardest. Strong axial ligands such as thiocyanate gave rise to weak correlations when compared with weak axial ligands such as chloride in the Ni(II) complexes. Their findings agree with earlier studies of Hathaway [100], Gazo [101] and Sugimoto [102].

The influence of the equatorial ligands on the hydrolysis rates of the axial ligands in Co(III) complexes of this type is another example which illustrates the interaction between in-plane and out of plane ligands [1]. Also, the electronic spectral studies of Busch and co-workers showed that for *trans*-NiX₂N₄ complexes, the ligand field strength of the axial ligands decreases with increasing in-plane ligand field. They introduced the term "electronic *cis* effect" to describe this observation [103]. The nature of all these phenomena are of electronic origin.

(c) Substituents on the Macrocycle

Carbon Substituents

Substituents on the carbon atoms of the five and six membered chelate rings can be described as equatorial or axial by analogy with substituted cyclopentanes and cyclohexanes. Substituents on isolated chelates normally adopt equatorial orientations because this minimizes intra-ligand strain [104]. For C-substituted linear polydentate ligands, the ideal arrangement is a balance between the minimum energy conformation/configuration of the unsubstituted ligand and equatorial orientation of a maximum number of substituents. The same principles apply to cyclic polyamines [105].

In general, a single substituent on a ring carbon atom introduces a chiral centre. Substituents in symmetri-

cal pairs lead to *C-rac* and *C-meso* configurations of the ligand. Often, *C-meso* ligands adopt a *trans*-III nitrogen configuration and planar coordination whereas *C-rac* ligands tend to adopt a *cis*-V configuration and folded coordination, leading to distinct stereochemical behaviour of the isomers of the macrocycle. A tetramine complex which illustrates this effect by providing a comprehensive set of structures is 5,5,7,12,12,14-hexamethylcyclam of which the *C-meso* and *C-rac* isomers are commonly known as tet a and tet b respectively [1].

Nitrogen Substituents

Isomerization of the nitrogen configuration of coordinated cyclic tertiary amines is impossible without breaking the metal-nitrogen bond [1].

The reaction between tetra-*N*-methylcyclam, nickel(II) ions and sodium azide results in a relatively unstable and labile cation, *trans*-I [Ni(tetra-*N*-methylcyclam)(N₃)]⁺ [106]. This is of square pyramidal geometry with the azide ion coordinated on the same side of the macrocycle as the four methyl groups, as shown in figure 7, with the nickel ion 33 pm away from the N₄ plane. Forcing the nickel ion in to the N₄ plane to give

Figure 7: Structures of *trans*-III (A) and *trans*-I (B) 1,4,8,11-tetra-*N*-methylcyclam [1]

planar coordination would cause severe interaction between the methyl groups. In comparison, *N*-methylation of presynthesized $[\text{Ni}(\text{cyclam})]^{2+}$ results in the tetra-*N*-methylated cation with a *trans*-III nitrogen configuration [74]. This cation is extremely stable and can not be demetallated with reagents such as cyanide. The reactivity differences between the cations of configurations I and III have been attributed to the exposed nature of the metal ion in configuration I [74] and the apparent inability of the tertiary nitrogens to change configuration [1]. However, Moore and co-workers have shown that the *trans*-I and *trans*-III isomers of $[\text{Ni}(\text{tetra-}N\text{-methylcyclam})]^{2+}$ undergo interconversion in the presence of strongly coordinating amines such as *n*-propylamine [107].

(f) Chelate Angles

Tetraazamacrocyclic complexes can also be regarded as derived from appropriate linear tetramines by bridging the terminal amino groups by a $-(\text{CH}_2)_2-$ or $-(\text{CH}_2)_3-$ bridge, with the formation of a ring-closing chelate ring. The level of strain due to ring closure can be estimated by comparing the "open" NMN angle with that for the particular chelate ring. The value of the chelate angle of bidentate ligands is a balance between the ideal value of the bonding angle at the central metal ion (generally 90°), the metal-donor distance and the preferred "chelate bite" or the N-N distance. For M(II) and M(III) ions of the latter half of the first transition series with diamine chelates, common values are about 85° for the five-membered and about 92° for the six membered chelate rings. Significant deviation from these values is indicative of a strained conformation.

Linking two or more five (or six) membered chelate

rings to form a linear polyamine results in cumulative strain which is greatest for planar coordination between the metal ion and the nitrogen donors. The alternate arrangement of five and six membered rings with alternate chelate angles greater than and less than 90° minimizes this strain. For planar coordinated cyclic polyamines, the strain is even greater, since the chelate angles must sum to 360° . Fourteen membered tetraazamacrocycles with two five and two six membered chelate rings, preferably alternating (cyclam-type) have the least amount of cumulative chelate angle strain and are most common. (Figure 8 shows the structure and some of the bond angles of *trans*-III [Ni(cyclam)Cl₂]). The chelate angles of cyclam-type

Figure 8: Structure of *trans*-III [Ni(cyclam)Cl₂] showing some of the bond angles

compounds are similar to those of diaminoethane and 1,3-diaminopropane, suggesting that chelate angle strain arising from cyclization is minimal.

Planar coordinated triethylenetetramine has terminal NMN angles of about 100° [94, 95]. For planar coordination, ring closure via a $-(CH_2)_3-$ bridge to give a [13]aneN₄ complex causes less strain than closure by a $-(CH_2)_2-$ to give a [12]aneN₄ complex. Relatively few planar complexes of [12]aneN₄ have been reported [108(a)-(d)] whereas a

number of planar and folded coordination [13]aneN₄ type compounds have been reported [1, 108(e), (f)].

Chelate angle strain is less for cyclic tetramines in folded coordination. Also, the chelate angles of cyclam compounds having planar and folded coordination are comparable; this is further proof for the minimal strain in the cyclam system in planar coordination.

Chelate angle strain can also be minimized by deviating from the coplanar arrangement of the metal ion and the donors. Structural data obtained by Ito and co-workers for *trans*-NiMN₄X₂ type complexes showed that [Ni([15]aneN₄)(NCS)₂], [Ni([16]aneN₄)Cl₂], and [Ni([16]aneN₄)(NCS)₂] display tetrahedral distortion of the NiN₄ set [93]. The distortion of the 16 membered ring was found to be greater than that of the 15 membered ring. However, in the complexes [Ni(cyclam)Cl₂], [Ni(cyclam)-(NCS)₂] and [Ni([15]aneN₄)Cl₂], the nickel ions were found to reside at an inversion centre.

SECTION 1.2: AZAMACROCYCLIC COMPLEXES CONTAINING PENDANT ARMS WITH ADDITIONAL LIGATING GROUPS

Introduction

Since the mid-1970s, coordination chemists have synthesized and studied ligands with kinetically inert, relatively rigid structural properties of macrocycles and also kinetically labile, flexible properties of open chain ligands [109]. The reasons for these investigations are numerous. The characteristics of a macrocycle can be modified by introducing additional ligating groups into its periphery; more stable complexes may be formed, metal ion selectivity or solubility properties may be changed. For example, the macrocycle shown in figure 9.1 with four pendant acetate groups forms thermodynamically stable complexes with alkali and alkaline earth metal ions whereas the same cyclic tetramine without these pendant arms can only bind transition metal ions [110-112]. Another interesting example is the pendant arm macrocycle shown in figure 9.2 which was synthesised by Raymond and co-workers specifically to bind iron(III) [113]. Hancock and co-workers have described a series of pendant arm macrocyclic compounds with high rates of complexation, high selectivity for lead and a low affinity for zinc and calcium [114]. These compounds have the potential to be efficient antidotes for lead poisoning with minimal depletion of trace elements such as zinc and calcium from the body. Also, the synthetic macrocycle with a long lipophilic chain, shown in figure 9.3, and its metal complexes are soluble in organic solvents. This property is useful for extracting metal ions from aqueous solution into an organic phase. [115]. Similarly, a polymer supported macrocycle has been prepared with cyclam and a polystyrene resin for which the retention capacity for copper is much

Figure 9: Analytically useful pendant arm macrocycles
[109]

Figure 9.1 A macrocycle that forms stable alkali and alkaline earth complexes

Figure 9.2 A macrocycle that specifically binds iron

Figure 9.3 A macrocycle that can extract metal ions from aqueous solution into an organic phase

greater than that for nickel and cobalt [116].

Apart from these analytically useful properties, pendant arm macrocycles can also be employed to study the selective influences of additional ligating groups on the properties of metal ions, such as coordination geometry, absorption spectra and oxidation state. For example, the redox potential of a coordinated metal ion can be changed by introducing an axial pendant arm [117,118]. As indicated earlier, coordination of a 3d metal ion by a polyamine macrocycle may stabilize unusual and generally unstable oxidation states [119]. An example of this is the low spin d^7 nickel(III) ion which forms stable complexes with cyclam [120]. The stability of this complex has been attributed to the unique tendency of the cyclam ring to exert a strong in-plane field, a property not shared by ligands of greater denticity (*i.e.*, penta- or hexaaza-rings). Fabbrizzi and co-workers have suggested that a cyclam ring with a pendant amine could stabilize the tetragonally distorted octahedral Ni(III) state further by coordination of a fifth nitrogen at an axial site of the distorted octahedron [121].

The selective coordination of another ligand may depend on the nature of the species already occupying the axial position. This is illustrated by the reversible oxygen binding properties of the iron in haemoglobin which are a result of the axially coordinated imidazole side chain of a histidine residue [122]. To model this natural system, Traylor and co-workers prepared an iron porphyrin with a long chain to which a histidine terminal has been attached [123]. The model was found to reversibly bind oxygen at low temperatures.

Another application of pendant arm macrocycles is to bring a metal ion within the reach of a weakly binding or non-coordinating organic group so that an interaction

between the two may take place [109]. By covalent coupling of the organic group to the macrocycle bound to the metal ion, metal ion promoted or catalyzed reactions can be investigated. (The metal ion behaves as a Lewis acid or a redox catalyst and the organic species as the substrate). By this type of application, mechanistic details of such processes can be elucidated.

Recently, Fabbrizzi and co-workers suggested the name *scorpiands* for these compounds owing to the active role played by the pendant arm or "tail", which can further "bite" an already chelated metal ion [121].

Categories of Pendant Arm Azamacrocycles

There are three main categories of azamacrocycles with additional ligating groups. They are (a) N-functionalized (b) C-functionalized and (c) bis-macrocycles [109].

(a) N-functionalized Macrocycles

Numerous N-functionalized tetraazamacrocycles and a lesser number of triazamacrocycles with pendant arms at coordinating nitrogen sites have been synthesised. In addition, a few polyaza, polymembered ligands with N-functionalized pendant arms have been reported [124-126]. Also, some diaza-, tri- and tetraoxa mixed donor ligands with N-functionalized pendant arms [127,128] and a few polydentate, mixed donor, large macrocyclic ligands with N-functionalized side arm participation [129] have been described. (Only tri- and tetraazamacrocyclic compounds will be discussed in this study).

N-functionalized Triazamacrocycles

Most N-functionalized triazamacrocycles are trisubstituted, with three pendant arms [130-147]. In general, these are synthesized by alkylation or acylation of the amino nitrogens of triazamacrocycles such as 1,4,7-triaza-

cyclononane, [9]aneN₃ or 1,5,9-triazacyclododecane, [12]aneN₃ [109]. A series of N-functionalized derivatives of 9ane[N]₃ are summarized in figure 10.

Figure 10: N-functionalized derivatives of [9]aneN₃ [146]

N-functionalized Tetraazamacrocycles

A variety of N-functionalized tetraazamacrocycles containing one, two and four pendant arms have been synthesized and studied [109-112, 116, 121, 147-171, 173-175].

By reacting an excess of alkylating agent with the unsubstituted macrocycle in the presence of a base, tetra-N-substituted tetraazamacrocycles can be prepared. Figure 11 shows some of these complexes.

Figure 11: Tetraazacycloalkanes with four N-functionalized pendant arms [109]

Murase and co-workers have prepared a series of unusual binuclear complexes of copper, nickel and cobalt with the ligand N,N',N''N'''-tetrakis(2-aminoethyl)cyclam (taec) [166, 171, 173]. In these complexes, the taec molecule incorporates two metal ions, each of which is coordinated by two ring and two pendant-nitrogen atoms. Preparation and coordination modes of taec are shown in figures 12(a) and 12(b) respectively.

Figure 12: Synthesis (a) and coordination modes (b) of taec [166]

Cyanomethylation of 1,4-dimethylcyclam gives the di-substituted species in figure 13 [151].

Figure 13: A disubstituted N-functionalized pendant arm macrocycle [109]

Mono-substituted, N-functionalized tetraazamacrocyclic compounds can be synthesized by various routes; (a) selective alkylation, (b) the cyclization with a side

chain containing precursor (c) the modification of a side-chain already present and (d) the alkylation of a selectively protected macrocycle [109]. Selective alkylation can also be used to prepare trisubstituted tetraazacycloalkanes.

(b) C-Functionalized Macrocycles

Additional ligating groups can also be introduced to macrocycles at carbon atoms of the ring [115, 117, 118, 172, 176-185]. Generally, these syntheses start with the side chain attached to one of the participants of the cyclization reaction. The C-functionalized pendant arm macrocycles synthesized by Tabushi and co-workers are shown in figure 14 [176].

Figure 14: C-Functionalized
macrocycles [109]

R = (CH₂)₃-OH

R = (CH₂)₄-NH₂

Kimura and co-workers have developed versatile synthetic methods to prepare tri- and tetraazamacrocyclic complexes with C-functionalized pendant phenol, catechol, hydroquinone, pyridine and imidazole donor groups [117, 118, 177, 178, 181, 184, 185]. These complexes have the potential to model enzyme systems since many biological tetramines have axial donor ligands such as imidazole, phenolate or cysteine. For example, an iron(III) complex of the macrocycle in figure 15, with axial coordination of phenolate may be a simple model for catalase [186] or abnormal heme [187].

Figure 15: A C-functionalized phenol pendant macrocycle [117]

(c) Bis-Macrocycles

The final category of pendant arm macrocycles are obtained by covalently linking two macrocycles so that binuclear metal complexes can be prepared [163,188-198]. The two macrocycles are linked together by bridging the amine nitrogens or the carbon atoms of the macrocyclic ring. The binuclear complexes can be homobimetallic, incorporating the same metallic element in both rings (for example, dinickel or dicopper) or heterobimetallic, incorporating two different metals such as nickel and copper. These bimetallic complexes have potential in being used as models for electron transfer metalloproteins containing two or more proximate metal centres [199]. The binuclear copper complex of the bis-macrocycle in figure 16 showed a weak metal-metal interaction and the two Cu(II) ions were

Figure 16: A bis-macrocycle [191]

easily oxidised to Cu(III) in two consecutive one-electron steps separated by 110 mV [190].

Equilibria in Solution

(a) Protonation

The protonation and complexation equilibria of the tetraacetate complexes shown in figure 17 have been

Figure 17: N,N',N'',N'''-tetraacetate complexes of tetra-azamacrocycles [109]

studied thoroughly [110-112, 200]. pH titration results have shown that all these compounds have two protonation constants (pK_H) above 9.7, two around 4 and two below 2 [109]. Desreux and co-workers have shown that protonation first occurs at two amino nitrogens which are *trans* to each other, then at the two carboxylates attached to the as yet unprotonated nitrogens and finally at the other two carboxylates [200]. The remaining nitrogens must have extremely low pK_H values ($\ll 2$). This is consistent with the finding that 12-14 membered tetraazamacrocycles without pendant arms have two high and two low pK_H values due to the strong electrostatic repulsion between the positively charged ammonium groups [201].

In this work, the protonation constants of diam and selected nickel, copper and palladium complexes of diam were measured.

(b) Equilibria Involving the Pendant Arm

The pH dependant internal equilibrium between open and coordinated forms of the pendant arm is an interesting phenomenon of macrocyclic complexes with additional ligating groups (Figure 18). Lotz and co-workers observed

Figure 18: Equilibrium between the open and apically coordinated forms of a pendant arm macrocyclic complex

that from a solution of the nickel complex of the macrocycle A shown in figure 19, two solids can be isolated depending on the pH [153,161]. When the pH is less than 6.3, the pendant nitrogen is protonated and a yellow, diamagnetic, square planar complex is obtained. When the pH is greater than 6.3, the pendant arm is not protonated and is available for axial coordination. A violet, paramagnetic, octahedral complex is formed under the latter conditions. Similarly, Fabbrizzi and co-workers observed that the nickel complex of the macrocycle B in figure 19 exists as the blue, high spin form at pH greater than 2.8 with the pendant amine apically coordinated [121]. At pH less than 2.8, the pendant arm is protonated and the predominant species is the yellow, low spin form. Similar phenomena have been observed with non-pendant arm cyclic amines and linear systems [202-208]. Two such examples are the isomerization of violet *cis*-[Ni(cyclam)-(H₂O)₂]²⁺ to yellow [Ni(cyclam)]²⁺ [203] and Jørgensen's

Figure 19: Pendant arm macrocycles that exhibit pH dependent high spin-low spin equilibria

early observation of an equilibrium mixture between blue $[\text{Ni}(\text{trien})(\text{H}_2\text{O})_2]^{2+}$ and yellow $[\text{Ni}(\text{trien})]^{2+}$ [205]. Blue-yellow equilibria were also observed in this work.

This type of acid-base equilibrium and the accompanying (possibly reversible) geometry changes are direct consequences of the combination of kinetically inert, structurally rigid macrocycles and the kinetically labile, structurally flexible pendant arms. Changes in pH may not affect the complexation capability of the macrocycle but the coordination potential of the pendant arm is highly dependent on pH [109].

Kinetic Aspects

Complex formation kinetics of the metal ions Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} , Ni^{2+} and Cu^{2+} with the macrocycles shown in figure 17.1 and 17.2 have been studied by Wilkins and co-workers [209]. In all cases, the monoprotonated form of the ligand, LH^{3-} was the reactive species. The rate constants for the complexation are 10^3 – 10^4 times larger than those for the unsubstituted species [201].

This can be explained by the different charges on the ligands; a charge of -3 on the monoprotinated tetraacetates and a charge of +1 on the monoprotinated unsubstituted macrocycle. However, the acetate groups also affect the rate of reaction by rapidly forming adducts with the metal ion. The high stability of these adducts suggests that a carboxylate anion and an amino nitrogen play a role in the binding. When the metal ion is coordinated and in the proximity of the macrocycle, it is rapidly incorporated. Similarly, Buckingham and co-workers observed that a picket fence porphyrin with four carboxylate substituents reacts much faster than the unsubstituted analogue [210]. The kinetics were also explained by a rapid pre-equilibrium mechanism; the metal ion is complexed by one or more of the carboxylates and then introduced into the macrocyclic ring. The latter is the rate determining step.

Little is known about kinetics of axial coordination of the pendant arm. For example, in the case of the nickel complex of the macrocycle A in figure 19, the reaction is too fast to be followed by stopped-flow or T-jump techniques [109].

In this work, the acid dissociation kinetics of $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ were investigated at 70°C and 50°C, in perchloric and hydrochloric acid. Acid dissociation kinetics of cyclam type pendant arm macrocyclic complexes have not been studied in great detail. Since the dissociation of (*trans*-III) copper(II) and nickel(II) complexes of 14 membered macrocycles is extremely slow, one would expect the rate of dissociation of similar pendant arm complexes to be as slow or even slower. The half life of $[\text{Ni}(\text{cyclam})]^{2+}$ is estimated to be 30 years at 25 °C in 1 mol dm⁻³ perchloric acid [202] and the dissociation of $[\text{Cu}(\text{II})(\text{cyclam})]^{2+}$ is extremely slow, even in 6 mol dm⁻³ hydrochloric acid [211]. However,

complexes of larger 17- or 18- membered tetraazamacrocycles dissociate quite readily in acidic solution [212,213]. Hay and co-workers have reported that at 25°C, Ni(II)[17]ane_4 dissociates 10^{10} times faster than $[\text{Ni(cyclam)}]^{2+}$ [214]. These figures suggest that pendant arm macrocyclic complexes with 17 or 18 members should dissociate quite readily in solution.

CHAPTER 2: EXPERIMENTAL

SECTION 2.1: INSTRUMENTATION

A Parr Instruments Pressure Reaction Apparatus (model no. 517) was used for catalytic hydrogenation of (6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane)nickel(II) chloride, $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ at a pressure of 60 lb/in², or a Parr Reaction Stirrer (A1120HC2 447 T 316, maximum operating pressure 1750 lb/in²) was used for higher pressure reductions.

Carbon, hydrogen, nitrogen, sulphur and halide analyses were performed by Professor A.D. Campbell and his associates, University of Otago. Metal analyses were performed on a Varian Techtron Model AA-4 Atomic Absorption Spectrophotometer.

Infrared spectra of the prepared compounds were recorded as nujol or hexachlorobutadiene (HCBd) mulls on potassium bromide plates using a Perkin Elmer 599B Infrared Spectrophotometer.

The electronic spectra were recorded as aqueous solutions at 25 or 50°C on a Perkin Elmer 330 Spectrophotometer.

The nuclear magnetic resonance spectra were determined on a Varian FT 80A Pulse Fourier Transform Spectrometer. An insert diameter of 5 mm and a sample temperature of ca. 30°C was used. The ¹H NMR data was obtained at 80 MHz, using D₂O or CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal reference. The ¹³C data were obtained at 20 MHz, using D₂O, CDCl₃ or DMSO as the solvent. Chemical shifts are reported relative to TMS using dioxane as the internal reference.

Magnetic measurements on solid samples were performed at 25°C using the Faraday Method and the apparatus

described in reference [215*].

Potentiometric pH titrations were performed at 25°C on a Radiometer automatic titration apparatus equipped with a PHM Research pH meter, a TTT 80 titrator, an ABU 80 autoburette, a REC 80 servograph and a TTA 80 titration assembly. The electrode system consisted of a Radiometer G2040B glass electrode and a Radiometer K401 calomel electrode. For calibration purposes, buffers of pH 4.01, 9.18 and 10.012 were used. The Gilbert Herron Method was used to calculate the protonation constants [215].

SECTION 2.2: SYNTHESSES

General Introduction

Commercially available reagents were used without further purification.

The unprotonated ligand, 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane hydrate, (diam). $3\frac{1}{2}\text{H}_2\text{O}$ was used for all metal complex preparations, with the exception of $[\text{Co}(\text{diam})]_8\text{Cl}_{14}(\text{CO}_3)_5 \cdot 56\text{H}_2\text{O}$ for which the protonated ligand, $(\text{diamH}_6)\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ was used. In all cases, the ligand and the metal salt were dissolved in a minimum volume of solvent (usually water) and mixed. During complex formation, additional acid or base were added after reacting the ligand and the metal salt in solution (a few minutes after mixing).

The metal complexes were recrystallized from a minimum volume of hot water, unless stated otherwise. When propan-2-ol was added to a solution of diam compound to aid crystallization, sufficient was added to render the solution turbid. Crystallization was carried out at room temperature in all cases.

Most compounds were hydrated and many occurred as different (and sometimes uncertain) hydrates. Since some of the water was lost on desiccation, all the compounds were air dried, and not vacuum desiccated.

Near quantitative yields of the metal complexes, based on the weight of the ligand were obtained (ca. 90%), unless stated otherwise.

The colours of the prepared compounds were described according to the standards in reference [216].

Elemental analyses, infrared, electronic and nuclear magnetic resonance spectral data and magnetic measurements for the prepared compounds are given in Sections 2.3-2.7.

Perchlorate salts of metal complexes are heat and

pressure sensitive and can be explosive. Only small quantities of these compounds should be prepared and handled with care. No such problems were encountered in this work.

Condensation Reaction

(6, 13-Dimethyl-6, 13-dinitro-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Chloride Hemihydrate,

$[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$

$[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (page 78; 11.5 g, 3.33×10^{-2} moles) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (4 g, 1.68×10^{-2} moles) were dissolved in hot methanol (200 cm^3) and magnetically stirred under reflux. Triethylamine (5 cm^3 , 3.59×10^{-2} moles), nitroethane (10 cm^3 , 1.39×10^{-1} moles) and lithium carbonate (5 g) were then added. Aqueous formaldehyde (37%, 30 cm^3 , 3.01×10^{-1} moles) was added dropwise over two hours. The reactants were refluxed for approximately eight hours. The mixture was then allowed to cool to room temperature while being stirred. The muddy yellow precipitate was filtered through (fast) filter paper and washed thoroughly with methanol until the washings were colourless. The solid was purified by stirring in a 1:1 ethanol/water mixture and adding concentrated hydrochloric acid dropwise until effervescence ceased. The greyish yellow product, $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ (15 g, 3.27×10^{-2} moles) was filtered off, washed with methanol until the washings were neutral. (A near quantitative yield based on the weight of $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was obtained).

Reduction of $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$

$[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ and Raney nickel catalyst (page 78) were suspended in water in a hydrogenating vessel under a gas pressure of ca. 60 lb/in² or 1000-1600 lb/in² (see SECTION 2.1: INSTRUMENTATION for details). The

exact quantities of the reactants were not critical; for every 50 g (1.09×10^{-1} moles) of $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, ca 250 cm³ water and 1 g Raney Nickel were added. The mixture was shaken or stirred until $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ had completely dissolved and the hydrogen gas pressure ceased to fall. (The reaction time depended on the quantities of $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ and Raney nickel, the activity of the catalyst and the gas pressure; taking approximately 12 to 72 hours). When the reaction was over, the hydrogenation vessel was depressurized and the catalyst was filtered off using fine filter paper (*Caution; pyrophoric!*). The filtration procedure was repeated thrice to remove traces of catalyst from the filtrate which was then rotary evaporated to dryness.

Separation of Reduction Reaction Products

a- (6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Chloride Sesquihydrate,

a- $[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$

The residue of the rotary evaporation was broken up and refluxed in ethanol. During refluxing, a lilac coloured precipitate, **a-** $[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, separated out from the bulk of the solution. This was filtered off and washed thoroughly with ethanol.

b- (6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Chloride Hexahydrate,

b- $[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$

Slow evaporation of the ethanolic filtrate from the **a-** isomer yielded large violet brown crystals of **b-** $[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$. These were filtered off and washed with cold ethanol.

b-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclo-tetradecane)diaquonickel(II) Chloride Dihydrate,

b-[Ni(diamH₂)(H₂O)₂]Cl₄. 2H₂O

The b- isomer could also be isolated as the protonated salt. The ethanolic filtrate from the a- isomer was rotary evaporated to dryness, dissolved in a minimum volume of hot water and filtered while hot. A few drops of concentrated hydrochloric acid was then added, followed by propan-2-ol. The resulting purple crystals of b-[Ni(diamH₂)(H₂O)₂]Cl₄. 2H₂O were filtered off and washed with ice cold water followed by ethanol. (This method of b- isomer separation was more effective since the protonated salt of the b- isomer was less soluble in ethanol and propan-2-ol than the nonprotonated salt).

c-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclo-tetradecane)nickel(II) Chloride Hydrate,

c-[Ni(diamH₂)]Cl₄. xH₂O (tentative formulation)

When all of the b- isomer had been precipitated out of solution, a brown filtrate remained. The rotary evaporation of this solution resulted in a dark brown, sticky material which was assumed to be largely crude, hygroscopic c-[Ni(diamH₂)]Cl₄. xH₂O and some impurities. (This formulation is tentative because of the impure and hygroscopic nature of the product).

Recrystallization of the a-, b- and c- isomers as perchlorate, thiocyanate and tetrachlorozincate salts will be discussed later.

The Relative Yields of a-, b- and c- Isomers

By varying the pH of the solution to be hydrogenated and the the hydrogen pressure, the relative yields of a- and b- isomers could be varied. In general, very high pressures, highly acidic solutions (ca. 1 mol dm⁻³

hydrochloric acid), and basic solutions (e.g. 0.4 mol dm⁻³ ammonia) resulted in very poor yields of the a- isomer. (These conditions led to high yields of the b- isomer). The yield of the a- isomer was increased by using a comparatively less acidic solution (ca. 0.05-0.1 mol dm⁻³ hydrochloric acid) or water, lower pressures (ca. 60 lb/in²) or higher pressures combined with large amounts of Raney nickel to decrease the reaction time. The true yield of the crude c- isomer was difficult to determine because of its tentative formulation; thus, only an estimate is given.

Some typical results are as follows. The starting material, [Ni(dini)]Cl₂ · ½H₂O is referred to as SM. The reaction time (in days) is given in parentheses.

Conditions	Yields
water, 15 g SM, 60 lb/in ² , (6)	46% a-, 39% b-, <15% c-
water, 300 g SM, 1000 lb/in ² , (1)	32% a-, 49% b-, <15% c-
water, 470 g SM, 1600 lb/in ² , (3)	0.5% a-, 84% b-, <15% c-
1 1 M HCl, 10g SM, 60 lb/in ² , (3)	0% a-, 80% b-, <20% c-
0.1 M HCl, 50 g SM, 60 lb/in ² , (3)	49% a-, 35% b-, <15% c-
0.05 M HCl, 10 g SM, 60 lb/in ² , (1)	33% a-, 42% b-, <20% c-
0.4 M NH ₃ , 10 g SM, 60 lb/in ² , (1)	0% a-, 75% b-, <20% c-
1 = The Raney Nickel was partially deactivated in 1 M HCl; however, 80% b- isomer and some c- isomer was obtained.	

Isolation of the Ligand

meso-(6,13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane) Hydrate, (diam). $3\frac{1}{2}\text{H}_2\text{O}$

Two methods were used to isolate the ligand (diam). $3\frac{1}{2}\text{H}_2\text{O}$; (a) Cyanide Method and (b) Acid Demetallation.

(a) Cyanide Method

Potassium or sodium cyanide was added to an aqueous solution of a- or b-[Ni(diam)]Cl₂, in a 1:6 mole ratio. The solution was heated in a water bath for about three hours. As the reaction proceeded, the purple colour changed to orange due to the formation of [Ni(CN)₅]³⁻. When demetallation was complete, the solution was rotary evaporated to dryness. The resulting residue was broken up and refluxed in petroleum ether to extract the ligand. (Other solvents that were used for extraction include ethanol, diethylether and chloroform, but were not as successful as petroleum ether). Slow evaporation of the petroleum ether extract resulted in colourless crystals of the ligand, (diam). $3\frac{1}{2}\text{H}_2\text{O}$. This was purified by dissolving in hot petroleum ether, filtering rapidly followed by slow evaporation. (The yield of the pure product was 70-80%). This method was limited in its success because of the high solubility of [Ni(CN)₅]³⁻ in polar solvents and the low solubility of diam in non-polar solvents. This led to the inconvenience of a large volume of solvent, reduced yields and the need for anhydrous solvents to avoid contamination from [Ni(CN)₅]³⁻. (The method of continuous extraction gave very low yields because of solubility problems).

(b) Acid Demetallation

A less troublesome method of demetallation involved acid dissociation of the nickel complex at a high temperature. a- or b-[Ni(diam)]Cl₂ was suspended in an excess of

concentrated hydrochloric acid in a Carius tube. The sealed tube was placed within a metal protective jacket in a Carius furnace at ca. 140°C. The reaction was simple and rapid. The reaction time was between 1 and 48 hours determined by the isomer, the amount of complex and the concentration of the hydrochloric acid. The a- isomer reacted up to 50 times faster than the b- isomer and the reaction in 36% acid was many times faster than that in 25% acid. Pale yellow crystals of the chloride salt of the fully protonated ligand, (6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane) hexahydrochloride dihydrate, $(\text{diamH}_6)\text{-Cl}_6 \cdot 2\text{H}_2\text{O}$ were filtered off and washed thoroughly with ethanol to remove all traces of nickel chloride. More product was isolated from the filtrate by the addition of propan-2-ol. The ligand salt was recrystallized from boiling water to which concentrated hydrochloric acid was added. (In contrast with the Cyanide Method, Acid Demetallation gave an almost quantitative yield of the ligand). The advantages of the latter method were high yields, simplicity, rapidity and the lack of need for highly poisonous chemicals such as sodium cyanide.

For nearly all subsequent preparations, the deprotonated or free base form of the ligand, (diam). $3\frac{1}{2}\text{H}_2\text{O}$ was used. When the nickel complex was demetallated with cyanide, the ligand could be used without further modifications. However, when acid demetallation was employed, deprotonation of the fully protonated ligand was necessary. $(\text{diamH}_6)\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ (20 g, 3.90×10^{-2} moles) was stirred in a saturated solution of sodium hydroxide. (*Care: exothermic reaction!*) When the mixture had cooled to room temperature, it was shaken with chloroform (ca. 125 cm³). About five extractions were performed. The chloroform extract was dried over anhydrous sodium sulphate for 24 hours, then decanted and rotary evaporated

to a small volume to which a few drops of diethylether was added. The resulting colourless crystals of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ were filtered off and recrystallized from chloroform and diethylether.

Characteristic infrared spectra showed that the ligand obtained from the a- and b- isomers of the nickel complex were identical, independent of the form of the complex (protonated or non-protonated) and the method of isolation used. Later, this was identified as the *meso*-isomer.

Acid Demetallation of c-[Ni(diamH₂)]Cl₄

The thiocyanate or perchlorate salt of the c- isomer was heated in concentrated hydrochloric acid at ca. 140°C for about 18 hours. The brown solution which turned a greenish brown colour yielded mostly the usual protonated *meso*- ligand. However, the addition of propan-2-ol to the filtrate yielded a small amount of brownish cream precipitate with unusual properties, discussed in Chapter 3 as the "c- ligand".

NICKEL(II) COMPOUNDS

All the nickel compounds discussed in this section were prepared by recrystallizing the three products of reduction of $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, a-, b- and c- isomers of the nickel complex of diam with anions such as perchlorate, thiocyanate and tetrachlorozincate under various conditions, as discussed below.

When nickel salts of the a- isomer are prepared, the products must be isolated without delay to avoid isomerization to the b- form in solution. Slow recrystallization of a- $[\text{Ni}(\text{diam})]\text{Cl}_2$ from hot or cold acidic and basic (or neutral) aqueous solution resulted in near quantitative yields of b- $[\text{Ni}(\text{diamH}_2)(\text{H}_2\text{O})_2]\text{Cl}_4$ and b- $[\text{Ni}(\text{diam})]\text{Cl}_2$ respectively. The half life of the a- to b- conversion reaction in water at 25°C was 8 hours. Heat and/or the presence of base or acid (0.2 mol dm^{-3} or more) increased the rate of conversion (see Section 2.9.1). Non-aqueous solvents (such as dimethylformamide, acetonitrile and 2-nitropropane) were found to be unsuitable media for recrystallization because of low solubility of the a- isomer. The solubility of the complex in dimethylsulphoxide was satisfactory; however, crystalline a- isomer was not obtained because of isomerization.

(a) COMPOUNDS OF THE a- ISOMER

Non-protonated Chloride Salt

a-(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Chloride Sesquihydrate,

a- $[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$

The lilac precipitate a- $[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, which was the first isomer to be separated from the solution of hydrogenated $[\text{Ni}(\text{dini})]\text{Cl}_2$, was recrystallized by dissolving in a minimum volume of cold water and then adding propan-2-ol or acetone.

Diprotonated Perchlorate Salt

a-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Perchlorate Hydrate,

a-[Ni(diamH₂)](ClO₄)₄. 2½H₂O

To a-[Ni(diam)]Cl₂. 1½H₂O (5 g, 1.20 x 10⁻² moles) dissolved in a minimum volume of cold water, an excess of concentrated perchloric acid (ca. 5 cm³) was added.

(*Caution; exothermic reaction!*) The resulting yellow precipitate was isolated without delay and washed with ice cold water followed by ethanol. The product was purified by dissolving in a small volume of cold water, adding a few drops of concentrated perchloric acid, followed by propan-2-ol until the solution appeared turbid. Yellow crystals of a-[Ni(diamH₂)](ClO₄)₄. 2½H₂O (8.6 g, 1.13 x 10⁻² moles) were obtained.

a-[Ni(diamH₂)](ClO₄)₄. 2½H₂O also isomerized to the b- form in solution; the half lives of the reaction in 0.1 mol dm⁻³ hydrochloric acid and 0.1 mol dm⁻³ sodium hydroxide at 50°C were ca. 7 hours and ¼ minute respectively (also see Section 2.9.1).

Non-protonated Mixed Chloride Perchlorate Salt

a-(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Chloride Perchlorate Monohydrate,

a-[Ni(diam)]Cl(ClO₄). H₂O

To a-[Ni(diam)]Cl₂. 1½H₂O (1 g, 2.41 x 10⁻³ moles), dissolved in a minimum volume of cold water, a concentrated solution of sodium perchlorate (0.74 g, 6.04 x 10⁻³ moles) was added slowly. On standing, flat, lustrous, lilac coloured crystals of a-[Ni(diam)]Cl(ClO₄). H₂O (1 g, 2.13 x 10⁻³ moles) appeared, within less than half an hour. (Under these conditions, contamination by the b-isomer was minimal). These were filtered off without delay and washed with ice cold water followed by ethanol.

Non-protonated Thiocyanato Compound

a-(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)dithiocyanatonickel(II) Hemihydrate,

a-[Ni(diam)(NCS)₂]. $\frac{1}{2}$ H₂O

A concentrated solution of sodium thiocyanate (0.49 g, 6.0×10^{-3} moles) was added to a-[Ni(diam)]Cl₂. $\frac{1}{2}$ H₂O (1 g, 2.41×10^{-3} moles) dissolved in a minimum volume of cold water. As the mixture was stirred, a greyish magenta precipitate, a-[Ni(diam)(NCS)₂]. $\frac{1}{2}$ H₂O (1.0 g, 2.26×10^{-3} moles) appeared. This was filtered off quickly and washed thoroughly with ice cold water and ethanol.

Non-protonated Tetrachlorozincate Salt

a-(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Tetrachlorozincate Dihydrate,

a-[Ni(diam)](ZnCl₄). 2H₂O

Zinc chloride (1.6 g, 1.17×10^{-2} moles) dissolved in a minimum volume^{of} cold water was added to a cold, concentrated solution of a-[Ni(diam)]Cl₂. $\frac{1}{2}$ H₂O (1 g, 2.41×10^{-3} moles). The pale lilac precipitate which appeared immediately, a-[Ni(diam)](ZnCl₄). 2H₂O (1.2 g, 2.14×10^{-3} moles) was filtered off and washed thoroughly with ice cold water followed by ethanol.

(b) COMPOUNDS OF THE b- ISOMER**Diprotanated Chloride Salt**

b-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)diaquonickel(II) Chloride Di- or Tetrahydrate, b-[Ni(diamH₂)(H₂O)₂]Cl₄. 2 or 4H₂O

The violet brown b-[Ni(diam)]Cl₂. 6H₂O which was the second isomer to be separated from the solution of hydrogenated [Ni(dini)]Cl₂ was recrystallized by dissolving in a small volume hot water to which a few drops of concentrated hydrochloric acid followed by propan-2-ol were

added. The purple product, $b\text{-Ni}(\text{diamH}_2)(\text{H}_2\text{O})_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ was washed with an ethanol/propan-2-ol mixture. When the product was recrystallized from water, the tetrahydrate salt was obtained.

Non-protonated Chloride Salt

$b\text{-(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Chloride Hexahydrate,}$

$b\text{-[Ni(diam)]Cl}_2 \cdot 6\text{H}_2\text{O}$

Recrystallizing $b\text{-[Ni(diamH}_2)(\text{H}_2\text{O})_2\text{]Cl}_4 \cdot 2\text{H}_2\text{O}$ from aqueous ammonia resulted in violet brown crystals of $b\text{-[Ni(diam)]Cl}_2 \cdot 6\text{H}_2\text{O}$.

Diprotonated Perchlorate Salt

$b\text{-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Perchlorate Di- or Hexahydrate,}$

$b\text{-[Ni(diamH}_2)](\text{ClO}_4)_4 \cdot 2 \text{ or } 6\text{H}_2\text{O}$

An excess of concentrated perchloric acid (ca. 10 cm^3) was added to $b\text{-[Ni(diamH}_2)(\text{H}_2\text{O})_2\text{]Cl}_4 \cdot 2\text{H}_2\text{O}$ (10 g, 1.88×10^{-2} moles) dissolved in a minimum volume of warm water (ca. 50°C). (*Caution; exothermic reaction!*) The orange precipitate that appeared immediately was filtered off and washed thoroughly with cold ethanol. Recrystallization of this compound from hot water acidified with concentrated perchloric acid resulted in dark orange crystals of $b\text{-[Ni(diamH}_2)](\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ (15 g, 1.83×10^{-2} moles). (Sometimes, the product crystallized from acidic solutions as the dihydrate).

Diprotonated Mixed Chloride Perchlorate Salt

b-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)diaquonickel(II) Chloride Perchlorate Monohydrate, $b-[Ni(diamH_2)(H_2O)_2]Cl_2(ClO_4)_2 \cdot H_2O$

$b-[Ni(diamH_2)(H_2O)_2]Cl_4 \cdot 2H_2O$ (2 g, 3.75×10^{-3} moles) was dissolved in hot water which was acidified by adding a few drops of concentrated perchloric acid. The pastel violet crystals of $b-[Ni(diamH_2)(H_2O)_2]Cl_2(ClO_4)_2 \cdot H_2O$ (2.3 g, 3.58×10^{-3} moles) were filtered off and washed with ice cold water and ethanol.

(When $b-[Ni(diamH_2)(H_2O)_2]Cl_4 \cdot 6H_2O$ was recrystallized from an aqueous solution of sodium perchlorate, the trihydrate of the mixed chloride perchlorate salt was obtained).

Non-protonated Perchlorate Salt

b-(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Perchlorate Sesquihydrate, $b-[Ni(diam)](ClO_4)_2 \cdot 1\frac{1}{2}H_2O$

$b-[Ni(diamH_2)(H_2O)_2]Cl_4 \cdot 2H_2O$ (2 g, 3.75×10^{-3} moles) was dissolved in hot water to which a few drops of concentrated ammonia was added. A solution of sodium perchlorate was added dropwise until crystallization commenced. The resulting pink crystals of $b-[Ni(diam)](ClO_4)_2 \cdot 1\frac{1}{2}H_2O$ (1.9 g, 3.50×10^{-3} moles) were filtered off and washed with ethanol.

Diprotonated Thiocyanate Thiocyanate Salt

b-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)dithiocyanatonickel(II) Thiocyanate Hemihydrate, $b-[Ni(diamH_2)(NCS)_2](SCN)_2 \cdot \frac{1}{2}H_2O$

$b-[Ni(diamH_2)(H_2O)_2]Cl_4 \cdot 2H_2O$ (2 g, 3.75×10^{-3} moles) was dissolved in a small volume of boiling water to which a few drops of concentrated hydrochloric acid was

added. An aqueous solution of sodium thiocyanate (1.6 g, 1.98×10^{-2} moles) was then added (dropwise). The pink product, $b\text{-}[\text{Ni}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ (2 g, 3.57×10^{-3} moles) which appeared immediately was filtered off and washed with ice cold water and ethanol.

Non-protonated Thiocyanato Compound

$b\text{-}(6, 13\text{-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane})\text{dithiocyanatonickel(II)}, b\text{-}[\text{Ni}(\text{diam})(\text{NCS})_2]$

The reaction between hot aqueous solutions of $b\text{-}[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (1 g, 2.02×10^{-3} moles) and sodium thiocyanate (0.35 g, 4.32×10^{-3} moles) yielded a greyish rose coloured precipitate of anhydrous $b\text{-}[\text{Ni}(\text{diam})(\text{NCS})_2]$ (0.8 g, 1.85×10^{-3} moles). This was filtered off and washed thoroughly with cold water, followed by ethanol.

Diprotonated Tetrachlorozincate Salt

$b\text{-}(6, 13\text{-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane})\text{nickel(II) Tetrachlorozincate Tetrahydrate}, b\text{-}[\text{Ni}(\text{diamH}_2)](\text{ZnCl}_4)_2 \cdot 4\text{H}_2\text{O}$

A mixture of concentrated hydrochloric acid (ca. 2 cm^3) and zinc chloride (1 g, 7.34×10^{-3} moles) was added to a hot aqueous solution of $b\text{-}[\text{Ni}(\text{diamH}_2)(\text{H}_2\text{O})_2]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ (2 g, 3.75×10^{-3} moles). The reddish brown crystals of $b\text{-}[\text{Ni}(\text{diamH}_2)](\text{ZnCl}_4)_2 \cdot 4\text{H}_2\text{O}$ (2.8 g, 3.53×10^{-3} moles) that appeared immediately were filtered off and washed thoroughly with cold ethanol.

Non-protonated Tetrachlorozincate Salt

$b\text{-}(6, 13\text{-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane})\text{nickel(II) Tetrachlorozincate Sesquihydrate}, b\text{-}[\text{Ni}(\text{diam})](\text{ZnCl}_4) \cdot 1\frac{1}{2}\text{H}_2\text{O}$

A concentrated aqueous solution of zinc chloride (0.29 g, 2.13×10^{-3} moles) was added to $b\text{-}[\text{Ni}(\text{diam})]\text{Cl}_2$.

$6\text{H}_2\text{O}$ (0.5 g, 1.01×10^{-3} moles) dissolved in a minimum volume of hot water. Pink fine crystals of $\text{h-}[\text{Ni}(\text{diam})]\text{-}(\text{ZnCl}_4)$. $1\frac{1}{2}\text{H}_2\text{O}$ (0.52 g, 9.44×10^{-4} moles) that appeared immediately were filtered off and washed with ethanol.

(c) COMPOUNDS OF THE c- ISOMER

The yields of the nickel salts prepared from crude $\text{c-}[\text{Ni}(\text{diamH}_2)]\text{Cl}_4$ were variable and in general, low; <20%. This estimate is based on the weight of unrecrystallized $\text{c-}[\text{Ni}(\text{diamH}_2)]\text{Cl}_4 \cdot \text{XH}_2\text{O}$. (A more accurate figure cannot be obtained because of the impure and hygroscopic nature of this material).

Diprotonated Perchlorate Salt

$\text{c-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) Perchlorate,}$

$\text{c-}[\text{Ni}(\text{diamH}_2)](\text{ClO}_4)_4$

The crude, hygroscopic $\text{c-}[\text{Ni}(\text{diamH}_2)]\text{Cl}_4 \cdot \text{XH}_2\text{O}$ (ca. 10 g) was dissolved in a small volume of boiling water or methanol. An excess of concentrated perchloric acid (ca. $2\text{-}3 \text{ cm}^3$) was added to the filtered solution. Brownish orange crystals of $\text{c-}[\text{Ni}(\text{diamH}_2)](\text{ClO}_4)_4$ were collected by slow evaporation. The product was washed with ethanol and recrystallized several times from hot water.

Diprotonated Thiocyanato Compound

$\text{c-(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)dithiocyanatonickel(II) Thiocyanate Trihydrate,}$

$\text{c-}[\text{Ni}(\text{diamH}_2)](\text{NCS})_2(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$

A concentrated solution of sodium thiocyanate (ca. 5 g) was added to a hot, filtered, aqueous or methanolic solution of crude $\text{c-}[\text{Ni}(\text{diamH}_2)]\text{Cl}_4 \cdot \text{XH}_2\text{O}$ (ca. 10 g). The addition of extra acid was not essential since the crude material contained sufficient residual acid from the h-

isomer crystallization step. Lustrous brown crystals of the formula $c\text{-}[\text{Ni}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ were collected many days later. These were washed thoroughly with ethanol and recrystallized several times from water.

Non-protonated Thiocyanato Compound

$c\text{-}(6, 13\text{-Diamino-}6, 13\text{-dimethyl-}1, 4, 8, 11\text{-tetraazacyclotetradecane})\text{dithiocyanatonickel(II) Hemihydrate,}$

$b\text{-}[\text{Ni}(\text{diam})(\text{NCS})_2] \cdot \frac{1}{2}\text{H}_2\text{O}$

When $c\text{-}[\text{Ni}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ (0.5 g, 8.26×10^{-4} moles) was recrystallized from an aqueous ammonia solution, a near quantitative yield of lustrous brown crystals of $c\text{-}[\text{Ni}(\text{diam})(\text{NCS})_2] \cdot \frac{1}{2}\text{H}_2\text{O}$ (0.35 g, 7.92×10^{-4} moles) were obtained.

Diprotonated Tetrachlorozincate Salt

$c\text{-}(6, 13\text{-Diammonio-}6, 13\text{-dimethyl-}1, 4, 8, 11\text{-tetraazacyclotetradecane})\text{nickel(II) Tetrachlorozincate,}$

$c\text{-}[\text{Ni}(\text{diamH}_2)](\text{ZnCl}_4)_2$

A solution of concentrated hydrochloric acid (ca. 2 cm³) and zinc chloride (2 g) was added to a hot aqueous solution of crude $c\text{-}[\text{Ni}(\text{diamH}_2)]\text{Cl}_4 \cdot \text{XH}_2\text{O}$ (5 g). Brownish orange crystals of $c\text{-}[\text{Ni}(\text{diamH}_2)](\text{ZnCl}_4)_2$ appeared over many months.

COPPER(II) COMPOUNDS

Diprotonated Chloride Salt

(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)copper(II) Chloride Hydrate, $[\text{Cu}(\text{diamH}_2)]\text{Cl}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$

The ligand, (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (10 g, 3.12×10^{-2} moles) was dissolved in a minimum volume of hot water to which a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (5.5 g, 3.23×10^{-2} moles) followed by a few drops of concentrated hydrochloric acid were added. The resulting deep violet crystals of $[\text{Cu}(\text{diamH}_2)]\text{Cl}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (15 g, 2.84×10^{-2} moles) were filtered off, washed with cold ethanol and recrystallized from a hot solution of dilute hydrochloric acid.

If an excess of hydrochloric acid and copper ions were present, fine brown crystals of the tetrachlorocuprate salt were obtained.

Non-protonated Chloride Salt

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)copper(II) Chloride Tetrahydrate,
 $[\text{Cu}(\text{diam})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

(Diam). $3\frac{1}{2}\text{H}_2\text{O}$ (0.5 g, 1.56×10^{-3} moles) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.27 g, 1.58×10^{-3} moles) were dissolved in a minimum volume of warm water. A few drops of concentrated ammonia followed by propan-2-ol were then added. The resulting purple precipitate of $[\text{Cu}(\text{diam})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (0.7 g, 1.5×10^{-3} moles) was filtered off, washed with ethanol and recrystallized from a dilute ammonia solution.

Diprotonated Perchlorate Salt

(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)copper(II) Perchlorate Monohydrate,

The addition of an excess of concentrated perchloric acid to a concentrated aqueous solution of $[\text{Cu}(\text{diamH}_2)]\text{Cl}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, yielded deep red crystals of $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$. These were filtered off and washed with ethanol. The same product was prepared by adding concentrated perchloric acid to (diam). $3\frac{1}{2}\text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ dissolved in a minimum volume of hot water.

Dark red crystals of the hexahydrate were obtained by recrystallizing the monohydrate from a dilute perchloric acid solution.

Diprotonated Mixed Chloride Perchlorate Salt

(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)copper(II) Chloride Perchlorate Tetrahydrate,

When $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ was recrystallized from warm dilute hydrochloric acid (ca. 0.2 mol dm^{-3}), deep violet, needle-like crystals of $[\text{Cu}(\text{diamH}_2)](\text{Cl})_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ were obtained. These were filtered off and washed with ethanol.

Non-protonated Perchlorate Salts

Several non-protonated perchlorate salts were prepared by recrystallizing $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ under basic conditions. Infrared and electronic spectra and solution properties of these compounds suggested that they were not just different hydrates of the same compound. Some of these were dark ruby coloured and others were purple or red.

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)copper(II) Perchlorate Hydrate,
 $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$

By recrystallizing $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ from a (heated or unheated) solution of sodium hydroxide or concentrated ammonia (pH ca. 14), dark ruby coloured crystals of $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ were obtained. These were filtered off and washed with ethanol.

The dihydrate of this compound was made by reacting (diam). $3\frac{1}{2}\text{H}_2\text{O}$ with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ under warm, neutral aqueous conditions and adding a few drops of propan-2ol.

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)copper(II) Perchlorate Tetrahydrate,
 $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$

When $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ was dissolved in hot water to which a few drops of ammonia was added (pH ca. 9), purple crystals of $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ were observed a few days later. These were filtered off and washed with ethanol. The same compound was obtained when the procedure was repeated with rapid isolation of the product (by dissolving the reactants in a acetone/water mixture and rotary evaporating) and when $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ was recrystallized from a dilute sodium bicarbonate solution.

Sometimes, under ammoniacal conditions, a purple perchlorate salt, most likely a diammine with (axially) coordinated ammonia, could be isolated. When this compound was washed with ethanol or exposed to the atmosphere, it rapidly turned red, indicating the loss of the ammonia. (These compounds were not characterized).

COBALT(III) COMPOUNDS

Diprotonated *trans*-Dichloro Chloride Salt

trans-(6,13-Diammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)dichlorocobalt(III) Chloride Dihydrate,
trans-[Co(diamH₂)Cl₂]Cl₃ · 2H₂O

A concentrated (aqueous or ethanolic) solution of CoCl₂·6H₂O (1.5 g, 6.31 × 10⁻³ moles) was added to (diam). 3½H₂O (1.5 g, 4.67 × 10⁻³ moles) dissolved in a minimum volume of solvent (water or ethanol). After a delay of a few minutes to permit the ligand to react with the cobalt(II) cation, concentrated hydrochloric acid (ca. 2 cm³) was added dropwise to the stirred solution, followed by a few drops of propan-2-ol. Within hours, emerald green crystals of *trans*-[Co(diamH₂)Cl₂]Cl₃ · 2H₂O (1.2-1.9 g, (2.26-3.57) × 10⁻³ moles) appeared. These were filtered off without delay, (to avoid contamination by compounds such as yellow [Co(diam)]Cl₃ and red, monoprotated, [Co(diamH)Cl]Cl₃), washed thoroughly with cold ethanol and recrystallized from hot water or a dilute hydrochloric acid solution. Using ethanol as the solvent and heating the reaction mixture minimized the formation of contaminants and improved the yield of *trans*-[Co(diamH₂)Cl₂]Cl₃. (In general, a yield of about 50 to 75% was obtained).

Monoprotated Monochloro Chloride Salt

(6-Amino-13-ammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)chlorocobalt(III) Chloride Dihydrate,
 [Co(diamH)Cl]Cl₃ · 2H₂O

From the filtrate from the preparation of green *trans*-[Co(diam)Cl₂]Cl₃ · 2H₂O, synthesized as above in water without heating, deep red crystals of [Co(diamH)Cl]Cl₃ · 2H₂O appeared over days or weeks. These were filtered off, washed with cold ethanol and recrystallized from hot

ethanol to which a few drops of water had been added. Propan-2-ol was then added or the solution was allowed to evaporated slowly to aid crystal growth. This compound could also be made by heating $[\text{Co}(\text{diam})(\text{OH})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ in hydrochloric acid (ca. 6 mol dm^{-3}). (The preparation of this hydroxo compound is discussed later). When the former method was used, the yields were low; around 10%. Much higher yields (ca. 75%) could be obtained by the latter method.

Diprotonated *trans*-Dichloro Perchlorate Salt

trans-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)dichlorocobalt(III) Perchlorate Trihydrate, $\text{trans}-[\text{Co}(\text{diamH}_2)\text{Cl}_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$

Recrystallizing $\text{trans}-[\text{Co}(\text{diamH}_2)\text{Cl}_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ from a warm, dilute perchloric acid solution yielded light green crystals of $\text{trans}-[\text{Co}(\text{diamH}_2)\text{Cl}_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$. These were filtered off and washed with ethanol.

Diprotonated *trans*-Dithiocyanato Thiocyanate Salt

trans-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)dithiocyanatocobalt(III) Thiocyanate Hydrate, $\text{trans}-[\text{Co}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$

When a concentrated solution of sodium thiocyanate (0.78 g, 9.63×10^{-3} moles) was added to green $\text{trans}-[\text{Co}(\text{diamH}_2)\text{Cl}_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (1 g, 1.88×10^{-3} moles) dissolved in a minimum volume of hot water, brownish violet crystals of $\text{trans}-[\text{Co}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (1.1 g, 1.68×10^{-3} moles) appeared. These were filtered off and washed with a mixture of ice cold water and ethanol.

Diprotonated, *cis*-Oxalato Mixed Chloride Oxalate Salt

cis-(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclo-tetradecane)oxalatocobalt(III) Chloride Oxalate Pentahydrate, *cis*-[Co(diamH₂)(C₂O₄)]Cl(C₂O₄). 5H₂O

The addition of a concentrated solution of sodium oxalate (0.32 g, 2.39×10^{-3} moles) to *trans*-[Co(diamH₂)-Cl₂]Cl₃. 2H₂O (0.5 g, 9.40×10^{-4} moles) dissolved in a minimum volume of hot water resulted in fine rose coloured crystals of *cis*-[Co(diamH₂)(C₂O₄)](C₂O₄)Cl. 5H₂O (0.55 g, 8.87×10^{-4} moles). These were filtered off and washed thoroughly with ice cold water followed by ethanol.

Diprotonated, *cis*-Diaminoethane Chloride Salt

cis-Diaminoethane-(6, 13-diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(III) Chloride Hydrate, *cis*-[Co(diamH₂)(en)]Cl₅. XH₂O (Tentative Formulation)

Diaminoethane (0.1 cm³, 3.0×10^{-3} moles) was added dropwise to *trans*-[Co(diamH₂)Cl₂]Cl₃. 2H₂O (0.1 g, 1.88×10^{-4} moles) dissolved in a hot solution of water and methanol (1:1 v/v). Brownish red crystals of *cis*-[Co(diamH₂)(en)]Cl₅. XH₂O (0.05 g) appeared after a few weeks. These were filtered off and washed with cold ethanol. (This compound was characterized by infrared spectroscopy only).

An Unusual Diprotonated Polyamino Chloride Salt

trans-(6, 13-diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)dichlorocobalt(III) Hepta-(6, 13-diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane) Chloride Hydrate Hydrochloride, *trans*-[Co(diamH₂)Cl₂](diamH₂)₇Cl₁₇. 28½HCl. 17H₂O (Tentative Formulation)

If a large quantity of propan-2-ol was added to a solution of (diam). 3½H₂O and CoCl₂. 6H₂O in a 1:1 molar

ratio, acidified with concentrated hydrochloric acid, (e.g. during the preparation of the green *trans*-dichloro complex), an extremely pale green precipitate with complex characteristic infrared and electronic spectra was obtained. This was filtered off and washed with ethanol. The elemental analysis results fitted the formula *trans*-Co[(diamH₂)Cl₂](diamH₂)₇Cl₁₇ · 28½HCl · 17H₂O. (The yield was about 30-40%). When this compound was recrystallized from a dilute hydrochloric acid solution, a slightly darker green compound (also with a characteristic infrared spectrum) was obtained.

Non-protonated Chloride Salt

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(III) Chloride Trihydrate, [Co(diam)]Cl₃ · 3H₂O

The reaction between neutral or basic aqueous solutions of (diam) · 3½H₂O (2 g, 6.23 × 10⁻³ moles) and CoCl₂ · 6H₂O (1.5 g, 6.31 × 10⁻³ moles) yielded yellow crystals of [Co(diam)]Cl₃ · 3H₂O (2.8 g, 5.86 × 10⁻³ moles), which were washed with cold ethanol. Low yields (between 20 and 50%) of the same compound were co-isolated with other products, such as *trans*-[Co(diamH₂)Cl₂]Cl₃ and [Co(diamH)Cl]Cl₃, prepared under acidic conditions.

Non-protonated, Mixed Carbonate Chloride Salt

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(III) Carbonate Chloride Hydrate
[Co(diam)]₈(CO₃)₅(Cl)₁₄ · 56H₂O

An aqueous slurry of Na₃[Co(CO₃)₃] · 3H₂O [217, 218] and the fully protonated macrocycle, (diamH₆)Cl₆ · 2H₂O in a 1:1 molar ratio was heated on a steam bath for 1 hour. The addition of propan-2-ol to this solution resulted in the precipitation of a yellow product. This was filtered

off and washed with ethanol. The compound was recrystallized by dissolving in hot water, filtering while hot and allowing to evaporate slowly. Large yellow crystals of $[\text{Co}(\text{diam})]_8(\text{CO}_3)_5(\text{Cl})_{14} \cdot 56\text{H}_2\text{O}$ were isolated in high yield.

Non-protonated Perchlorate Salt

(6-13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(III) Perchlorate Hemihydrate,

The reaction between hot, concentrated aqueous solutions of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (5 g, 1.56×10^{-2} moles) and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (5.7 g, 1.56×10^{-2} moles) to which a few drops of concentrated perchloric acid was added yielded light yellow crystals of $[\text{Co}(\text{diam})](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (9 g, 1.44×10^{-2} moles). These were filtered off and washed thoroughly with cold ethanol.

Non-protonated, Mixed Chloride Perchlorate Salt

(6-13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(III) Chloride Perchlorate,

When $[\text{Co}(\text{diam})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ was recrystallized from a perchloric acid or sodium perchlorate/ammonia solution, vivid yellow crystals of $[\text{Co}(\text{diam})](\text{ClO}_4)\text{Cl}_2$ were obtained. These were filtered off and washed with ethanol.

Non-protonated, Monohydroxo Perchlorate Salt

(6-13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)hydroxocobalt(III) Perchlorate Monohydrate,

Concentrated aqueous solutions of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (1 g, 3.12×10^{-3} moles) and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.15 g, 3.14×10^{-3} moles) were mixed and heated with stirring for approxi-

mately 15 minutes. From the hot dark orange solution, rather insoluble deep reddish orange coloured crystals of $[\text{Co}(\text{diam})(\text{OH})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ appeared. These were filtered off and washed thoroughly with water. To remove any contaminants present (such as yellow $[\text{Co}(\text{diam})](\text{ClO}_4)_3$), the orange crystals were stirred in boiling water and filtered off while hot. Under favourable conditions, the yield of $[\text{Co}(\text{diam})(\text{OH})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was around 1.20 g, 2.17×10^{-3} moles or 70%. (The addition of propan-2-ol to the filtrate resulted in crystallization of a mixture of orange $[\text{Co}(\text{diam})(\text{OH})](\text{ClO}_4)_2$ and yellow $[\text{Co}(\text{diam})](\text{ClO}_4)_3$). The optimum pH (to obtain the pure orange compound in high yield) was ca. 10, and the diam-cobalt perchlorate solution was of this pH. Under acidic ($\text{pH} < 5$) and highly basic conditions (pH ca. 14) the proportion of $[\text{Co}(\text{diam})](\text{ClO}_4)_3$ was higher (ca. 60%).

Non-protonated, Peroxo Bridged Perchlorate Salt

de-Aqua-bis(6-13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)- μ -peroxodicobalt(III) Perchlorate Trihydrate, $[(\text{H}_2\text{O})\text{Co}(\text{diam})-\text{O}_2-\text{Co}(\text{diam})(\text{H}_2\text{O})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$

To an unheated, concentrated aqueous solution of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (1 g, 3.12×10^{-3} moles), $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.14 g, 3.12×10^{-3} moles) was added with stirring. The solution was filtered to remove undissolved impurities and allowed to stand at room temperature. Dark brown crystals of $[(\text{H}_2\text{O})\text{Co}(\text{diam})-\text{O}_2-\text{Co}(\text{diam})(\text{H}_2\text{O})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (3.1 g, 2.77×10^{-3} moles) that appeared were filtered off and washed with ethanol. The filtrate appeared to contain more product.

Non-protonated, Perchlorate Salt of Unusual Colour

(6-13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(III) Perchlorate Monohydrate,
 $\text{Co}(\text{diam})(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (Tentative Formulation)

An aqueous solution of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (1 g, 3.12×10^{-3} moles), $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.14 g, 3.12×10^{-3} moles) and perchloric acid (2 mol dm^{-3} , 3.13 cm^3 , 6.25×10^{-3} moles) were stirred under nitrogen for four days. At the end of this period, a concentrated solution of sodium perchlorate followed by propan-2-ol were added dropwise. A shiny grey precipitate of the formula $\text{Co}(\text{diam})(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (1.6 g, 2.5×10^{-3} moles) was filtered off without delay and washed with ethanol. (The yield was 85%). When this compound was heated in water for a prolonged period, the yellow $[\text{Co}(\text{diam})]^{3+}$ cation was obtained.

Non-protonated Bromide Salt

(6-13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(III) Bromide Hemihydrate, $[\text{Co}(\text{diam})]\text{Br}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$

When hot, concentrated aqueous solutions of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (1 g, 3.12×10^{-3} moles) and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ (1.02 g, 3.12×10^{-3} moles) were reacted under slightly acidic or basic conditions (using a few drops of concentrated hydrobromic acid or ammonia), yellow $[\text{Co}(\text{diam})]\text{Br}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (1.6 g, 2.82×10^{-3} moles) was obtained. This was filtered off and washed thoroughly with cold ethanol.

COBALT(II) COMPOUNDSNon-protonated, Mixed Chloride Tetrachlorocobaltate (or Mixed Chloride Dioxygen Tetrachlorocobaltate) Salt

(6-13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(II) Chloride Tetrachlorocobaltate

Hexahydrate, $[\text{Co(II)(diam)}]\text{Cl}(\text{CoCl}_4)_4 \cdot 6\text{H}_2\text{O}$

or

(6-13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(II) Chloride Dioxygen Tetrachlorocobaltate Hydrate, $[\text{Co(II)(diam)}]\text{Cl}(\text{O}_2)(\text{CoCl}_4)_4 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ (Tentative Formulae)

A concentrated aqueous solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (3.7 g, 1.56×10^{-2} moles) was added to (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (3 g, 9.35×10^{-3} moles) dissolved in a minimum volume of cold water, with stirring. The mixture was allowed to stand at room temperature. Over a period of weeks, brownish red paramagnetic crystals of the formulae $[\text{Co(II)(diam)}]\text{Cl}(\text{CoCl}_4)_4 \cdot 6\text{H}_2\text{O}$ or $[\text{Co(II)(diam)}]\text{Cl}(\text{O}_2)(\text{CoCl}_4)_4 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ (1.06 g, 1.89×10^{-3} moles) appeared. These were filtered off and washed with a mixture of ice cold water and ethanol. The yield was variable and relatively low (ca. 20-40%). If the reaction mixture was heated for long periods or if propan-2-ol is added to the filtrate, yellow $[\text{Co(diam)}]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ (or a mixture of the two) was isolated.

Diprottonated Bromide Salt

(6-13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cobalt(II) Bromide Hydrate, $[\text{Co(II)(diamH}_2)]\text{Br}_4 \cdot 1$ or $2\frac{1}{2}\text{H}_2\text{O}$ (Tentative Formulation)

From concentrated aqueous or ethanolic solutions of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (0.5 g, 1.56×10^{-3} moles) and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ (0.51 g, 1.56×10^{-3} moles) acidified with an excess of concentrated hydrobromic acid (ca. 1 cm³), olive

yellow coloured $[\text{Co(II)}(\text{diamH}_2)]\text{Br}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (0.76 g, 1.16×10^{-3} moles) was obtained. (The same compound was isolated from heated and unheated solutions). This compound was filtered off and washed thoroughly with ethanol. (This was not recrystallized; the yield was *ca.* 74%). When $[\text{Co(II)}(\text{diamH}_2)]\text{Br}_4$ was heated in water (or base), the yellow $[\text{Co}(\text{diam})]^{3+}$ cation was detected in solution. When the olive yellow compound was heated in hydrochloric acid, the electronic spectrum of this solution indicated the presence of the green *trans*- $[\text{Co}(\text{diamH}_2)\text{Cl}_2]^{3+}$ cation.

Non-protonated, Mixed Bromide Tetrabromocobaltate (or Mixed Bromide, Dioxygen and Tetrabromocobaltate) Salt

(6-13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(II) Bromide Tetrabromocobaltate Tetrahydrate, $[\text{Co}(\text{diam})]\text{Br}(\text{CoBr}_4)\frac{1}{2} \cdot 4\text{H}_2\text{O}$

or

(6-13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(II) Bromide Dioxygen Tetrabromocobaltate Trihydrate, $[\text{Co}(\text{diam})]\text{Br}(\text{O}_2)(\text{CoBr}_4)\frac{1}{2} \cdot 3\text{H}_2\text{O}$ (Tentative Formulae)

From an unheated, concentrated aqueous solution of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (0.60 g, 1.87×10^{-3} moles) and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ (0.61 g, 1.87×10^{-3} moles) a brownish orange precipitate of paramagnetic $[\text{Co}(\text{diam})]\text{Br}(\text{CoBr}_4)\frac{1}{2} \cdot 4\text{H}_2\text{O}$ or $[\text{Co}(\text{diam})]\text{Br}(\text{O}_2)(\text{CoBr}_4)\frac{1}{2} \cdot 3\text{H}_2\text{O}$ (0.55 g, 8.35×10^{-4} moles) was isolated quickly by scratching the surface of the reaction vessel. This was filtered off and washed with a mixture of ice cold water and ethanol. (The addition of propan-2-ol to the filtrate caused precipitation of yellow $[\text{Co}(\text{diam})]\text{Br}_3$). (The yield of the paramagnetic species was *ca.* 45%).

CHROMIUM(III) COMPOUNDSNon-protonated Chloride Salt

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)chromium(III) Chloride Hydrate,
 $[\text{Cr}(\text{diam})]\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$

Anhydrous CrCl_3 (2 g, 1.26×10^{-2} moles) was suspended in dimethylsulphoxide (100 cm^3). To the heated reaction mixture, (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (3 g, 9.35×10^{-3} moles) was added portionwise. The resulting reddish brown solution was heated for another hour. The solution was then cooled to room temperature. The yellow product which had precipitated was filtered off and washed thoroughly with ethanol to remove all traces of dimethylsulphoxide. This was recrystallized from hot water, or an unheated dilute hydrochloric acid solution to which ethanol or propan-2-ol was added. The resulting primrose yellow crystals of $[\text{Cr}(\text{diam})]\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (4 g, 8.67×10^{-3} moles) were filtered off and washed with ethanol.

Non-protonated Mixed Chloride Perchlorate Salt

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)chromium(III) Chloride Perchlorate
 $[\text{Cr}(\text{diam})]\text{Cl}_2(\text{ClO}_4)$

When $[\text{Cr}(\text{diam})]\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ was dissolved in an unheated perchloric acid solution to which ethanol or propan-2-ol was added, yellow crystals of the mixed anionic species $[\text{Cr}(\text{diam})](\text{ClO}_4)\text{Cl}_2$ were obtained. These were filtered off and washed with ethanol. (Rapid isolation of the product is essential to avoid pendant arm protonation).

Monoprotonated Monoaquo Chloride Salt

(6-Amino-13-ammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclo-tetradecane)aquochromium(III) Chloride Trihydrate,

The recrystallization of $[\text{Cr}(\text{diam})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ from hot aqueous hydrochloric acid resulted in needle-like, reddish orange crystals of $[\text{Cr}(\text{diamH})(\text{H}_2\text{O})]\text{Cl}_4 \cdot 3\text{H}_2\text{O}$. These were filtered off, washed with ethanol and purified by recrystallization from dilute hydrochloric acid. (This reaction also took place at room temperature within days in acidic solution).

Monoprotonated Monoaquo Mixed Chloride Perchlorate Salt

(6-Amino-13-ammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclo-tetradecane)aquochromium(III) Chloride Perchlorate

The synthesis and purification procedure for $[\text{Cr}(\text{diamH})(\text{H}_2\text{O})]\text{Cl}_4$ was followed, with perchloric acid in place of hydrochloric acid. Deep orange crystals of monoprotonated $[\text{Cr}(\text{diamH})(\text{H}_2\text{O})]\text{Cl}(\text{ClO}_4)_3 \cdot 2\% \text{ or } 3\% \text{H}_2\text{O}$ were obtained.

PALLADIUM(II) COMPOUNDS

Diprotonated, Mixed Chloride Tetrachloropalladate Salt

(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)palladium(II) Chloride Tetrachloropalladate Hydrate,
 $[\text{Pd}(\text{diamH}_2)](\text{PdCl}_4)_2\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$

Palladium chloride (0.40 g , 2.26×10^{-3} moles) was refluxed in concentrated hydrochloric acid until completely dissolved, and the solution rotary evaporated to dryness. The residue was dissolved in a small volume of water and added to an aqueous solution of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (0.5 g , 1.56×10^{-3} moles). The solution was boiled for a few minutes and filtered while hot. Lustrous golden brown crystals of $[\text{Pd}(\text{diamH}_2)](\text{PdCl}_4)_2\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (0.91 g , 1.42×10^{-3} moles) were filtered off on slow cooling to room temperature, and washed with cold ethanol.

Non-protonated Mixed Chloride Tetrachloropalladate Salt

$\text{Di}[(6, 13\text{-diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane})\text{palladium(II)}]$ Chloride Tetrachloropalladate
 $[\text{Pd}(\text{diam})]_2\text{Cl}_3(\text{PdCl}_4)_2$

Recrystallization of $[\text{Pd}(\text{diamH}_2)](\text{PdCl}_4)_2\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ from an aqueous solution of ammonia resulted in pale yellow crystals of $[\text{Pd}(\text{diam})]_2\text{Cl}_3(\text{PdCl}_4)_2$. These were filtered off and washed with ethanol.

Diprotonated Perchlorate Salt

(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)palladium(II) Perchlorate Hydrate,
 $[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 5\frac{1}{2}\text{H}_2\text{O}$

When $[\text{Pd}(\text{diamH}_2)](\text{PdCl}_4)_2\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ was recrystallized from a dilute aqueous solution of perchloric acid, ivory coloured crystals of $[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ were obtained. These were filtered off and washed with ethanol.

Non-protonated Perchlorate Salt

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)palladium(II) Perchlorate Hydrate,

Recrystallization of $[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ from an aqueous ammonia solution resulted in beige coloured crystals of $[\text{Pd}(\text{diam})](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$. These were filtered off and washed with ethanol.

ZINC(II) COMPOUNDSNon-protonated Hydroxide Pentachlorodizincate Salt

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)zinc(II) Hydroxide Pentachlorodizincate Dihydrate, $[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot 2\text{H}_2\text{O}$ (Tentative Formulation)

Hot aqueous solutions of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (1 g, 3.12×10^{-3} moles) and ZnCl_2 (1 g, 7.34×10^{-3} moles) were mixed together and stirred. An immediate white precipitate of composition $[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot 2\text{H}_2\text{O}$ (1.6 g, 2.34×10^{-3} moles) appeared. This was filtered off and washed with ethanol (The yield was 75%).

Tetraprotonated, Tetrachlorozincate Salt of Diam

(6, 13-Diammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane) Tetrachlorozincate Hydrate, $(\text{diamH}_4)(\text{ZnCl}_4)_2 \cdot 4\frac{1}{2}\text{H}_2\text{O}$

Aqueous solutions of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (2 g, 6.23×10^{-3} moles) and ZnCl_2 (2 g, 1.47×10^{-2} moles) were mixed and a small volume of concentrated hydrochloric acid (ca. 0.5 cm^3) was added to this. The addition of propan-2-ol aided the formation of white crystals of the tetrachlorozincate salt of diam, $(\text{diamH}_4)(\text{ZnCl}_4)_2 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ (4.2 g, 5.61×10^{-3} moles). These were filtered off and washed with ethanol.

When $[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot 2\text{H}_2\text{O}$ was recrystallized from dilute hydrochloric acid, the same compound was obtained.

RHODIUM(III) COMPOUNDSNonprotonated Mixed Chloride Perchlorate Salt

Di[(6, 13-diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)rhodium(III)] Chloride Perchlorate Heptahydrate, $[\text{Rh}(\text{diam})]_2\text{Cl}_5(\text{ClO}_4) \cdot 7\text{H}_2\text{O}$

An aqueous or methanolic solution (ca. 50 cm³) of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (1 g, 3.12×10^{-3} moles) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1 g, 3.80×10^{-3} moles) were refluxed for about ten hours. The reddish orange solution slowly turned a yellowish brown. The small amount of metallic rhodium which appeared was filtered off. When an aqueous solution of sodium perchlorate (1.5 g, 1.22×10^{-2} moles) was added dropwise to the filtrate, a yellow precipitate appeared immediately. This compound was recrystallized by dissolving in hot water and adding perchloric acid or sodium perchlorate followed by propan-2-ol. The resulting product was a light yellow precipitate of $[\text{Rh}(\text{diam})]_2\text{Cl}_5(\text{ClO}_4) \cdot 7\text{H}_2\text{O}$ (1.7 g, 3.02×10^{-3} moles). This was filtered off and washed with ethanol. Larger crystals were difficult to achieve; the compound was not very soluble in ethanol and slow evaporation of aqueous solutions resulted in a glassy layer.

Nonprotonated, Mixed Perchlorate Tetrachlorozincate Salt

Tri[(6, 13-diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)rhodium(III)] Perchlorate Tetrachlorozincate trihydrate, $[\text{Rh}(\text{diam})]_3(\text{ClO}_4)_5(\text{ZnCl}_4)_2 \cdot 3\text{H}_2\text{O}$

When $[\text{Rh}(\text{diam})]_2(\text{ClO}_4)\text{Cl}_5 \cdot 7\text{H}_2\text{O}$ was recrystallized from an acidified aqueous tetrachlorozincate solution, a yellow precipitate of $[\text{Rh}(\text{diam})]_3(\text{ClO}_4)_5(\text{ZnCl}_4)_2 \cdot 3\text{H}_2\text{O}$ was obtained. This was filtered off and washed with ethanol.

CADMIUM(II) COMPOUNDSNon-protonated Chloride Salt

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane)cadmium(II) Chloride Dihydrate, $[\text{Cd}(\text{diam})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

Hot aqueous solutions of (diam), $3\frac{1}{2}\text{H}_2\text{O}$ (2 g, 6.23×10^{-3} moles) and cadmium chloride (1.2 g, 6.55×10^{-3} moles) were mixed and heated with stirring for ten minutes. As the solution cooled to room temperature, fine, white crystals of $[\text{Cd}(\text{diam})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (2.7 g, 5.64×10^{-3} moles) separated. These were filtered off and washed thoroughly with cold water.

Pentaprotonated Tetrachlorocadmium Salt of Diam

(6, 13-Diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane) Tetrachlorocadmium Trichloride Dihydrate, $(\text{diamH}_5)(\text{CdCl}_4)\text{Cl}_3 \cdot 2\text{H}_2\text{O}$

Recrystallization of $[\text{Cd}(\text{diam})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ from dilute hydrochloric acid resulted in colourless crystals of $(\text{diamH}_5)(\text{CdCl}_4)\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. These were filtered off and washed with ethanol.

LEAD(II) COMPOUNDSTriprotonated, Mixed Acetate Perchlorate Salt

(1, 6, 13-Triammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclo-tetradecane)lead(II) Acetate Perchlorate Hydrate

$\text{Pb}(\text{diamH}_3)(\text{CH}_3\text{COO})_3(\text{ClO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (Tentative Formulation)

A few drops of acetic acid was added to a hot aqueous solution of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (0.8 g, 2.49×10^{-3} moles); pH slightly below 7. (This was to prevent the formation of lead hydroxide when lead ions were added). An aqueous solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ (1 g, 2.64×10^{-3} moles) was then added dropwise to the ligand solution. Since slow evaporation or the addition of propan-2-ol did not result in crystal formation, a solution of sodium perchlorate was added until the solution appeared turbid. A white precipitate of composition $\text{Pb}(\text{diamH}_3)(\text{CH}_3\text{COO})_3(\text{ClO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (1.7 g, 1.87×10^{-3} moles) appeared within an hour. (A yield of 75% was obtained). This was filtered off and washed with ethanol.

Triprotonated Nitrate Salt

(1, 6, 13-Triammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclo-tetradecane)lead(II) Tetra(1, 6, 13-Triammonio-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclotetradecane) Nitrate

Octahydrate $[\text{Pb}(\text{diamH}_3)](\text{diamH}_3)_4(\text{NO}_3)_{17} \cdot 8\text{H}_2\text{O}$
(Tentative Formulation)

To an aqueous solution of (diam). $3\frac{1}{2}\text{H}_2\text{O}$ (0.5 g, 1.56×10^{-3} moles) neutralized with acetic acid (pH slightly below 7), a solution of lead nitrate (0.56 g, 1.69×10^{-3} moles) was added. A white precipitate of the formula $[\text{Pb}(\text{diamH}_3)](\text{diamH}_3)_4(\text{NO}_3)_{17} \cdot 8\text{H}_2\text{O}$ (0.53 g, 1.96×10^{-4} moles) appeared when the solution was heated. (The yield was 63%). This was filtered off and washed with ethanol.

Ni(en)₃Cl₂·2H₂O

Diaminoethane (100 cm³, 1.50 moles) was dissolved in ethanol (500 cm³). NiCl₂·6H₂O (125 g, 5.26 x 10⁻¹ moles) was added portionwise with stirring. (*Care; exothermic reaction!*) When cooled to room temperature, the purple crystalline product, [Ni(en)₃]Cl₂·2H₂O (172 g, 4.98 x 10⁻¹ moles) was filtered off and washed with ethanol.

Raney Nickel Catalyst

A modified version of the method described by Linstead et al [219] was used to prepare the Raney nickel. Sodium hydroxide pellets (32.5 g) was dissolved in water (125 cm³) in a wide mouthed conical flask fitted with a mechanical or magnetic stirrer and a thermometer. The flask was cooled in ice water. When the temperature of the solution had fallen to 50°C, the nickel-aluminium alloy (25 g) was added portionwise (1-2 g) to the rapidly stirred solution. The temperature was maintained at 50 ± 5°C. Excessive foaming during the reaction was controlled by the addition of a few drops of ethanol. When all the alloy had been added, the contents of the flask were digested at 50°C for an hour in a thermostatted water bath. Without delay, the active nickel was washed by decantation with distilled water until the washings were neutral. This was followed by washing with ethanol and finally with absolute ethanol. The catalyst was stored in a glass jar under absolute ethanol in the refrigerator. The catalyst retained activity for many months and could even be reused.

The reaction which takes place is as follows.

$\text{Ni-Al}(\text{alloy}) + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Ni}(\text{act}) + \text{Na}^+ + \text{AlO}_2^- + \frac{1}{2}\text{H}_2$
 The active nickel is a black suspension saturated with hydrogen (50-100 cm³/ g) [220].

SECTION 2.3: ELEMENTAL ANALYSES

Table 1 contains calculated values for the percentages of carbon, hydrogen, nitrogen, halogen, sulphur and metal with experimental (found) values in parentheses.

Carbon, hydrogen, nitrogen, chlorine and sulphur analyses were performed by Professor A.D. Campbell and his associates at University of Otago.

The following standard solutions ($1\text{ cm}^{-3} = 1.00\text{ mg}$ metal) were used for metal analysis by atomic absorption; nickel ; Spectrosol (BDH Limited) Nickel Nitrate
copper ; Spectrosol (BDH Limited) Cupric Nitrate
cobalt ; BDH Lab Reagent Cobaltous Nitrate
zinc ; Spectrosol (BDH Limited) Zinc Nitrate
cadmium; Spectrosol (BDH Limited) Cadmium Nitrate
lead ; Spectrosol (BDH Limited) Lead Nitrate

For chromium analyses, chromium metal (99.5%) and AR potassium chromate were used.

The oxidation states of the metals (unless stated otherwise) are as follows: Ni(II), Cu(II), Co(III), Cr(III), Pd(II), Zn(II), Rh(III), Cd(II) and Pb(II). Colours of the compounds in table 1 are described according to standards [216].

Abbreviations

HAL = halogen

rec. = recrystallized

(T) = tentative formulation

TABLE 1 : ELEMENTAL ANALYSIS

COMPOUND	CALCULATED (FOUND) %						FORMULA	COLOUR
	C	H	N	HAL	S	H		
<u>LIGAND</u>								
a- diam. 3H ₂ O	44.9	11.6	26.1	-	-	-	C ₁₂ H ₃₇ N ₆ O ₃ H	white
(cyanide method)	(45.1)	(11.7)	(26.1)	-	-	-		
b- diam. 3H ₂ O	44.9	11.6	26.1	-	-	-	C ₁₂ H ₃₇ N ₆ O ₃ H	white
(cyanide method)	(45.0)	(11.9)	(26.1)	-	-	-		
diam. 3H ₂ O	44.9	11.6	26.1	-	-	-	C ₁₂ H ₃₇ N ₆ O ₃ H	white
(acid demetallation)	(45.2)	(12.0)	(26.0)	-	-	-		
(diam ₂ H ₉)Cl ₉ . 5H ₂ O	30.8	8.5	18.0	34.2	-	-	C ₂₄ H ₇₉ N ₁₂ Cl ₉ O ₅	white
	(30.8)	(8.5)	(18.0)	(34.9)	-	-		
(diamH ₆)Cl ₆ . 2H ₂ O	28.1	7.9	16.4	41.4	-	-	C ₁₂ H ₄₀ N ₆ Cl ₆ O ₂	pale yellow
	(28.0)	(8.1)	(16.3)	(41.3)	-	-		
(diamH ₅)Cl ₃ (CdCl ₄). 1½H ₂ O	22.2	5.9	12.9	38.2	-	17.3	C ₁₂ H ₃₉ N ₆ CdCl ₇ O ₂	white
(acid rec. [Cd(diam)] ²⁺)	(22.2)	(6.2)	(12.8)	(38.3)	-	(16.9)		
(diamH ₄)(ZnCl ₄) ₂ . 4½H ₂ O	19.0	5.7	11.1	37.4	-	17.3	C ₁₂ H ₄₃ N ₆ Zn ₂ Cl ₈ O _{4½}	white
(diam + ZnCl ₂ /HCl)	(19.4)	(5.6)	(11.4)	(37.2)	-	(17.2)		
(diamH ₄)(ZnCl ₄) ₂ . 4½H ₂ O	19.0	5.7	11.1	37.4	-	17.3	C ₁₂ H ₄₃ N ₆ Zn ₂ Cl ₈ O _{4½}	white
(acid rec. [Zn(diam)] ²⁺)	(18.8)	(5.5)	(11.1)	(37.4)	-	(17.5)		
<u>NICKEL COMPOUNDS</u>								
[Ni(dini)]Cl ₂ . H ₂ O	31.6	6.0	18.4	15.5	-	12.9	C ₁₂ H ₂₇ N ₆ NiCl ₂ O _{4½}	greyish yellow
	(31.7)	(6.1)	(18.4)	-	-	-		

TABLE 1 CONTINUED

TABLE 1 CONTINUED		CALCULATED (FOUND) %						
COMPOUND	C	H	N	HAL	S	H	FORMULA	COLOUR
NICKEL COMPOUNDS								
a-[Ni(diam)]Cl ₂ . 1½H ₂ O	34.7	8.0	20.2	17.1	-	14.1	C ₁₂ H ₃₃ N ₆ NiCl ₂ O _{1½}	lilac
(made under 0.1M HCl)	(34.2)	(7.4)	(19.9)	-	-	(14.0)		
a-[Ni(diam)]Cl ₂ . 1½H ₂ O	34.7	8.0	20.2	17.1	-	14.1	C ₁₂ H ₃₃ N ₆ NiCl ₂ O _{1½}	lilac
(made under aqueous)	(34.5)	(7.5)	(20.1)	-	-	-		
a-[Ni(diamH ₂)](ClO ₄) ₄ . 2½H ₂ O	18.9 (19.0)	4.9 (4.9)	11.0 (11.4)	18.6 -	- -	7.7 (7.6)	C ₁₂ H ₃₇ N ₆ NiCl ₄ O _{18½}	yellow
a-[Ni(diam)]Cl(ClO ₄). H ₂ O	30.7 (30.8)	6.9 (7.3)	17.9 (17.9)	15.1 (15.1)	- -	12.5 -	C ₁₂ H ₃₂ N ₆ NiCl ₂ O ₅	lilac
a-[Ni(diam)](HCS) ₂ . ½H ₂ O	38.0 (38.0)	7.1 (7.1)	25.4 (25.4)	- -	14.5 -	13.3 -	C ₁₂ H ₃₁ N ₆ NiS ₂ O _½	greyish magenta
a-[Ni(diam)](ZnCl ₄). 2H ₂ O	25.7 (25.9)	6.1 (6.0)	15.0 (15.0)	25.3 (25.3)	- -	10.5 -	C ₁₂ H ₃₄ N ₆ NiZnCl ₄ O ₂	lilac
b-[Ni(diam)]Cl ₂ . 6H ₂ O	29.0 (29.0)	8.5 (8.4)	16.9 (16.9)	14.3 -	- -	11.8 (11.8)	C ₁₂ H ₄₂ N ₆ NiCl ₂ O ₆	violet brown
b-[Ni(diamH ₂)](H ₂ O) ₂ Cl ₄ . 2H ₂ O	27.0 (26.8)	7.6 (7.9)	15.8 (15.7)	26.6 -	- -	11.0 (11.0)	C ₁₂ H ₄₀ N ₆ NiCl ₄ O ₄	purple
b-[Ni(diam)H ₂](H ₂ O) ₂ Cl ₄ . 4H ₂ O	25.4 (25.5)	7.8 (7.8)	14.8 (15.1)	24.9 (24.9)	- -	10.3 -	C ₁₂ H ₄₄ N ₆ NiCl ₄ O ₆	purple
b-[Ni(diamH ₂)](ClO ₄) ₄ . 6H ₂ O	17.5 (17.5)	5.4 (5.4)	10.2 (10.2)	17.2 -	- -	7.1 (7.1)	C ₁₂ H ₄₄ N ₆ NiCl ₄ O ₂₂	dark orange

TABLE 1 CONTINUED

TABLE 1 CONTINUED		CALCULATED (FOUND) %						FORMULA	COLOUR
COMPOUND	C	H	N	HAL	S	H			
NICKEL COMPOUNDS									
b-[Ni(diamH ₂)](ClO ₄) ₄ . 2H ₂ O	19.1 (19.0)	4.8 (4.4)	11.2 (11.1)	18.8 (18.8)	-	7.8 -	C ₁₂ H ₃₆ N ₆ NiCl ₄ O ₁₈	dark orange	
b-[Ni(diamH ₂)(H ₂ O) ₂]Cl ₂ (ClO ₄) ₂ . H ₂ O	22.4 (22.5)	6.0 (6.0)	13.1 (13.1)	22.1 -	-	9.1 (9.2)	C ₁₂ H ₃₈ N ₆ NiCl ₄ O ₁₁	pastel violet	
b-[Ni(diamH ₂)(H ₂ O) ₂]Cl ₂ (ClO ₄) ₂ . 3H ₂ O	21.2 (21.2)	6.2 (6.4)	12.4 (12.4)	20.8 (20.8)	-	8.7 -	C ₁₂ H ₄₂ N ₆ NiCl ₄ O ₁₃	pastel violet	
b-[Ni(diam)](ClO ₄) ₂ . 1½H ₂ O	26.6 (26.6)	6.1 (6.1)	15.5 (15.8)	13.1 -	-	10.8 (10.7)	C ₁₂ H ₃₃ N ₆ NiCl ₂ O _{9½}	pink	
b-[Ni(diam)](ClO ₄) ₂ . H ₂ O	27.0 (27.0)	6.0 (6.4)	15.7 (15.7)	13.3 -	-	11.0 -	C ₁₂ H ₃₂ N ₆ NiCl ₂ O ₉	pink	
b-[Ni(diamH ₂)](NCS) ₂ (SCN) ₂ . ½H ₂ O	34.3 (34.6)	5.9 (6.0)	25.0 (25.1)	-	22.9 (22.3)	10.5 (10.5)	C ₁₆ H ₃₃ N ₁₆ S ₄ NiO ₄	pink	
b-[Ni(diam)](NCS) ₂	38.8 (38.6)	7.0 (7.5)	25.9 (25.9)	-	14.8 (14.4)	13.6 (13.5)	C ₁₄ H ₃₀ N ₈ S ₂ Ni	greyish rose	
b-[Ni(diamH ₂)](ZnCl ₄) ₂ . 4H ₂ O	17.9 (18.1)	5.0 (5.1)	10.4 (10.2)	35.2 (34.7)	-	7.3 (7.4)	C ₁₂ H ₄₀ N ₆ NiZn ₂ Cl ₈ O ₄	reddish brown	
b-[Ni(diam)](ZnCl ₄) ₂ . 1½H ₂ O	26.1 (25.8)	6.4 (6.3)	15.3 (15.2)	25.7 (25.9)	-	10.7 -	C ₁₂ H ₃₃ N ₆ NiZnCl ₄ O _{1½}	pink	
c-[Ni(diamH ₂)](ClO ₄) ₄	20.1 (20.2)	4.5 (4.7)	11.7 (11.7)	19.8 -	-	8.2 (8.0)	C ₁₂ H ₃₂ N ₆ NiCl ₄ O ₁₆	brownish orange	

TABLE 1 CONTINUED

CALCULATED (FOUND) %

COMPOUND	C	H	N	HAL	S	M	FORMULA	COLOUR
<u>NICKEL COMPOUNDS</u>								
c-[Ni(diamH ₂)(NCS) ₂] (SCN) ₂ · 3H ₂ O	31.8 (31.9)	6.3 (6.3)	23.1 (22.8)	-	21.2 (21.1)	9.7 (9.4)	C ₁₆ H ₃₈ N ₁₀ S ₄ NiO ₃	dark brown
c-[Ni(diam)(NCS) ₂] · 4H ₂ O	38.1 (38.3)	7.1 (7.3)	25.4 (25.3)	-	14.5 (14.4)	13.3 -	C ₁₄ H ₃₁ N ₈ S ₂ NiO ₄	dark brown
<u>COPPER COMPOUNDS</u>								
[Cu(diamH ₂)]Cl ₄ · 3H ₂ O	27.2 (27.1)	7.4 (7.1)	15.9 (15.9)	27 (28)	- -	12.0 (12.5)	C ₁₂ H ₃₉ N ₆ CuCl ₄ O ₃	deep violet
[Cu(diam)]Cl ₂ · 4H ₂ O	30.9 (30.6)	8.2 (8.4)	18.0 (18.0)	15.2 -	- -	13.6 -	C ₁₂ H ₃₈ N ₆ CuCl ₂ O ₄	purple
[Cu(diamH ₂)](ClO ₄) ₄ · H ₂ O	19.5 (19.1)	4.6 (4.3)	11.4 (11.3)	19.2 -	- -	8.6 (8.5)	C ₁₂ H ₃₄ N ₆ CuCl ₄ O ₁₇	deep red
[Cu(diamH ₂)](ClO ₄) ₄ · 6H ₂ O	17.4 (17.3)	5.3 (4.8)	10.1 (10.2)	17.1 -	- -	7.7 (7.4)	C ₁₂ H ₄₄ N ₆ CuCl ₄ O ₂₂	dark red
[Cu(diamH ₂)]Cl ₂ (ClO ₄) ₂ · 4H ₂ O	21.7 (21.7)	6.1 (6.4)	12.7 (12.8)	21.3 -	- -	9.6 (9.2)	C ₁₂ H ₄₀ N ₆ CuCl ₄ O ₁₂	deep violet
[Cu(diam)](ClO ₄) ₂ · 2H ₂ O (OH ⁻ rec. [Cu(diamH ₂)] ⁴⁺)	25.9 (25.9)	6.2 (6.3)	15.1 (15.0)	12.7 -	- -	11.4 (10.9)	C ₁₂ H ₃₄ N ₆ CuCl ₂ O ₁₀	dark ruby
[Cu(diam)](ClO ₄) ₂ · 2H ₂ O (Cu ²⁺ + diam + H ₂ O)	25.5 (25.6)	6.2 (6.2)	14.9 (14.8)	12.5 -	- -	11.2 (11.1)	C ₁₂ H ₃₅ N ₆ CuCl ₂ O ₁₀	dark ruby
[Cu(diam)](ClO ₄) ₂ · 4H ₂ O [Cu(diamH ₂)] ⁴⁺ rec. pH 9)	24.3 (24.4)	6.5 (6.5)	14.2 (14.1)	12.0 -	- -	10.72 -	C ₁₂ H ₃₅ N ₆ CuCl ₂ O ₁₀	deep violet

TABLE 1 CONTINUED

CALCULATED (FOUND) %

COMPOUND	C	H	N	HAL	S	M	FORMULA	COLOUR
COBALT COMPOUNDS								
[Co(diam)]Cl ₃ . 3H ₂ O	30.2 (30.2)	7.6 (7.3)	17.6 (17.4)	22.3 -	- -	12.3 -	C ₁₂ H ₃₆ N ₆ CoCl ₃ O ₃	greyish yellow
[Co(diam)](ClO ₄) ₃ . 2H ₂ O	23.1 (23.0)	5.0 (5.0)	13.5 (13.6)	17.0 -	- -	9.4 (9.6)	C ₁₂ H ₃₁ N ₆ CoCl ₃ O ₁₂	light yellow
[Co(diam)]Cl ₂ (ClO ₄) (from a- ligand)	29.6 (29.6)	6.2 (6.2)	17.3 (17.2)	21.8 (21.8)	- -	12.1 -	C ₁₂ H ₃₀ N ₆ CoCl ₃ O ₄	vivid yellow
[Co(diam)]Cl ₂ (ClO ₄) (from b- ligand)	29.6 (29.3)	6.2 (6.2)	17.3 (17.4)	21.8 (21.8)	- -	12.1 -	C ₁₂ H ₃₀ N ₆ CoCl ₃ O ₄	vivid yellow
[Co(diam)] ₈ Cl ₁₄ (CO ₃) ₅ . 56H ₂ O	27.9 (27.8)	8.2 (7.7)	15.5 (15.3)	11.4 (11.0)	- -	10.8 (10.6)	C ₁₀₁ H ₃₅₂ N ₄₈ Co ₈ Cl ₁₄ O ₇₁	yellow
trans-[Co(diamH ₂)Cl ₂]Cl ₃ . 2H ₂ O	27.1 (27.0)	6.8 (6.8)	15.8 (15.8)	33.3 -	- -	11.1 (11.3)	C ₁₂ H ₃₆ N ₆ CoCl ₅ O ₂	deep green
trans-[Co(diamH ₂)Cl ₂] (ClO ₄) ₃ . 3H ₂ O	19.4 (19.6)	5.2 (5.3)	11.3 (11.3)	23.9 -	- -	7.9 -	C ₁₂ H ₃₈ N ₆ CoCl ₅ O ₁₅	light green
cis-[Co(diamH ₂)(C ₂ O ₄)] Cl(C ₂ O ₄). 5H ₂ O	31.0 (30.8)	6.8 (6.3)	13.6 (13.5)	5.7 -	- -	9.5 -	C ₁₆ H ₄₂ N ₆ CoClO ₁₃	rose
trans-[Co(diamH ₂)(SCN) ₂] (SCN) ₃ . 2H ₂ O	31.2 (31.1)	5.7 (5.6)	23.6 (23.8)	- -	24.5 (23.8)	9.0 -	C ₁₇ H ₃₇ N ₁₁ S ₅ CoO ₂	brownish violet
[Co(diamH)Cl]Cl ₃ . 2H ₂ O	29.1 (29.4)	7.1 (6.9)	16.9 (16.9)	28.6 (29.0)	- -	11.9 (11.8)	C ₁₂ H ₃₅ N ₆ CoCl ₄ O ₂	deep red

check

TABLE 1 CONTINUED

CALCULATED (FOUND) %

COMPOUND	C	H	N	HAL	S	M	FORMULA	COLOUR
<u>CORALY COMPOUNDS</u>								
$[\text{Co}(\text{diamH}_2)\text{Cl}_2](\text{diamH}_2)_7$	27.7	7.7	16.2	40.5	-	1.42	$\text{C}_{96}\text{H}_{318}\text{N}_{48}\text{CoCl}_{47}\text{O}_{17}$	pale green
$\text{Cl}_{17} \cdot 20\% \text{HCl} \cdot 17\text{H}_2\text{O}$ (T)	(27.7)	(8.1)	(16.4)	(40.6)	-	(1.41)		
$[(\text{H}_2\text{O})\text{Co}(\text{diam})-\text{O}_2-\text{Co}(\text{diam})(\text{H}_2\text{O})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	25.8	6.0	15.0	12.7	-	10.5	$\text{C}_{24}\text{H}_{66}\text{N}_{12}\text{Co}_2\text{Cl}_4\text{O}_{21}$	dark brown
	(25.9)	(6.0)	(15.0)	(12.7)	-	(10.1)		
$[\text{Co}(\text{diam})(\text{OH})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	26.2	6.0	15.3	12.9	-	10.7	$\text{C}_{12}\text{H}_{33}\text{N}_6\text{CoCl}_2\text{O}_{10}$	orange red
	(26.0)	(6.2)	(15.3)	(12.9)	-	(10.3)		
$[\text{Co}(\text{II})(\text{diam})](\text{O}_2)\text{Cl}(\text{CoCl}_4)_4 \cdot 4\text{H}_2\text{O}$ or $[\text{Co}(\text{II})(\text{diam})]\text{Cl}(\text{CoCl}_4)_4 \cdot 6\text{H}_2\text{O}$ (T)	25.5	6.9	14.9	18.8	-	15.6	$\text{C}_{12}\text{H}_{39}\text{N}_6\text{Co}_1\text{Cl}_3\text{O}_6$	brownish red
	(25.5)	(6.8)	(14.8)	(18.9)	-	(15.9)		
$[\text{Co}(\text{diam})]\text{Br}_3 \cdot \text{H}_2\text{O}$	25.5	5.5	14.9	42.4	-	10.4	$\text{C}_{12}\text{H}_{31}\text{N}_6\text{CoBr}_3\text{O}_4$	yellow
	(25.2)	(5.5)	(14.8)	-	-	(10.4)		
$[\text{Co}(\text{II})(\text{diamH}_2)]\text{Br}_4 \cdot 2\text{H}_2\text{O}$ (T)	21.1	5.5	12.3	46.8	-	8.6	$\text{C}_{12}\text{H}_{37}\text{N}_6\text{CoBr}_4\text{O}_2$	olive yellow
	(21.1)	(5.4)	(12.3)	(46.8)	-	(8.4)		
$[\text{Co}(\text{II})(\text{diamH}_2)]\text{Br}_4 \cdot \text{H}_2\text{O}$	21.9	5.2	12.8	48.7	-	9.0	$\text{C}_{12}\text{H}_{34}\text{N}_6\text{CoBr}_4\text{O}$	olive yellow
	(21.9)	(5.4)	(12.9)	-	-	-		
$[\text{Co}(\text{II})(\text{diam})](\text{O}_2)\text{Br}(\text{CoBr}_4)_4 \cdot 3\text{H}_2\text{O}$ or $[\text{Co}(\text{II})(\text{diam})]\text{Br}(\text{CoBr}_4)_4 \cdot 4\text{H}_2\text{O}$ (T)	21.5	5.4	12.5	35.7	-	13.1	$\text{C}_{12}\text{H}_{36}\text{N}_6\text{Co}_1\text{Br}_3\text{O}_5$	brownish orange
	(21.8)	(5.0)	(12.6)	(35)	-	-		
$[\text{Co}(\text{diam})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (grey) (T)	22.8	5.1	13.3	16.8	-	9.3	$\text{C}_{12}\text{H}_{33}\text{N}_6\text{CoCl}_5\text{O}_8$	grey
	(22.9)	(5.1)	(13.5)	-	-	(9.3)		

TABLE 1 CONTINUED

TABLE 1 CONTINUED		CALCULATED (FOUND) %							
COMPOUND	C	H	N	HAL	S	H	FORMULA	COLOUR	
CHROMIUM COMPOUNDS									
[Cr(diam)]Cl ₃ . 2H ₂ O	31.2 (31.1)	7.6 (7.9)	18.2 (18.1)	23.0 (22.8)	-	11.3 (11.1)	C ₁₂ H ₃₅ N ₆ CrCl ₃ O ₂	primrose yellow	
[Cr(diam)]Cl ₃ . 3H ₂ O	30.7 (31.0)	7.7 (8.0)	17.9 (18.1)	22.7 (22.9)	-	11.1 (11.1)	C ₁₂ H ₃₆ N ₆ CrCl ₃ O ₃	primrose yellow	
[Cr(diam)](ClO ₄)Cl ₂	30.0 (30.3)	6.3 (6.6)	17.5 (17.5)	22.1 (22.2)	-	10.8 (10.8)	C ₁₂ H ₃₀ N ₆ CrCl ₃ O ₄	primrose yellow	
[Cr(diam)](H ₂ O)]Cl ₄ . 3H ₂ O	27.4 (27.3)	7.5 (7.7)	16.0 (15.8)	27.0 (27.4)	-	9.9 (9.9)	C ₁₂ H ₃₉ N ₆ CrCl ₄ O ₄	reddish orange	
[Cr(diam)](H ₂ O)]Cl (ClO ₄) ₃ . 3H ₂ O	19.9 (19.8)	5.5 (5.1)	11.6 (11.6)	19.5 -	-	7.1 (7.2)	C ₁₂ H ₄₀ N ₆ CrCl ₄ O ₁₆	deep orange	
[Cr(diam)](H ₂ O)]Cl (ClO ₄) ₃ . 2H ₂ O	20.4 (20.6)	5.4 (5.3)	11.9 (11.9)	20.0 (20.0)	-	7.3 (7.1)	C ₁₂ H ₃₈ N ₆ CrCl ₄ O ₁₅	deep orange	
PALLADIUM COMPOUNDS									
[Pd(diamH ₂)]Cl ₃ (PdCl ₄) ₂ . 2H ₂ O	22.5 (22.5)	5.8 (6.0)	13.1 (13.1)	27.6 (27.3)	-	24.9 -	C ₁₂ H ₃₇ N ₆ Pd ₁₂ Cl ₁₅ O ₂₂	golden brown	
[Pd(diam)] ₂ (PdCl ₄) ₂ Cl ₃	30.1 (30.3)	6.3 (6.8)	17.5 (17.5)	18.5 (18.4)	-	22.2 -	C ₂₄ H ₆₀ N ₁₂ Pd ₂ Cl ₅	pale yellow	
[Pd(diamH ₂)](ClO ₄) ₄ . 5H ₂ O	16.7 (16.7)	5.0 (4.9)	9.7 (9.7)	16.4 -	-	12.3 -	C ₁₂ H ₄₃ N ₆ PdCl ₄ O ₂₁	ivory	
[Pd(diam)](ClO ₄) ₂ . H ₂ O	25.4 (25.4)	5.4 (5.7)	14.8 (15.2)	12.5 -	-	18.7 -	C ₁₂ H ₃₀ N ₆ PdCl ₂ O ₈	beige	

TABLE 1 CONTINUED

CALCULATED (FOUND) %

COMPOUND	C	H	N	HAL	S	H	FORMULA	COLOUR
RHODIUM COMPOUNDS								
$[\text{Rh}(\text{diam})]_2\text{Cl}_5(\text{ClO}_4) \cdot 7\text{H}_2\text{O}$	25.6 (25.6)	6.6 (6.4)	14.9 (14.7)	18.9 (19.3)	-	18.3 -	$\text{C}_{24}\text{H}_{74}\text{N}_{12}\text{Rh}_2\text{Cl}_6\text{O}_{11}$	light yellow
$[\text{Rh}(\text{diam})]_3(\text{ClO}_4)_5 (\text{ZnCl}_4)_2 \cdot 3\text{H}_2\text{O}$	21.1 (21.2)	4.7 (5.3)	12.3 (12.3)	22.5 (22.9)	-	15.1 -	$\text{C}_{36}\text{H}_{96}\text{N}_{18}\text{Rh}_3\text{Cl}_{13}\text{Zn}_2\text{O}_{23}$	light yellow
ZINC COMPOUNDS								
$[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot 2\text{H}_2\text{O} (\text{T})$	21.1 (21.0)	5.2 (5.4)	12.3 (12.5)	25.9 (25.7)	-	28.7 (28.4)	$\text{C}_{12}\text{H}_{35}\text{N}_6\text{Zn}_3\text{Cl}_5\text{O}_3$	white
CADMIUM COMPOUNDS								
$[\text{Cd}(\text{diam})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	30.2 (30.5)	7.2 (7.3)	17.6 (17.6)	14.9 (15.0)	-	23.5 (23.2)	$\text{C}_{12}\text{H}_{34}\text{N}_6\text{CdCl}_2\text{O}_2$	white
LEAD COMPOUNDS								
$[\text{Pb}(\text{diamH}_3)](\text{CH}_3\text{COO})_3 (\text{ClO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O} (\text{T})$	23.8 (23.9)	5.4 (5.0)	9.3 (8.9)	7.8 (7.7)	-	22.8 (22.9)	$\text{C}_{18}\text{H}_{49}\text{N}_6\text{PbCl}_2\text{O}_{17}\frac{1}{2}$	white
$[\text{Pb}(\text{diamH}_3)](\text{diamH}_3)_4 (\text{NO}_3)_{17} \cdot 8\text{H}_2\text{O} (\text{T})$	26.6 (26.1)	6.7 (6.3)	24.4 (24.6)	-	-	7.7 (7.8)	$\text{C}_{60}\text{H}_{181}\text{N}_{47}\text{PbO}_{59}$	white

SECTION 2.4: INFRARED SPECTRA

The major infrared bands compounds of diam (Table 2), the complete list of infrared spectral bands of diam. $3\frac{1}{2}\text{H}_2\text{O}$ (Table 3), the main infrared bands of the "c-ligand" (Table 4), a comparison of the fingerprint regions of a-/b-(diamH₆)Cl₆. 2H₂O and "c-ligand" (Table 5), and a complete list of infrared spectral bands of a-, b- and c-[Ni(diam)(NCS)₂] (Table 6) are given. All bands were assigned according to [221]. Experimental details were discussed in SECTION 2.1: Instrumentation.

Anionic Stretches

<u>anion</u>	<u>IR band/cm⁻¹</u>
ClO ₄ ⁻	≈1100, 620
SCN ⁻ (ionic)	≈2050
M-SCN	≈2100
M-NCS	<2050
NO ₃ ⁻	≈1400, 850, 720
CH ₃ COO ⁻	≈1550, 1350
CO ₃ ²⁻	≈1420

Symbols Used;

+ = NH bend due to -NH₂⁺ or NH₃⁺

* = NH /OH

s = strong

sh = sharp

m = medium

w = weak

(T)= tentative formulation

The five major bands in the fingerprint region of the compounds of diam are listed in Table 2 for identification purposes.

TABLE 2: INFRARED SPECTRAL DATA OF COMPOUNDS OF DIAM

COMPOUND	NH stretch	NH bend	OH stretch	anion	fingerprint
<u>LIGAND</u>					
(diamH ₆)Cl ₆ · 2H ₂ O	3400(s, w), 3340(s), 3250(m)	1610(s), 1570(s, +), 1530(s, +)	3480(s, w)	-	1150(s, sh), 1040(s, sh), 1005(s, sh), 970(s, sh), 800(s, sh)
(diamH ₅)Cl ₃ (CdCl ₄) · 2H ₂ O	3540(s, w), 3470(s), 3330(s), 3270(m)	1625(s), 1580(s), 1540(s, +), 1515(s, w)	3540(s, w)	-	1330(s, sh), 1050(s, sh), 940(s, sh), 855(s, sh), 795(s, sh)
(diamH ₄)(ZnCl ₄) ₂ · 4H ₂ O	3060(s), 3130(s), 3270(s)	1630(m), 1610(s), 1585(m, +), 1508(s, +) 1655(m, w)	3480(s, b)	-	1090(s, sh), 960(s, sh), 945(s, sh), 895(s, sh), 855(s, sh)
<u>NICKEL COMPOUNDS</u>					
[Ni(dini)]Cl ₂ · H ₂ O	3200(s, sh), 3290(s)	1550(s, C-HO ₂ also)	3380(m, b)	-	1370(s, sh), 1340(s, sh), 1325(s, sh), 960(s, sh), 940(s, sh)
a-[Ni(diam)]Cl ₂ · 1H ₂ O	3140(s, sh), 3250(s)	1610(s)	3400(s, b)	-	1065(s, sh), 1025(s), 940(s), 920(s, sh), 900(s, sh)
a-[Ni(diamH ₂)](ClO ₄) ₄ · 2H ₂ O	3210(s), 3280(s)	1620(s, w), 1540(s, +)	3560(s, b)	1080(s, b), 625(s)	1325(w), 1300(w), 1280(w), 870(w), 720(m)
a-[Ni(diam)]Cl(ClO ₄) · H ₂ O	3170(s), 3250(s), 3340(s)	1600(m)	3530(m), 3610(s)	1085(s, b), 620(s, sh)	1320(s), 1255(m), 835(m), 785(m), 720(m)
a-[Ni(diam)(HCS) ₂] · H ₂ O	3160(s), 3195(s), 3240(s), 3340(m, sh)	1610(m)	3520(w, b)	2005(s, sh), 1100(s, sh), 1090(s, sh), 1030(s, sh), 2050(s, sh)	965(s, sh), 910(s)
a-[Ni(diam)](ZnCl ₄) · 2H ₂ O	3130(s), 3190(m), 3230(s), 3290(s)	1605(s)	3500(m, b)	-	1100(s, sh), 1015(s, sh), 975(s, sh), 965(s, sh), 900(s, sh)
b-[Ni(diam)]Cl ₂ · 6H ₂ O	3160(s)	1605(s), 1635(s, w)	3300(s, b)	-	1140(s), 1080(s), 1010(s), 985(s), 945(s)

TABLE 2 CONTINUED

COMPOUND	NH stretch	NH bend	OH stretch	anion	fingerprint
NICKEL COMPOUNDS					
b-[Ni(diamH ₂)(H ₂ O) ₂]Cl ₄ .	3190(s), 3220(s),	1640(s, r), 1625(s),	3420(s, b)	-	1320(s, sh), 1190(s), 1085(s),
2H ₂ O	3300(s)	1570(s, sh, +),			1025(s), 980(s)
		1530((s, sh, +),			
b-[Ni(diamH ₂)](ClO ₄) ₄ .	3230(s), 3410(s)	1610(s), 1550(s),	3550(s, b)	1070(s, b),	1330(s), 1200(s), 910(s), 880(m),
6H ₂ O				615(s)	790(m)
b-[Ni(diamH ₂)]Cl ₂ (ClO ₄) ₂ .	3180(s), 3215(s),	1620(s), 1535(s, +),	3550(s, b)	1075(s, b),	1350(m), 1315(m, sh), 1285(w),
3H ₂ O	3280(s, sh), 3340(s)	1498(s, +)		610(s)	905(s, sh), 855(w)
b-[Ni(diam)](ClO ₄) ₂ .	3180(s), 3280(s),	1610(s)	3540(s),	1070(s, b),	1300(m), 870(s, sh), 815(m, sh),
1½H ₂ O	3310(s)		3600(s)	615(s)	775(m, sh), 645(s)
b-[Ni(diamH ₂)](NCS) ₂	3030(m), 3080(m),	1615(w), 1490(s, +)	3500(w, b)	2054(s, sh), 1170(m),	1090(s), 1005(s),
(SCN) ₂ . ½H ₂ O	3200(m, sh), 3230(m)			2094(s, sh)	965(s, sh), 905(m)

TABLE 2 CONTINUED

COMPOUND	NH stretch	NH bend	OH stretch	anion	fingerprint
<u>NICKEL COMPOUNDS</u>					
c-[Ni(diamH ₂)](NCS) ₂ (SCN) ₂ · 3H ₂ O	3200(s, b)	1620(m), 1595(m, +), 1510(m)	3400(s, b)	2014(s), 2054(s)	1175(m), 1085(s), 1025(m), 965(s), 885(m)
c-[Ni(diam)](NCS) ₂ · 2H ₂ O	3240(s), 3290(m), 3340(s)	1590(m)	3420(w, b)	2039(s)	1095(s), 980(s, sh), 960(s, sh), 945(s, sh), 855(s)
<u>COPPER COMPOUNDS</u>					
[Cu(diamH ₂)]Cl ₄ · 3H ₂ O	3090(s), 3190(s)	1615(s, +), 1545(s, +), 1503(s, +)	3340(s, b)	-	1315(s, sh), 1180(s, sh), 1100(s, sh), 970(s, sh), 910(s, sh)
[Cu(diam)]Cl ₂ · 4H ₂ O	3190(s), 3255(s), 3310(s)	1625(m), 1600(m)	3460(s, b)	-	1300(m), 1085(m), 1060(m), 1030(w), 960(s)
[Cu(diamH ₂)](ClO ₄) ₄ · H ₂ O	3150(s), 3240(s), 3510(m, +), 3600(s)	1610(m), 1520(s, +)	3510(m, +)	1050(s, b), 605(s, sh)	1320(m, sh), 920(m, sh), 905(w, sh), 885(m, sh), 860(w, sh)
[Cu(diamH ₂)](ClO ₄) ₄ · 6H ₂ O	3150(s), 3240(s), 3520(s)	1610(s), 1535(s, +), 1520(s, +)	3600(s, b)	1050(s, b), 610(s)	1315(s, sh), 920(s, sh), 910(s, sh), 900(m, sh), 870(m, sh)
[Cu(diamH ₂)]Cl ₂ (ClO ₄) ₂ · 4H ₂ O	3150(s), 3240(s), 3500(s)	1620(s), 1530(s, sh, +)	3400(s, b)	1080(s, b), 610(s)	1320(s, sh), 1285(m), 915(w), 900(s, sh), 865(m)
[Cu(diam)](ClO ₄) ₂ · 2H ₂ O	3250(s, sh), 3340(s), 3460(s, b, +)	1635(s, +), 1615(s)	3530(s, b)	1100(s, b), 610(s)	1285(w), 1275(m), 925(s), 895(s), 795(s)
[Cu(diam)](ClO ₄) ₂ · 4H ₂ O	3250(s), 3290(m), 3340(s), 3440(s, b, +)	1610(s), 1685(s, H-H?)	3440(b, +) 3610(s, ?)	1090(s, b), 615(s)	1310(m), 1270(w), 1200(m), 900(m), 875(m)
<u>COBALT COMPOUNDS</u>					
[Co(diam)]Cl ₃ · 3H ₂ O	3030(s), 3120(s, b), 3390(s)	1610(s, +), 1580(s)	3460(s, b)	-	1240(s), 1100(s), 1055(s), 1040(s), 995(s)

TABLE 2 CONTINUED

COMPOUND	NH stretch	NH bend	OH stretch	anion	fingerprint
<u>CORALY COMPOUNDS</u>					
$[\text{Co}(\text{diam})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$	3240(s), 3160(m)	1595(s, sh)	3550(w, b)	1065(s, b), 1275(m), 1250(m), 1210(s), 830(m), 600(s, sh) 810(m)	
$[\text{Co}(\text{diam})](\text{ClO}_4)\text{Cl}_2$	3260(s), 3100(s), 3020(s)	1610(s, sh)	-	1100(s, b), 1260(m, sh), 1235(s, sh), 930(m, sh), 620(s, sh) 855(m, sh), 830(w, sh)	
$[\text{Co}(\text{diam})]_8(\text{CO}_3)_5\text{Cl}_{14} \cdot 56\text{H}_2\text{O}$	3050(s, b)	1615(s, +)	3340(s, b)	1420(s, b) 1220(s), 1125(s), 1070(m), 1050(s), 1000(s)	
<i>trans</i> - $[\text{Co}(\text{diamH}_2)\text{Cl}_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$	3120(s), 3200(m), 3390(s)	1615(m, +), 1595(m), 1545(s, +), 1490(s, +)	3460(s, +)	-	1345(m, sh), 1110(s, sh), 1075(s, sh), 1035(s, sh), 1020(s, sh)
<i>trans</i> - $[\text{Co}(\text{diamH}_2)\text{Cl}_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	3140(s), 3220(s), 3300(m, sh)	1610(s, +), 1525(s, +)	3530(s), 3600(s)	1100(s, b), 1345(m, sh), 1325(m, sh), 900(m, sh), 615(s) 875(m, sh), 850(m, sh)	
<i>cis</i> - $[\text{Co}(\text{diamH}_2)(\text{C}_2\text{O}_4)](\text{C}_2\text{O}_4)\text{Cl} \cdot 5\text{H}_2\text{O}$	3170(m), 3080(m)	1640(s), 1515(s, +)	3400(s, b)	1720(s)	1215(s), 1125(s), 1040(s), 1030(s), 720(s)
<i>cis</i> - $[\text{Co}(\text{diamH}_2)(\text{en})]\text{Cl}_5 \cdot 2\text{H}_2\text{O}$ (T)	3080(s, b), 3170(s)	1620(s), 1460(s, b, +)	3350(s, b)	-	1160(s), 1135(s), 1055(s), 1010(m), 850(m)
<i>trans</i> - $[\text{Co}(\text{diamH}_2)(\text{SCN})_2](\text{SCN})_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	3060(m), 3100(w)	1605(m), 1545(m, +)	3415(m)	2054(s)	1150(m), 1120(s), 1075(m), 1035(s), 840(m)
$[\text{Co}(\text{diamH})\text{Cl}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$	3320(m), 3140(s)	1650(m), 1610(s), 1530(m, +)	3450(m, +)	-	1110(s), 1070(s), 1055(m), 1040(s), 990(m)
$\text{Co}[(\text{diamH}_2)\text{Cl}_2](\text{diamH}_2)_7\text{Cl}_{17} \cdot 20\frac{1}{2}\text{HCl} \cdot 17\text{H}_2\text{O}$ (T)	3330(s), 3260(m), 3100(m)	1645(s), 1620(s), 1585(s, +), 1550(s, +), 1530(s, +)	3400(s, +)	-	1335(s), 1120(s), 1055(s), 950(s), 860(s)

TABLE 2 CONTINUED

COMPOUND	NH stretch	NH bend	OH stretch	anion	fingerprint
<u>COPALY COMPOUNDS</u>					
$[(H_2O)Co(diam)-O_2-Co$ $(diam)(H_2O)](ClO_4)_4.$ H_2O	3100(m), 3160(m), 3240(m), 3280(s), 3330(m)	1630(m, s), 1610(m)	3550(m, b)	1080(s, b), 620(s, sh)	1275(m), 1205(m), 940(m), 920(m), 890(m)
$[Co(diam)(OH)](ClO_4)_2.$ H_2O	3120(s), 3240(s), 3360(m, sh)	1605(s, s)	3550(s, b) 3595(s, sh)	1070(s, b), 610(s, sh)	1245(m), 1210(m), 930(s), 870(w), 840(m)
$[Co(II)(diam)](O_2)Cl$ $(CoCl_4)_4. 4H_2O$ or $[Co(II)(diam)]Cl(CoCl_4)_4.$ $6H_2O$ (T)	3150(s), 3050(s)	1620(m, s), 1605(s)	3440(s, b)	-	1215(m), 1110(m), 1095(m), 1065(s), 980(s)
$[Co(diam)](ClO_4)_3. 4H_2O$ (grey) (T)	3130(s), 3240(s)	1610(s)	3580(m, b, s)	1100(s, b), 612(s, sh)	1255(w), 1225(w), 840(w), 795(w), 715(w)
$[Co(diam)]Br_3. 4H_2O$	3025(s), 3100(s)	1605(s, sh)	3440(m, b)	-	1235(s, sh), 1100(s, sh), 1065(s, sh), 1040(s, sh), 1000(m, sh)
$[Co(II)(diamH_2)]Br_4.$ $2H_2O$ (T)	3100(s), 3230(m), 3370(s, s)	1610(m), 1530(m, +), 1490(s, +)	3370(s, s)	-	1315(m, sh), 1100(s, sh), 1020(s, sh), 1005(s, sh), 960(m, sh)
$[Co(II)(diamH_2)]Br_4. H_2O$ (T)	3090(s), 3130(m)	1615(w, s), 1605(m), 1550(s, +)	3420(w, b)	-	1110(s, sh), 1075(m, sh), 1040(s, sh), 1025(s, sh), 980(m, sh)
$[Co(II)(diam)](O_2)Br$ $(CoBr_4)_4. 3H_2O$ or $[Co(II)(diam)]Br(CoBr_4)_4.$ $4H_2O$ (T)	3050(s), 3130(s), 3210(s)	1600(s)	3400(s, b)	-	1240(m, sh), 1105(s, sh), 1090(m), 1065(s), 975(m, sh)
<u>CHROMIUM COMPOUNDS</u>					
$[Cr(diam)]Cl_3. 2H_2O$	3420(s), 3310(s), 3210(s)	1645(m, s), 1610(s, sh)	3080(s, b)	-	1225(s, sh), 1155(s, sh), 1080(s, sh), 1040(s, sh), 1020(s, sh)

TABLE 2 CONTINUED

COMPOUND	NH stretch	NH bend	OH stretch	anion	fingerprint
<u>CHROMIUM COMPOUNDS</u>					
$[\text{Cr}(\text{diam})](\text{ClO}_4)\text{Cl}_2$	3250(s, sh), 3200(s) 3150(m)	1615(s, sh)	-	1110(s, b), 1225(s, sh), 985(s, sh), 975(s, sh), 625(s, sh) 845(m, sh), 520(m, sh)	
$[\text{Cr}(\text{diamH})(\text{H}_2\text{O})]\text{Cl}_4 \cdot 3\text{H}_2\text{O}$	3070(s), 3170(s)	1630(s, v), 1605(s), 1545(s, +)	3350(b, s)	-	1230(s, sh), 1085(s, sh), 1030(s), 1010(s), 850(s)
$[\text{Cr}(\text{diamH})(\text{H}_2\text{O})](\text{ClO}_4)_3$	3260(s), 3200(w)	1625(s, v), 1605(s)	3540(s, b)	1060(s, b)	1325(m, sh), 1235(m), 845(s, sh),
$\text{Cl} \cdot 2\text{H}_2\text{O}$	3070(s)	1530(s, +)		610(s, sh)	815(m), 750(m)
<u>PALLADIUM COMPOUNDS</u>					
$[\text{Pd}(\text{diamH}_2)]\text{Cl}_3(\text{PdCl}_4)_4 \cdot 2\text{H}_2\text{O}$	3150(s), 3430(s) 3480(m)	1625(m, v), 1600(m), 1510(s, +)	3560(m)	-	1180(m), 1160(w), 1120(m), 1070(m), 1030(s)
$[\text{Pd}(\text{diam})]_2\text{Cl}_3(\text{PdCl}_4)$	3400(s), 3240(s) 3070(s)	1610(s), 1640(s)	-	-	1285(m, sh), 1270(m, sh), 1070(s, sh), 1055(s, sh), 940(m, sh)
$[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 5\text{H}_2\text{O}$	3240(s), 3400(s, b, v)	1610(s), 1545(s, +)	3540(s, b)	1080(s, b), 610(s)	1410(m, sh), 1330(w, sh), 1320(m, sh), 890(m, sh), 865(m, sh)
$[\text{Pd}(\text{diam})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	3170(s), 3240(s), 3310(s), 3360(s)	1610(s)	3630(w)	1085(s, b), 620(s)	1350(m), 1320(s), 1265(m), 1205(m), 800(s)
<u>ZINC COMPOUNDS</u>					
$[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot 2\text{H}_2\text{O}$	3110(s), 3280(s), 3245(s)	1583(m), 1605(m, v)	3590(m), 3400(m, b)	-	1085(s, sh), 1060(s, sh), 1045(s, sh), 965(s, sh), 945(s, sh)
<u>CADMIUM COMPOUNDS</u>					
$[\text{Cd}(\text{diam})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	3390(s), 3350(s), 3310(s), 3250(s)	1595(s), 1630(s, v)	3430(s, b)	-	1135(s, sh), 1085(s, sh), 1045(s, sh), 1015(s, sh), 885(s, sh)

TABLE 2 CONTINUED

COMPOUND	NH stretch	NH bend	OH stretch	anion	fingerprint
<u>LEAD COMPOUNDS</u>					
$[\text{Pb}(\text{diamH}_3)](\text{CH}_3\text{COO})_3$	3290(s), 3340(m)	1600(m, +), 1580(s),	3530(m, b)	1070(s, b), 1220(s), 900(s), 850(s), 800(s),	
$(\text{ClO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (T)		1560(s, b, +, $\text{C}_2\text{H}_3\text{O}_2^-$)		615(s)	660(s)
				1320(s)	
				1335(s)	
$[\text{Pb}(\text{diamH}_3)](\text{diamH}_3)_4$	3295(s, sh), 3050(s)	1615(s), 1510(s, +)	3500(w, b)	1390(s), 1100(s, sh), 960(s, sh), 950(s, sh),	
$(\text{NO}_3)_{17} \cdot 8\text{H}_2\text{O}$ (T)				850(s, sh), 900(s), 820(s, sh)	
				720(w)	
<u>RHODIUM COMPOUNDS</u>					
$[\text{Rh}(\text{diam})]_2\text{Cl}_5(\text{ClO}_4) \cdot 7\text{H}_2\text{O}$	3100(s, b)	1600(s)	3370(s, b)	1150(m)	1300(w), 1220(w), 1500(w), 970(m), 800(w)
$[\text{Rh}(\text{diam})]_3(\text{ClO}_4)_5$	3290(s), 3190(s)	1600(s)	3400(s, b)	1085(s, b), 1300(w), 1225(w), 970(m), 835(w),	
$(\text{ZnCl}_4)_2 \cdot 3\text{H}_2\text{O}$				620(s)	715(m)

Table 3: Infrared Spectral Bands of (diam). $3\frac{1}{2}\text{H}_2\text{O}$

ASSIGNMENT	FREQUENCY (cm^{-1})
NH stretch	3440(s), 3370(s), 3240(s, b, +)
OH stretch	3260(s, b, +)
CH stretch	2955(m), 2920(m), 2860(m), 2810(m)
NH bend	1585(m), 1615(w)
OH bend	1675(m)
CH bend	1460(s) 1380(m)
Fingerprint	1335(m), 1315(m), 1295(w), 1235(m), 1190(w), 1155(s, sh), 1120(s, sh), 1100(s), 1060(w), 1035(w), 990(s), 955(s), 930(s), 905(m), 885(w), 865(s), 815(s), 775(s)

Table 4: The Main Infrared Bands of "c- Ligand"

NH stretch	3490(s), 3300(s) [split, b]
NH bend	1605(s), 1590(s), 1565(s, +), 1540(s, +)

Table 5: A Comparison of the Fingerprint Regions of a-/b-
(diamH₆)Cl₆. 2H₂O and "c- ligand"

** denotes major differences (in cm⁻¹)

a-/b-	c-
1320(s) **	1330(m) **
1310(s)	1310(m)
1290(s)	1290(m)
	1275(w) **
1245(s)	1245(w)
1215(s)	1220(m)
1190(m)	
	1170(m, doublet) **
1150(s)	1150(m)
1085(w) **	
	1070(w) **
1050(s)	1045(s)
1035(s)	
1025(m)	1020(w)
1000(s)	1000(s)
	980(w) **
965(s)	965(w)
935(m)	930(m)
905(m)	910(w)
	870(m) **
860(m)	
	845(w, doublet) **
830(m)	830(w)
785(s)	785(s)
	780(m) **
750(w)	750(w)

Table 6: A Complete List of Infrared Spectral Bands of
a-, b- and c-[Ni(diam)(NCS)₂]

ASSIGNMENT	FREQUENCY (cm ⁻¹)		
	a-	b-	c-
NH stretch	3340 (m, sh)		3340 (s)
		3290 (s)	3290 (m)
		3270 (s)	
	3240 (s)		3240 (s)
		3230 (s)	
	3195 (s)		
		3180 (s)	
	3160 (s)		
NH bend	1610 (m)	1610 (s, sh)	1590 (m)
CN stretch	2065 (s, sh)		2055 (s)
	2020 (s, sh)	2030 (s, sh)	
OH stretch	3520 (w, b)	-	3420 (w, b)
Fingerprint		1435 (s, sh)	
	1400 (w, sh)		
		1375 (s, sh)	
		1365 (s, sh)	
			1350 (m)
	1330 (w)	1330 (m)	
	1320 (m, sh)		1320 (s)
	1310 (w)	1300 (m)	
		1275 (m)	1280 (m)
	1265 (m)	1260 (w)	1263 (m)
	1255 (m)		
	1225 (w)		
	1215 (w)	1210 (w)	

Table 6 Continued

<u>ASSIGNMENT</u>	<u>a-</u>	<u>b-</u>	<u>c-</u>
Fingerprint	1185(s)	1185(m, sh)	1180(m)
	1145(m)	1145(s, sh)	
		1125(s)	
		1110(m)	
	1100(s, sh)		1095(s)
	1090(s, sh)	1080(s, sh)	
	1065(s, sh)		1058(s)
	1050(m)		
	1030(s, sh)		1020(m)
	995(m)	1005(s)	
	990(m)		980(s, sh)
	965(s, sh)		
	960(s, sh)	955(m)	960(s, sh)
	940(s, sh)	940(s, sh)	945(s, sh)
		930(s, sh)	
		920(s, sh)	925(s, sh)
	910(s)		905(s, sh)
		890(w)	895(s)
	880(s)		
	875(m)	870(s, sh)	
			855(s)
	830(m, sh)	830(w)	
		815(m)	
	785(m, sh)	780(w)	785(m)
	775(m, sh)		775(s)
	745(m, sh)	740(w)	
		730(w)	
		715(w)	715(m)
		675(m)	

SECTION 2.5: ELECTRONIC SPECTRA

The electronic spectra of fresh aqueous solutions of the metal complexes of diam were measured at 25°C (unless stated otherwise).

Table 7 contains the electronic spectral data for the nickel, copper, cobalt, chromium, palladium, zinc and rhodium complexes of diam. Absorption maxima ($\lambda_{\max}$) are in nanometers and molar absorptivities (ϵ) shown in parentheses are in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.

Symbols Used;

sh = shoulder

b = broad

*d = doublet

W/A = water/acetone mixture

(T) = tentative formulation

TABLE 7: ELECTRONIC SPECTRA OF METAL COMPLEXES OF DIAM

COMPOUND	$\lambda_{\max}/\epsilon (\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$
<u>COMPOUNDS OF NICKEL</u>	
a-[Ni(diam)]Cl ₂ . 1½H ₂ O	328(4), 494(5), 586(3, b), 685(3, b), 925(4), 974(4, b)
a-[Ni(diamH ₂)](ClO ₄) ₄ . 2½H ₂ O	191, 326(7), 453(9), 692(2), 910(2), 990(2)
a-[Ni(diam)]Cl(ClO ₄). H ₂ O	326(15.8), 491(10.6), 575(7.3, b), 678(6.5, b)
a-[Ni(diam)(SCN) ₂]. ½H ₂ O	264, 494(10), 800(11), 971(22), 1180(56) (W/A)
a-[Ni(diam)](ZnCl ₄). 2H ₂ O	325(15), 487(9.5), 580(6.4, b), 682(5.7, b)

TABLE 7 CONTINUED

COMPOUND	$\lambda_{\max}/\mu\text{m}(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$
<u>COMPOUNDS OF NICKEL</u>	
b-[Ni(diam)]Cl ₂ . 6H ₂ O	315(5), 485(5), 790(4.8), 860(3.6, sh)
b-[Ni(diamH ₂)(H ₂ O) ₂] Cl ₄ . 2H ₂ O	340(10.6), 513(6), 665(3), 1123(1.7, b) & 1167(1.6, b) *d, 1260(1.2, b, sh)
b-[Ni(diamH ₂)](ClO ₄) ₄ . 6H ₂ O	335(10), 506(6), 666(3), 1069(1.2, b, sh), 1158(1.4, b, sh), 1260(0.5, b, sh)
b-[Ni(diam)](ClO ₄) ₂ . H ₂ O	315(5.5), 485(5.9), 780(5.5, b)
b-[Ni(diamH ₂)(NCS) ₂]	485(5), 770(6, b), 960(4, b), 1155(4, b)
b-[Ni(diamH ₂)](NCS) ₄ . ½H ₂ O	214(17400, sh), 326(16), 497(11.5) 264, 495(12), 780(10), 972(26), 1183(52) (W/A)
b-[Ni(diam)]ZnCl ₄ . 1½H ₂ O	316((11.6), 486(10.4), 780(9, b)
c-[Ni(diamH ₂)](ClO ₄) ₄	194, 330, 460, 640 (50°C)
c-[Ni(diamH ₂)(NCS) ₂] (SCN) ₂ . 3H ₂ O	215(17200, sh), 321(90), 489(29.5)

TABLE 7 CONTINUED

COMPOUND	$\lambda_{\max}(\text{nm})(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$
<u>COMPOUNDS OF COPPER</u>	
$[\text{Cu}(\text{diamH}_2)]\text{Cl}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$	251(7050), 527(75)
$[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	250(7060), 520(65)
$[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	253(6660), 508(87)
<u>COMPOUNDS OF COBALT</u>	
$[\text{Co}(\text{diam})](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	214(20500), 322(94), 448(74)
$[\text{Co}(\text{diam})](\text{ClO}_4)\text{Cl}_2$	214(19800), 329(69), 449(70)
$[\text{Co}(\text{diam})]_8\text{Cl}_{14}(\text{CO}_3)_5 \cdot 56\text{H}_2\text{O}$	214(18100), 323(75), 448(66)
<i>trans</i> - $[\text{Co}(\text{diamH}_2)]\text{Cl}_5 \cdot 2\text{H}_2\text{O}$	226(17800), 379(50, sh), 440(34, sh), 620(32.6)
<i>trans</i> - $[\text{Co}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	219(23300, sh), 320(3200, b), 533(370)
$[\text{Co}(\text{diamH})\text{Cl}_4 \cdot 2\text{H}_2\text{O}$	224(17100), 354(100), 445(45, sh), 520(73)
$[\text{Co}(\text{diamH}_2)\text{Cl}_2(\text{diamH}_2)_7\text{Cl}_{17} \cdot 28\frac{1}{2}\text{HCl} \cdot 17\text{H}_2\text{O} \text{ (T)}$	230(13900) & 249(14150) *d, 311(1600), 378(42, sh), 438(32, sh), 620(25.5)

TABLE 7 CONTINUED

COMPOUND	$\lambda_{\max}/m(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$
<u>COMPOUNDS OF COBALT</u>	
$[(\text{H}_2\text{O})\text{Co}(\text{diam})-\text{O}_2-\text{Co}]$ $(\text{diam})(\text{H}_2\text{O})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	217(32400), 300(8800, sh), 420(720, sh)
$[\text{Co}(\text{diam})(\text{OH})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	223(8450), 363(90), 483(76)
$[\text{Co}(\text{II})(\text{diam})](\text{O}_2)\text{Cl}$ $(\text{CoCl}_4)_\frac{1}{2} \cdot 4\frac{1}{2}\text{H}_2\text{O}$ or $[\text{Co}(\text{II})(\text{diam})]\text{Cl}$ $(\text{CoCl}_4)_\frac{1}{2} \cdot 6\text{H}_2\text{O} (\text{T})$	217(13700), 354(92), 485(67)
$[\text{Co}(\text{diam})]\text{Br}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	191(44100), 220(17900, sh), 328(70), 450(69)
$[\text{Co}(\text{II})(\text{diamH}_2)]\text{Br}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O} (\text{T})$	228(10100, sh), 374(463), 524(21, sh)
$\text{Co}(\text{diam})(\text{ClO}_4)_3 \cdot 1\text{H}_2\text{O} (\text{grey}) (\text{T})$	220(12900), 304(6600), 390(800, sh)
<i>cis</i> - $[\text{Co}(\text{diamH}_2)(\text{C}_2\text{O}_4)]\text{Cl}(\text{C}_2\text{O}_4) \cdot 5\text{H}_2\text{O}$	237, 300(sh), 447(35), 550(60)
<u>COMPOUNDS OF CHROMIUM</u>	
$[\text{Cr}(\text{diam})]\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	335(44), 429(50), 500(16, sh)
$[\text{Cr}(\text{diamH})]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$	340(34, sh), 406(43, b), 480(26, sh)
$[\text{Cr}(\text{diamH})]\text{Cl}(\text{ClO}_4)_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$	339(36, sh), 408(46, b), 480(26, sh)

TABLE 7 CONTINUED

COMPOUND	$\lambda_{\max}(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$
<u>COMPOUNDS OF PALLADIUM</u>	
$[\text{Pd}(\text{diamH}_2)](\text{PdCl}_4)\frac{1}{2}$ $\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	195(18600, sh), 391(640)
$[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot$ $5\frac{1}{2}\text{H}_2\text{O}$	200(20900), 276(480)
<u>COMPOUNDS OF ZINC</u>	
$[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot$ $2\text{H}_2\text{O} \text{ (T)}$	247(140)
<u>COMPOUNDS OF RHODIUM</u>	
$[\text{Rh}(\text{diam})](\text{ClO}_4)\frac{1}{2}\text{Cl}_2\frac{1}{2} \cdot$ $3\frac{1}{2}\text{H}_2\text{O}$	207(30500), ≈ 340 (sh)

SECTION 2.6: MAGNETIC DATA

The magnetic susceptibilities of selected nickel, copper, cobalt, chromium and palladium complexes of diam were measured at 25°C, using the Faraday Method.

Table 8 lists the molar susceptibility (X_m), the diamagnetic component (X_d), paramagnetic component (X_p) the effective magnetic moment (μ_{eff}) assuming Curie Law and the number of unpaired electrons (n).

$Hg[Co(NCS)_4]$ ($X_g = 16.44 \times 10^{-6} \text{ emu g}^{-1}$) was used to calibrate the magnetic susceptibility apparatus.

CGS units are used in the calculations; X_D values are in emu g-ion^{-1} [222(a)] and μ_{eff} values are in Bohr magnetons, μ_B ($1 \mu_B = 9.274 \times 10^{-24} \text{ Am}$) [222(b)].

TABLE 8: MAGNETIC DATA FOR SELECTED DIAM COMPLEXES

COMPOUND	$X_m/10^{-3}$	$-X_D/10^{-6}$	$X_P/10^{-3}$	μ_{eff}/μ_B	n
<u>NICKEL COMPOUNDS</u>					
$a-[Ni(diam)]Cl_2 \cdot 1\frac{1}{2}H_2O$	3.81	278	4.89	3.12	2
$a-[Ni(diam)_2](ClO_4)_4 \cdot 2\frac{1}{2}H_2O$	-0.346	383	0.037	0.3	0
$b-[Ni(diam)_2](H_2O)_2]Cl_4 \cdot 2H_2O$	3.47	375	3.85	3.03	2
$c-[Ni(diam)_2](NCS)_2](SCN)_2 \cdot 3H_2O$	3.74	395	4.14	3.14	2
<u>COPPER COMPOUNDS</u>					
$[Cu(diam)_2]Cl_4 \cdot 3\frac{1}{2}H_2O$	1.08	366	1.44	1.85	1
$[Cu(diam)_2](ClO_4)_4 \cdot 6H_2O$	0.938	430	1.38	1.81	1
$[Cu(diam)](ClO_4)_2 \cdot 2H_2O$	1.066	301	1.37	1.81	1
<u>COBALT COMPOUNDS</u>					
$[Co(diam)](ClO_4)_3 \cdot H_2O$	-0.170	310	0.140	0.58	0
$trans-[Co(diam)_2]Cl_2]Cl_3 \cdot 2H_2O$	-0.221	367	0.146	0.59	0
$trans-[Co(diam)_2](NCS)_2](SCN)_3 \cdot 2\frac{1}{2}H_2O$	-0.294	420	0.126	0.55	0
$[Co(diam)Cl]Cl_3 \cdot 2H_2O$	0.232	330	0.570	1.17	0
$[Co(diam)_2]Cl_2](diam)_2]_7Cl_{17} \cdot 28\frac{1}{2}H_2O$	-2.61	3163	0.553	1.15	0

$17H_2O$ (7)

TABLE 8 CONTINUED

COMPOUND	$\chi_M/10^{-3}$	$-\chi_D/10^{-6}$	$\chi_P/10^{-3}$	μ_{eff}/μ_B	n
<u>COBALT COMPOUNDS</u>					
$[(H_2O)Co(diam)-O_2-Co(diam)(H_2O)](ClO_4)_4 \cdot H_2O$	-0.449	607	0.158	0.61	0
$[Co(diam)(OH)](ClO_4)_2 \cdot H_2O$	-0.157	296	0.139	0.58	0
$[Co(II)(diam)](O_2)Cl(CoCl_4)_4$ $4H_2O$ or $[Co(II)(diam)]Cl(CoCl_4)_4$ $6H_2O$ (T)	6.37	382	6.75	4.01	3
$[Co(diam)]Br_3 \cdot 2H_2O$	-0.240	316	0.076	0.43	0
$[Co(II)(diam)_2]Br_4 \cdot 2H_2O$	1.37	367	1.74	2.04	1
$[Co(II)(diam)](O_2)Br(CoBr_4)_4 \cdot 3H_2O$ or $[Co(II)(diam)]Br(CoBr_4)_4 \cdot 4H_2O$ (T)	6.53	388	6.92	4.06	3
$Co(diam)(ClO_4)_3 \cdot 2H_2O$ (grey) (T)	-0.392	316	-0.076	0	0
<u>CHROMIUM COMPOUNDS</u>					
$[Cr(diam)]Cl_3 \cdot 3H_2O$	6.18	327	6.51	3.94	3
$[Cr(diam)](ClO_4)Cl_2$	6.00	287	6.29	3.87	3
$[Cr(diam)](H_2O)]Cl_4 \cdot 3H_2O$	5.88	371	6.25	3.86	3
$[Cr(diam)](H_2O)]Cl(ClO_4)_3 \cdot 3H_2O$	5.96	403	6.36	3.89	3
<u>PALLADIUM COMPOUNDS</u>					
$[Pd(diam)_2](ClO_4)_4 \cdot 5H_2O$	-0.375	444	0.069	0.41	0

SECTION 2.7: ^1H and ^{13}C Nuclear Magnetic Resonance Data of Compounds of Diam

Instrumentation and experimental conditions were discussed in SECTION 2.1: INSTRUMENTATION. D_2O was used as the solvent for ^1H and ^{13}C nuclear magnetic resonance spectra, unless stated otherwise. Reference [221] was used to assign all ^1H and ^{13}C resonances according to the atom designation in figure 20.

^1H NMR DATA

Tetramethylsilane (TMS) was used as the internal reference.

Table 9 contains the ^1H NMR data for the ligand (diam). $3\frac{1}{2}\text{H}_2\text{O}$ and selected complexes of cobalt, zinc and rhodium. The chemical shifts (δ) are in ppm (and in Hertz within parentheses). The number of protons in each peak (n) was calculated by integration.

^{13}C NMR DATA

Chemical shifts are reported relative to TMS using dioxane as an internal reference.

Table 10 contains the ^{13}C NMR data for the ligand (diam). $3\frac{1}{2}\text{H}_2\text{O}$ and selected complexes of cobalt and zinc. The chemical shifts (δ) are in ppm (and in Hertz within parentheses).

Symbols Used

(B) = broad

(T) = tentative formulation

Figure 20: Atom designation for ^1H and ^{13}C nuclear magnetic resonance spectra

TABLE 9: ^1H NMR DATA OF SELECTED COMPOUNDS OF DIAM

Compound	δ/ppm (Hz)	Assignment	n
a-(diam). $3\frac{1}{2}\text{H}_2\text{O}$ (CDCl_3)	2.66 (212.07)	b	8
	2.54 (202.07)	a	8
	1.86 (148.18)	NH/NH_2 (B)	8
	1.07 (85.56)	CH_3	6
	(D_2O)		
	2.65 (211.13)	b	8
	2.54 (202.10)	a	8
	1.07 (85.48)	CH_3	6
b-(diam). $3\frac{1}{2}\text{H}_2\text{O}$ (D_2O)	2.66 (211.86)	b	8
	2.54 (202.44)	a	8
	1.07 (85.60)	CH_3	6
$(\text{diamH}_4)(\text{ZnCl}_4)_2 \cdot 4\text{H}_2\text{O}$	3.78 (301.27)	b	8
	3.60 (286.12)	a	8
	2.05 (163.45)	CH_3	6
$[\text{Co}(\text{diam})](\text{ClO}_4)\text{Cl}_2$	4.05 (322.88)		
	3.97 (316.01)	b	8
	3.94 (313.51)		
	3.81 (303.11)		
	3.43 (272.88)		
	3.31 (263.44)	a	8
	3.23 (257.30)		
	3.06 (243.93)		
	1.83 (146.10)	CH_3	6

Table 9 continued

Compound	δ /ppm (Hz)	Assignment	n
[Co(diam)]Cl ₃ · 3H ₂ O	3.99 (317.57)		
	3.88 (308.81)	b	8
	3.79 (301.66)		
	3.71 (295.62)		
	3.34 (265.56)		
	3.22 (255.98)	a	8
	3.13 (249.49)		
	2.96 (235.90)		
	1.74 (138.49)	CH ₃	6
[Co(diam)] ₈ (CO ₃) ₅ Cl ₁₄ · 56H ₂ O	4.00 (318.18)		
	3.91 (311.26)	b	8
	3.88 (308.85)		
	3.74 (298.20)		
	3.37 (268.69)		
	3.25 (259.21)	a	8
	3.16 (252.02)		
	3.00 (238.73)		
	1.78 (142.15)	CH ₃	6
[Co(diam)]Br ₃ · ½H ₂ O	4.12 (328.47)		
	4.03 (321.25)	b	8
	4.01 (319.13)		
	3.87 (307.98)		

TABLE 9 continued

Compound	δ /ppm (Hz)	Assignment	n
[Co(diam)]Br ₃ · ½H ₂ O	3.48 (277.51)		
continued	3.36 (267.87)	a	8
	3.27 (260.58)		
	3.10 (247.32)		
	1.88 (150.22)	CH ₃	6
<i>trans</i> -[Co(diamH ₂)Cl ₂]Cl ₃ · 2H ₂ O	3.65 (290.81)		
	3.62 (287.83)	b	8
	3.54 (282.01)		
	3.48 (277.25)		
	3.34 (265.68)		
	3.16 (251.50)	a	8
	3.01 (239.72)		
	1.98 (157.53)	CH ₃	6
[Co(diamH ₂)Cl ₂](diamH ₂) ₇ Cl ₁₇ · 28½HCl · 17H ₂ O (T)	3.40 (270.54)	b	8
	3.20 (254.93)	a	8
	1.66 (132.51)	CH ₃	6
[Co(diamH)Cl]Cl ₃ · 2H ₂ O	3.99 (317.41)		
	3.78 (300.95)	b	8
	3.64 (289.92)		
	3.37 (268.61)	a	8
	3.17 (252.70)		
	2.21 (176.17)	CH ₃	6
	1.82 (144.99)		

TABLE 9 continued

Compound	δ /ppm (Hz)	Assignment	n
[Co(II)diamH ₂)]Br ₄ .	3.84 (306.03)		
2 $\frac{1}{2}$ H ₂ O (T)	3.72 (296.16)	a & b	16
	3.66 (291.93)		
	3.56 (283.92)		
	2.11 (168.24)	CH ₃	6
	2.01 (160.31)		
[Co(II)(diam)](O ₂)Cl	3.39-3.63	a and b	16
(CoCl ₄) $\frac{1}{2}$. 4 $\frac{1}{2}$ H ₂ O or	(269.76-289.22)	(B)	
[Co(II)(diam)]Cl(CoCl ₄) $\frac{1}{2}$.			
6H ₂ O (T)	1.66-1.79	CH ₃ (B)	6
	(132.33-143.01)		
[Zn(diam)](OH)(Zn ₂ Cl ₅).	3.79 (302.09)		
2H ₂ O (T)	3.67 (292.59)	b	8
	3.62 (288.61)		
	3.59 (285.59)		
	3.30 (262.96)		
	3.23 (257.54)		
	3.08 (245.69)	a	8
	3.00 (239.30)		
	2.92 (232.31)		
	1.72 (137.21)	CH ₃	6
[Rh(diam)] ₂ Cl ₅ (ClO ₄). 7H ₂ O	3.54-3.57	a & b (B)	16
	(281.77-284.53)		
	1.85-1.98	CH ₃ (B)	6
	(147.81-157.78)		

TABLE 10: ^{13}C NMR DATA OF SELECTED COMPOUNDS OF DIAM

Compound	δ/ppm (Hz)	Assignment
a-(diam). $3\frac{1}{2}\text{H}_2\text{O}$ (CDCl_3)	60.78 (1215.69)	c
	51.50 (1030.05)	b
	48.86 (977.36)	a
	27.41 (548.41)	<u>CH</u> ₃
b-(diam). $3\frac{1}{2}\text{H}_2\text{O}$ (CDCl_3)	60.68 (1213.80)	c
	51.46 (1029.26)	b
	48.77 (975.52)	a
	27.34 (546.90)	<u>CH</u> ₃
(diamH ₄)(ZnCl ₄) ₂ . $4\frac{1}{2}\text{H}_2\text{O}$	55.58 (1118.81)	c
	53.90 (1078.19)	b
	47.83 (956.75)	a
	20.78 (415.63)	<u>CH</u> ₃
[Co(diam)]Cl ₂ (ClO ₄)	65.59 (1312.05)	c
	60.73 (1214.73)	b
	54.25 (1085.23)	a
	19.46 (389.28)	<u>CH</u> ₃
[Co(diam)]Cl ₃ . $3\text{H}_2\text{O}$	65.54 (1310.95)	c
	60.64 (1213.05)	b
	54.20 (1084.09)	a
	19.48 (389.69)	<u>CH</u> ₃
[Co(diam)] ₈ (CO ₃) ₅ Cl ₁₄ . $56\text{H}_2\text{O}$	65.48 (1309.73)	c
	60.78 (1215.74)	b
	54.15 (1083.16)	a
	19.59 (391.88)	<u>CH</u> ₃

TABLE 10 continued

Compound	δ /ppm (Hz)	Assignment
[Co(diam)]Br ₃ · ½H ₂ O	65.71 (1314.31)	c
	60.77 (1215.54)	b
	54.36 (1087.25)	a
	19.65 (393.08)	<u>CH</u> ₃
<i>trans</i> -[Co(diamH ₂)Cl ₂]Cl ₃ · 2H ₂ O	58.10 (1162.07)	c
	54.92 (1098.59)	b
	53.58 (1071.63)	a
	23.29 (465.81)	<u>CH</u> ₃
[Co(diamH ₂)Cl ₂](diamH ₂) ₇ Cl ₁₇ · 28½HCl · 17H ₂ O (T)	55.24 (1104.93)	c
	53.77 (1075.45)	b
	47.56 (951.40)	a
	20.73 (414.68)	<u>CH</u> ₃
[Co(II)(diamH ₂)]Br ₄ · 2½H ₂ O (T)	64.03 (1280.80)	c
	61.72 (1234.52)	
	61.29 (1226.01)	b
	59.67 (1193.52)	
	59.51 (1190.43)	
	53.54 (1071.02)	a
	28.86 (577.30)	<u>CH</u> ₃
	26.43 (528.78)	
[Co(diam)(OH)](ClO ₄) ₂ · H ₂ O (DMSO)	63.57 (1271.53)	c
	60.77 (1215.52)	b
	52.28 (1045.79)	a

TABLE 10 continued

<u>Compound</u>	<u>δ/ppm (Hz)</u>	<u>Assignment</u>
[Co(diam)(OH)](ClO ₄) ₂ · H ₂ O	19.58 (391.77)	<u>CH</u> ₃
(DMSO) continued	28.06 (561.32)	
[Co(II)(diam)](O ₂)Cl	60.56 (1211.26)	c
(CoCl ₄) _{1/2} · 4 ^{1/2} H ₂ O or	54.07 (1081.59)	b
[Co(II)(diam)]Cl(CoCl ₄) _{1/2} ·	52.36 (1047.32)	a
6H ₂ O (T)	19.29 (386.00)	<u>CH</u> ₃
[Zn(diam)](OH)(Zn ₂ Cl ₅) ·	57.91 (1158.38)	c
2H ₂ O (T)	54.43 (1088.87)	b
	50.25 (1005.12)	a
	23.92 (478.44)	<u>CH</u> ₃

SECTION 2.8: PROTONATION CONSTANTS OF SELECTED COMPOUNDS OF DIAM

Diam compounds for which pendant arm protonation constants were determined from potentiometric titration results and the salts used are given in table 11.

Table 11: Diam Compounds for which Protonation Constants Were Determined and the Salts Used

<u>Compound</u>	<u>Salt(s)</u>
diam	(diam). $3\frac{1}{2}\text{H}_2\text{O}$, (diamH ₆)Cl ₆ . $2\text{H}_2\text{O}$
b-[Ni(diam)(H ₂ O) ₂] ²⁺	b-[Ni(diam)]Cl ₂ . $6\text{H}_2\text{O}$, b-[Ni(diamH ₂)]Cl ₄ . $4\text{H}_2\text{O}$ b-[Ni(diamH ₂)](ClO ₄) ₄ . $6\text{H}_2\text{O}$
b-[Ni(diam)(NCS) ₂] ²⁺	b-[Ni(diamH ₂)(NCS) ₂](SCN) ₂ . $\frac{1}{2}\text{H}_2\text{O}$
c-[Ni(diam)] ²⁺	c-[Ni(diamH ₂)](ClO ₄) ₄
c-[Ni(diam)(NCS) ₂] ²⁺	c-[Ni(diamH ₂)(NCS) ₂](SCN) ₂ . $3\text{H}_2\text{O}$
[Cu(diam)] ²⁺	[Cu(diam)](ClO ₄) ₂ . $2\text{H}_2\text{O}$, [Cu(diamH ₂)](ClO ₄) ₄ . H_2O
[Pd(diam)] ²⁺	[Pd(diamH ₂)](ClO ₄) ₄ . $5\frac{1}{2}\text{H}_2\text{O}$

See SECTION 2.1 for instrumentation. Accurately weighed (ca. 5.5×10^{-5} moles) samples of the above compounds were dissolved in 0.1 mol dm^{-3} sodium perchlorate solution (30 cm^3) to which a calculated amount of standardized hydrochloric acid ($0.1100 \text{ mol dm}^{-3}$; $0.4\text{--}4.0 \text{ cm}^3$) was added. The solutions were stirred under nitrogen for half an hour and titrated with carbonate free $0.0998 \text{ mol dm}^{-3}$ sodium hydroxide solution. The temperature was maintained at $25 \pm 0.05^\circ\text{C}$. The calomel/hydrogen electrode system was calibrated with the following freshly prepared buffers; 0.05 mol dm^{-3} potassium hydrogenphthalate (pH 4.01) [223], 0.01 mol dm^{-3} borax (pH 9.18) [223] and 0.025

mol dm⁻³ sodium bicarbonate/0.025 mol dm⁻³ sodium carbonate (pH 10.012) [224]. All solutions were protected from air by a stream of nitrogen throughout the titration. The nitrogen flow and stirring were ceased and the solution was allowed to equilibrate before each reading to minimize disturbances. The protonation constants for selected compounds of diam calculated in the pH range 2-11 by the Gilbert Herron Method [215] are listed in table 12. These results are discussed in CHAPTER 3: DISCUSSION.

Table 12(i): The Protonation Constants and Standard Deviations for Diam (I = 0.1 mol dm⁻³ NaClO₄, 25°C)

<u>Salt</u>	<u>Log K₁</u>	<u>Log K₂</u>	<u>Log K₃</u>	<u>Log K₄</u>
(diam). 3½H ₂ O	11.20±0.05	9.8±0.1	6.2±0.1	5.3±0.1
(diamH ₆). 2H ₂ O	11.10±0.05	9.6±0.1	6.1±0.1	5.28±0.05

Table 12(ii): The Protonation Constants and Standard Deviations for Selected Nickel, Copper and Palladium Complexes of Diam (I = 0.1 mol dm⁻³ NaClO₄, 25°C)

<u>Salt</u>	<u>Log K₁</u>	<u>Log K₂</u>
b-[Ni(diam)]Cl ₂ . 6H ₂ O	4.49±0.06	3.97±0.05
b-[Ni(diamH ₂)(H ₂ O) ₂]Cl ₄ . 2H ₂ O	4.52±0.04	3.98±0.05
b-[Ni(diamH ₂)](ClO ₄) ₄ . 6H ₂ O	4.50±0.03	3.91±0.05
b-[Ni(diamH ₂)(NCS) ₂](SCN) ₂ . ½H ₂ O	5.08±0.03	4.88±0.05
c-[Ni(diamH ₂)](ClO ₄) ₄	5.73±0.02	3.94±0.02
c-[Ni(diamH ₂)(NCS) ₂](SCN) ₂ . 3H ₂ O	6.17±0.02	4.91±0.03
[Cu(diam)](ClO ₄) ₂ . 2H ₂ O	5.28±0.02	4.29±0.02
[Cu(diamH ₂)](ClO ₄) ₄ . H ₂ O	6.68±0.02	5.70±0.02
[Pd(diamH ₂)](ClO ₄) ₄ . 5½H ₂ O	6.08±0.02	5.10±0.02

SECTION 2.9.1: KINETICS OF ISOMERIZATION AND DISSOCIATION OF THE a-ISOMER OF THE NICKEL COMPLEX OF DIAM

Introduction

In solution, the a- isomer of the nickel complex of diam slowly isomerizes to the b- form. When a-[Ni(diamH₂)]-(ClO₄)₄ is dissolved in neutral or dilute hydrochloric acid solutions, a yellow solution containing square planar singlet state nickel(II) species is obtained. This yellow solution slowly turns pink as a- --> b- isomerization occurs, because of the formation of the triplet ground state nickel(II) species, b-[Ni(diamH₂)(H₂O)₂]⁴⁺. This results in a significant change in the electronic spectrum. In basic solution, both a- and b- isomers occur as the pink, triplet ground state [Ni(diam)]²⁺ cation with similar electronic spectra. However, the addition of a small volume of concentrated hydrochloric acid results in the reformation of the yellow, singlet ground state a-[Ni(diamH₂)]⁴⁺ but not the analogous square planar b-form. Thus, the a- --> b- isomerization rates in acidic, and basic solutions can be followed spectrophotometrically.

In addition to isomerization, the a- isomer was also observed to undergo dissociation in neutral and acidic solutions. Since the rate of reaction of diam with copper(II) is rapid in 2 mol dm⁻³ ^{HCl} at 50°C while the reaction with nickel(II) is extremely slow, the rate of dissociation of the nickel complex can be determined by monitoring the formation of the [Cu(diamH₂)]⁴⁺ cation.

The following reactions of the a- isomer of the nickel complex of diam were studied spectrophotometrically: (a) the rate of disappearance of yellow, square planar a-[Ni(diamH₂)]⁴⁺ in acidic and basic solutions at 50°C; (b) the effect of different salts on the rate of this reaction; (c) the parallel acid dissociation reaction

of $a\text{-[Ni(diamH}_2\text{)]}^{2+}$ at 50°C ; and (d) the rate of disappearance of tetragonal $a\text{-[Ni(diam)]}^{2+}$ in water at 25°C . These results are discussed in CHAPTER 3: DISCUSSION.

(a) The Rate of Disappearance of Yellow, Square Planar $a\text{-[Ni(diamH}_2\text{)]}^{4+}$ in Acidic and Basic Solutions at 50°C

In Aqueous Acid Solutions

Samples of $a\text{-[Ni(diamH}_2\text{)](ClO}_4\text{)}_4 \cdot 2\text{H}_2\text{O}$ (0.063 g, 8.27×10^{-5} moles) were dissolved in standardized hydrochloric acid, ($0.1\text{--}2.0 \text{ mol dm}^{-3}$; 5 cm^3 ; $I = 2.00 \text{ mol dm}^{-3} \text{ NaCl}$). The solutions were thermostatted at $50 \pm 0.5^\circ\text{C}$ and electronic spectra measured periodically (in the range $640\text{--}360 \text{ nm}$). The decrease in intensity of the band at 453 nm of singlet state nickel(II) was used to calculate the rate of disappearance of $a\text{-[Ni(diamH}_2\text{)]}^{4+}$ (as a result of isomerization and dissociation) by plotting $\ln(A_\infty - A_t)$ versus t . The observed first order rate constants (k_{obs}) for these reactions in hydrochloric acid are given in table 13. These results are plotted in figure 21.

In Basic Solutions

Accurately weighed $a\text{-[Ni(diamH}_2\text{)](ClO}_4\text{)}_4 \cdot 2\text{H}_2\text{O}$ (0.378 g, 4.96×10^{-4} moles) was dissolved in sodium hydroxide (0.1 mol dm^{-3} ; 30 cm^3 ; $I = 2.0 \text{ mol dm}^{-3} \text{ NaCl}$) and thermostatted at 50°C . Periodically, a drop of hydrochloric acid was added to a 5 cm^3 sample and the absorbance at 453 nm was recorded. The observed first order rate constant was $2.0(3) \times 10^{-2} \text{ s}^{-1}$.

Table 13: The Observed First Order Rate Constants for the Disappearance of $a\text{-[Ni(diamH}_2\text{)](ClO}_4\text{)}_4$ in Hydrochloric Acid at 50°C, I = 2.00 mol dm⁻³ NaCl

$[\text{HCl}]/\text{mol dm}^{-3}$	$k_{\text{obs}}/10^{-4} \text{ s}^{-1}$
0.1	0.28
0.2	0.60
0.4	1.12
0.65	1.71
1.0	2.39
1.4	2.70
1.75	2.91
2.0	3.05 ¹

¹ = The rate of disappearance of the chloride salt, $a\text{-[Ni(diam)]Cl}_2$ was also followed in 2.0 mol dm⁻³ hydrochloric acid at 50°C. The observed first order rate constant was $3.34 \times 10^{-4} \text{ s}^{-1}$.

(b) Specific Salt Effects on the Rate of Disappearance of $a\text{-[Ni(diamH}_2\text{)]}^{4+}$

Samples of $a\text{-[Ni(diamH}_2\text{)](ClO}_4\text{)}_4 \cdot 2\text{H}_2\text{O}$ (0.063 g, 8.27×10^{-5} moles) were dissolved in sodium chloride (2.0 mol dm⁻³; 5 cm³) and sodium nitrate (2.0 mol dm⁻³; 5 cm³) and thermostatted at 50°C. The electronic spectrum (in the range 640-360 nm) was recorded periodically and the decrease in absorbance at 453 nm was used for rate calculations. The observed first order rate constants in 2 mol dm⁻³ sodium chloride and 2 mol dm⁻³ sodium nitrate were $5.0(5) \times 10^{-5}$ and $5.6(5) \times 10^{-5} \text{ s}^{-1}$ respectively.

(c) Dissociation of $a\text{-[Ni(diam)]Cl}_2$ in 2.0 mol dm⁻³ Hydrochloric acid at 50°C

Accurately weighed $a\text{-[Ni(diam)]Cl}_2 \cdot \text{H}_2\text{O}$ (0.500 g, 1.205×10^{-3} moles) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.043 g, 2.511×10^{-4}

Figure 21: The relationship between the observed first order rate constant, K_{obs} , and acid concentration, $[\text{H}^+]$, for the disappearance of $\alpha\text{-[Ni(diamH}_2\text{)](ClO}_4\text{)}_4$ in acidic solutions at 50°C , $I = 2.00 \text{ mol dm}^{-3} \text{ NaCl}$

moles) were dissolved in hydrochloric acid (2.0 mol dm^{-3} ; 25 cm^3) and kept in a thermostatted water bath at 50°C . The electronic spectrum was periodically measured between 800 and 360 nm at 50°C . The observed first order rate constant calculated from the increase in absorption at 527 nm ($\epsilon = 75 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) due to the formation of the $[\text{Cu}(\text{diamH}_2)]^{4+}$ cation was $1.82 \times 10^{-7} \text{ s}^{-1}$. Since the rate of reaction between Ni^{2+} and diam in 2 mol dm^{-3} hydrochloric acid at 50°C was extremely slow, interference from the formation of $\text{b-}[\text{Ni}(\text{diamH}_2)]^{4+}$ ($\lambda_{\text{max}} = 513 \text{ nm}$, $\epsilon = 6 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) was not a problem.

(d) The Rate of Disappearance of Lilac Coloured Tetragonal $\text{a-}[\text{Ni}(\text{diam})]\text{Cl}_2$ in Water at 25°C

The electronic spectrum of aqueous $\text{a-}[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ($0.1112 \text{ mol dm}^{-3}$) was measured periodically in the range 800 to 400 nm at 25°C . The decrease in intensity of the band at 586 nm ($\epsilon = 3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) of the triplet state $\text{a-}[\text{Ni}(\text{diam})]^{2+}$ cation was used for the rate calculations. A first order rate constant of $2.35 \times 10^{-5} \text{ s}^{-1}$ was obtained.

SECTION 2.9.2: ACID DISSOCIATION KINETICS OF

$[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$

The acid dissociation kinetics of $[\text{Cu}(\text{diamH}_2)]^{4+}$ were studied in 0.2-2 mol dm⁻³ perchloric acid and 0.1 mol dm⁻³ hydrochloric acid at 50°C and 70°C.

$[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (0.2200 g, 2.97×10^{-4} moles) were dissolved in standardized perchloric acid or hydrochloric acid (25.00 cm³) in volumetric flasks with teflon screw caps. These caps were heat (up to 260°C) and acid resistant. The acid concentrations and the reaction temperatures are given in table 14. The ionic strength of the solutions was maintained at 2.0 mol dm⁻³ with NaClO₄ or NaCl respectively.

Table 14: Temperatures and Acid Concentrations Used for Acid Dissociation Kinetics of $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$

<u>Temperature</u>	<u>Acid</u>	<u>Concentrations/mol dm⁻³</u>
50°C	HClO ₄	0.2, 0.6, 1.0, 2.0
70°C	HClO ₄	0.2, 0.6, 1.0, 2.0
	HCl	0.1

A well insulated metallic container equipped with its own water supply, thermostatted heating/stirring unit, level indicator and thermometer was used for the 70°C water bath. (A standard thermostatted water bath was used for the 50°C kinetics). The electronic spectra (800-360 nm) of the solutions were measured periodically at 50°C. The times and the absorbance at λ_{max} (527 nm for the reaction in hydrochloric acid and 512 nm for the reaction in perchloric acid) were recorded. A small decrease in absorbance was found (ca. 2% over the year at 50°C and 14% at 70°C). Since the reactions were extremely slow, the

infinity value for the calculations had to be estimated some other way. This was done by dissociating the copper complex $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (0.2200 g, 2.97×10^{-4} moles) in concentrated hydrochloric acid (25 cm^3) at 70°C . (The reaction took about 2 days). An infinity value of 0.22 was thus obtained. The results are summarized in Table 15. These results are discussed in CHAPTER 3: DISCUSSION.

Table 15: Observed First Order Rate Constants (k_{obs}) for the Acid Dissociation Kinetics of $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ ($I = 2.0 \text{ M NaCl}$)

(i) in perchloric acid

Conc /mol dm ⁻³	$k_{\text{obs}}/10^{-9} \text{ s}^{-1}$	
	(50 °C)	(70 °C)
0.2	1.3(5)	7.3
0.6	1.3(3)	8.0
1.0	1.3(0)	7.2
2.0	1.2(6)	7.5

average k_{obs} at $50^\circ\text{C} = (1.3 \pm 0.1) \times 10^{-9} \text{ s}^{-1}$

average k_{obs} at $70^\circ\text{C} = (7.5 \pm 0.5) \times 10^{-9} \text{ s}^{-1}$

(ii) in 0.1 mol dm^{-3} hydrochloric acid at 70°C

$k_{\text{obs}} = 6.5 \times 10^{-9} \text{ s}^{-1}$

CHAPTER 3: DISCUSSION

Since a large number of complexes were synthesized during the course of this research, it is not proposed to discuss every compound in detail. The emphasis will be on the more "important" and "interesting" compounds. The syntheses and results (elemental analyses, infrared spectra, electronic spectra, magnetic susceptibilities, ^1H and ^{13}C nuclear magnetic resonance spectra, pendant amine protonation constants and kinetic data) were discussed in CHAPTER 2: EXPERIMENTAL.

DIAM (6, 13-Dimethyl-6, 13-Diamino-1, 4, 8, 11-Tetraazacyclo-tetradecane)

The following protonated and non-protonated forms of diam were synthesized and characterized by elemental analysis, infrared, ^1H and ^{13}C nuclear magnetic resonance spectroscopy; (diam). $3\frac{1}{2}\text{H}_2\text{O}$, $(\text{diam}_2\text{H}_9)\text{Cl}_9$. $5\text{H}_2\text{O}$, $(\text{diamH}_6)\text{Cl}_6$. $2\text{H}_2\text{O}$, $(\text{diamH}_5)(\text{CdCl}_4)\text{Cl}_3$. $2\text{H}_2\text{O}$ and $(\text{diamH}_4)(\text{ZnCl}_4)_2$. $4\frac{1}{2}\text{H}_2\text{O}$. The protonation constants of diam which were calculated from potentiometric titration measurements will be discussed separately (page 181).

Metal-directed condensation reactions with formaldehyde and carbon acids or ammonia leading to azamacrocyclic and polycyclic ligands have been thoroughly investigated [21, 22, 60, 65-72, 172, 225]. In this work, *bis*(diaminoethane) nickel(II) chloride, formaldehyde and nitroethane reacted in the presence of the non-coordinating base triethylamine to produce (6, 13-dimethyl-6, 13-dinitro-1, 4, 8, 11-tetraazacyclotetradecane)nickel(II) chloride, $[\text{Ni}(\text{dini})]\text{Cl}_2$ in high yield (figure 4.6(b)). $[\text{Ni}(\text{dini})]\text{Cl}_2$ was greyish yellow, square planar and sparingly soluble in hot water. An aqueous suspension of $[\text{Ni}(\text{dini})]\text{Cl}_2$ was reduced by

catalytic hydrogenation to form a-, b- and c- isomers of $[\text{Ni}(\text{diam})]\text{Cl}_2$. Demetallation of a- or b- $[\text{Ni}(\text{diam})]^{2+}$ in concentrated acid at 140°C or by reaction with cyanide led to the pendant arm macrocycle 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane, diam in high yield (figure 3).

The chiral carbon atoms at positions 6 and 13 of the ligand give rise to *C-meso* and *C-rac* diastereoisomerism, with the two amino groups on opposite sides, or the same side, of the macrocyclic plane. The structural data for the nickel, cobalt and copper complexes of diam and nuclear magnetic resonance spectra indicated that the isolated ligand was of *C-meso* configuration.

As observed with other coordinated cyclic tetramines, complexes of diam can occur in several configurations arising from the four chiral secondary amine nitrogens, as shown in figure 5 for cyclam. It has been established that the thermodynamically most stable nitrogen donor configuration of planar coordinated cyclam type macrocyclic complexes of metal ions with ideal M-N distances of 1.9-2.2 Å (for example nickel(II), copper(II) and cobalt(II) and (III)) is *trans*-III [98]. This has the six and five membered chelate rings in the chair and gauche conformations respectively, giving rise to minimal hydrogen-hydrogen interactions in the chelate rings and negligible torsional bond strain. This configuration is adopted by uncoordinated cyclam, its diprotonated salt and virtually all *trans*-octahedral and planar substituted and unsubstituted cyclam complexes of nickel, copper, cobalt, palladium, silver and zinc [1,7,93]. ^1H and ^{13}C nuclear magnetic resonance data and X-ray crystal structures of $[\text{Ni}(\text{diam})]^{2+}$, $[\text{Ni}(\text{diamH}_2)]^{4+}$ and $[\text{Co}(\text{diam})]^{3+}$ cations can be used to assign a *trans*-III configuration to most of the prepared complexes of diam.

Two of the most important properties of diam are the ability of the non-protonated pendant amine groups to coordinate to the (central) metal ion and its similarity to cyclam, which is perhaps the most thoroughly investigated synthetic azamacrocyclic, particularly when the pendant arms are protonated.

Infrared Spectra

The infrared spectrum of diam is complex and as expected, distinctly different from that of other cyclam type ligands because of the pendant primary amino groups. In general, the high and low frequency amine bands can be assigned to free and intra-molecularly hydrogen bonded amines respectively [226]. The $\nu(\text{NH})$ of selected cyclam type ligands are given in table 16.

The bands at 1615 and 1585 cm^{-1} in the infrared spectrum of diam are assigned to $\delta(\text{NH}_2)$. The additional bands at 1570 and 1530 cm^{-1} in the spectrum of $(\text{diamH}_6)\text{Cl}_6$ are assigned to $\delta(\text{NH}_2^+)$ and $\delta(\text{NH}_3^+)$ modes.

Table 16: $\nu(\text{NH})$ of Cyclam Type Ligands

<u>Ligand</u>	<u>$\nu(\text{NH})/\text{cm}^{-1}$</u>	
cyclam	3186, 3270	[226]
C-meso-5,12-Me ₂ -cyclam	3285, 3258, 3205	[226]
diam	3440, 3370, 3240	

^1H and ^{13}C Nuclear Magnetic Resonance Spectra

All nuclear magnetic resonances are assigned according to the atom designation in figure 20.

diam. $3\text{H}_2\text{O}$

The ^1H and ^{13}C spectra of the ligand isolated from the demetallation reaction of a- and b-[Ni(diam)]Cl₂ are simple, indicating a highly symmetric environment. ^1H and

^{13}C spectral data for diam, the assignments according to the atom designation in figure 20, and a comparison with the ^1H and ^{13}C spectra of cyclam are given in table 17.

Table 17: ^1H and ^{13}C Spectral Data for Diam and Cyclam in CDCl_3 Relative to TMS

diam

^1H	Assignment	n ¹	^{13}C	Assignment
2.66	b	8	60.73	c
2.54	a	8	51.48	b
1.86	NH/NH_2	8	48.82	a
1.07	CH_3	6	27.38	CH_3

cyclam

^1H	Assignment	n	^{13}C	Assignment
1.74	β	4	47.0, 47.1	$\text{N}-\text{CH}_2$
2.36	$\text{NH}'\text{s}$	4	27.8	$\text{C}-\text{CH}_2-\text{C}$
2.74	α	16		

¹ = number of protons

The ^1H and ^{13}C data for cyclam are from references [103] and [230] respectively.

The resonance of the primary and secondary amine protons was broad because of quadrupole coupling and possibly some intra-molecular hydrogen bonding, as also observed with cyclam [7]. The formation of the hydrogen bond causes the resonance of the bonded proton to move downfield (*i.e.* to larger values of δ) [227]. The chemical shift for RNH_2 and R_2NH (where R is an alkyl group) vary in the range 0.6-5 ppm [221]. The relatively low chemical shift of the amine protons of diam, 1.86 ppm, (identified by its disappearance in D_2O), suggests a low level of hydrogen bonding.

It has been found that protons that lie over the N_4 plane of the ligand (axial) experience low field shifts while those that lie in plane (equatorial) experience high field shifts (i.e. higher and lower values of δ respectively) [105b, 228]; axial methyl protons resonate at 1.9-2.2 ppm and equatorial methyl protons resonate at 1.1-1.3 ppm [229]. The resonance at 1.07 ppm is therefore assigned to equatorially oriented methyl groups. The single methyl resonance confirms that the six membered chelate ring conformations are pairwise equivalent.

$(diamH_4)(ZnCl_4)_2 \cdot 4\frac{1}{2}H_2O$

Protonation of the ligand has resulted in all the proton resonances shifting downfield (to higher chemical shifts) with respect to non-protonated diam because of the deshielding effect arising from the high positive charge. The methyl proton resonance at 2.05 ppm is indicative of axially oriented methyl groups, since bulkier NH_3^+ groups tend to adopt equatorial orientations.

The methyl carbon resonance of $(diamH_4)^{4+}$ is shielded with respect to that of diam, possibly as a result of steric repulsion between itself and the bulky NH_3^+ group.

NICKEL(II)

The following nickel(II) complexes of dini and diam were synthesized and characterized by elemental analysis, magnetic susceptibility measurements, electronic and infrared spectroscopy; $[\text{Ni}(\text{dini})]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, $a\text{-}[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, $a\text{-}[\text{Ni}(\text{diam})](\text{ClO}_4)\text{Cl} \cdot \text{H}_2\text{O}$, $a\text{-}[\text{Ni}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, $a\text{-}[\text{Ni}(\text{diam})(\text{NCS})_2] \cdot \frac{1}{2}\text{H}_2\text{O}$, $a\text{-}[\text{Ni}(\text{diam})](\text{ZnCl}_4) \cdot 2\text{H}_2\text{O}$, $b\text{-}[\text{Ni}(\text{diam})]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, $b\text{-}[\text{Ni}(\text{diamH}_2)(\text{H}_2\text{O})_2]\text{Cl}_4 \cdot 2 \text{ or } 4\text{H}_2\text{O}$, $b\text{-}[\text{Ni}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 2 \text{ or } 6\text{H}_2\text{O}$, $b\text{-}[\text{Ni}(\text{diamH}_2)(\text{H}_2\text{O})_2]\text{Cl}_2(\text{ClO}_4)_2 \cdot 1 \text{ and } 3\text{H}_2\text{O}$, $b\text{-}[\text{Ni}(\text{diam})](\text{ClO}_4)_2 \cdot 1 \text{ or } 1\frac{1}{2}\text{H}_2\text{O}$, $b\text{-}[\text{Ni}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, $b\text{-}[\text{Ni}(\text{diam})(\text{NCS})_2]$, $b\text{-}[\text{Ni}(\text{diamH}_2)](\text{ZnCl}_4)_2 \cdot 4\text{H}_2\text{O}$, $b\text{-}[\text{Ni}(\text{diam})](\text{ZnCl}_4) \cdot 1\frac{1}{2}\text{H}_2\text{O}$, $c\text{-}[\text{Ni}(\text{diamH}_2)](\text{ClO}_4)_4$, $c\text{-}[\text{Ni}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ and $c\text{-}[\text{Ni}(\text{diam})(\text{NCS})_2] \cdot \frac{1}{2}\text{H}_2\text{O}$. The pendant amine protonation constants of selected nickel complexes will be discussed separately (page 183).

Isomers of $[\text{Ni}(\text{diam})]^{2+}$

All the nickel complexes of diam discussed in this work were prepared from the three isomeric products of hydrogenation of $[\text{Ni}(\text{dini})]\text{Cl}_2$, designated a-, b- and c- $[\text{Ni}(\text{diam})]\text{Cl}_2$, which were lilac, violet brown and dark brown in colour respectively. The differences in solubility of the chloride salts of the three isomers permitted their successful separation.

The initial major product of the hydrogenation reaction was metastable $a\text{-}[\text{Ni}(\text{diam})]^{2+}$ which slowly isomerized in solution to $b\text{-}[\text{Ni}(\text{diam})]^{2+}$. The isomerization reaction was rapid in base, slower in water and acidic solutions and even slower in non-aqueous solutions such as dimethylsulphoxide, dimethylformamide, acetonitrile or 2-nitropropane. Apart from isomerizing to the b- isomer, the a- isomer was observed to hydrolyse slowly

in water and acidic solutions at room temperature. (It was demetallated in concentrated hydrochloric acid at 140°C in less than two hours). The rate constant for the disappearance (by conversion and hydrolysis) of lilac coloured a -[Ni(diam)]Cl₂ in water at 25°C was $2.3(5) \times 10^{-5} \text{ s}^{-1}$. (section 2.9.1). (The rates of disappearance of a -[Ni(diamH₂)]⁴⁺ at 50°C in various aqueous media will be discussed later; page 186).

The b - isomer was highly resistant to acid hydrolysis, remaining unreacted in concentrated hydrochloric acid at room temperature for prolonged periods. However, it was demetallated in concentrated hydrochloric acid at 140°C within *ca.* 48 hours.

When a -[Ni(diam)]Cl₂ was recrystallized from cold water with other anions such as perchlorate, thiocyanate and tetrachlorozincate, lilac coloured, octahedral salts were obtained. Recrystallizing a -[Ni(diam)]²⁺ from concentrated perchloric acid yielded the yellow square planar salt, a -[Ni(diamH₂)](ClO₄)₄. (The a - compounds could not be recrystallized from hot or basic solutions because of rapid isomerization to the b - form).

The recrystallization of b -[Ni(diam)]Cl₂ or diprotonated b -[Ni(diamH₂)(H₂O)₂]Cl₄ from water or basic solutions with the aforesaid anions resulted in pink hexacoordinated salts with pendant amines (of the non-protonated compound), water or anions completing octahedral coordination. By recrystallizing b -[Ni(diam)]²⁺ from concentrated perchloric acid or a solution of zinc chloride and concentrated hydrochloric acid, orange or reddish brown square planar salts of b -[Ni(diamH₂)]⁴⁺ were obtained respectively. The b - compounds were isolated as many different hydrates, with zero to six moles of water per mole of compound.

Attempts to prepare compounds of [Ni(diamH₂)]⁴⁺ with

the macrocycle in folded coordination with a chelate such as oxalate, diaminoethane or acetylacetonate coordinated were unsuccessful.

The behaviour of *a*- and *b*- isomers in acidic, basic and aqueous solution was distinctly different. When $a\text{-[Ni(diam)]Cl}_2$ was dissolved in water, a lilac solution ($\text{pH} = 7.50$) with mainly triplet ground state octahedral Ni(II) was observed. In the absence of competing ligands such as thiocyanate, pendant amino groups of the *a*- isomer could coordinate under these conditions. In acidic solutions ($\text{pH} < 5$), the *a*- isomer existed mainly as yellow, singlet ground state, square planar nickel(II) with the pendant arms protonated and uncoordinated. In solution, yellow $a\text{-[Ni(diamH}_2\text{)]}^{4+}$ slowly turned pink on isomerization to the *b*- form. In basic solutions, the *a*- $\rightarrow$ *b*- isomerization occurred rapidly and the triplet ground state, octahedrally coordinated violet brown *b*- isomer was obtained. The observed rate constants for the disappearance of yellow $a\text{-[Ni(diamH}_2\text{)](ClO}_4\text{)}_4$ at 50°C in 2 mol dm^{-3} hydrochloric acid, 0.1 mol dm^{-3} sodium hydroxide and 2 mol dm^{-3} sodium chloride solutions were 3.05×10^{-4} , $2.0(3) \times 10^{-2}$ and $5.0(5) \times 10^{-5} \text{ s}^{-1}$ respectively (SECTION 2.9.1).

In water ($\text{pH} = 7.08$), or basic solutions in the absence of thiocyanate, the *b*- isomer had the pendant arms coordinated. In acidic solutions, the pendant arms were protonated and uncoordinated. Dilute or concentrated hydrochloric acid and dilute perchloric acid solutions of the *b*- isomer were pink or purple because of axially coordinated water (or possibly chloride ions in concentrated hydrochloric acid). Unlike square planar $a\text{-[Ni(diamH}_2\text{)]}^{4+}$ which formed with ease in acidic solutions, the square planar $b\text{-[Ni(diamH}_2\text{)]}^{4+}$ was observed in significant amounts only in the absence of potential axial coordi-

nators, under strongly acidic conditions; in concentrated perchloric acid or excess tetrachlorozincate and concentrated hydrochloric acid. Also in contrast with the a-analogue, when square planar b-[Ni(diamH₂)]⁴⁺ salts were dissolved in water, the pink octahedrally coordinated [Ni(diamH₂)(H₂O)₂]⁴⁺ cation was observed.

In the presence of the thiocyanate anion, non-protonated or diprotonated octahedral nickel salts with the axial sites occupied by the nitrogen of the thiocyanate molecule were obtained. (Structural and electronic spectral evidence to support this is discussed later).

From the filtrate after the isolation of the a- and b- isomers, a sticky dark brown material designated crude c-[Ni(diamH₂)]⁴⁺ was obtained. The properties and experimental data of the c- compounds will be discussed separately because of their unusual nature (page 143).

Octahedral-Square Planar Conversion

Nickel(II) complexes of linear or cyclic tetramines can be high spin or low spin. The "bluish" paramagnetic form is of tetragonally distorted octahedral geometry. The four (usually coplanar) coordination sites are occupied by the amine nitrogens and the (usually) axial sites are occupied by counter ions, solvent molecules or in the case of macrocycles containing axial ligating groups, pendant arms. The yellow diamagnetic form has the four nitrogen donors in a coplanar arrangement giving a square planar stereochemistry.

The equilibrium between high and low spin forms of a nickel(II)-tetramine complex (NiL) in water is shown below. The kinetics and thermodynamics of this equilibrium have been studied extensively [91, 121, 153, 161, 202-208, 231-253].

The blue-yellow reaction is endothermic and displaced to the right by an increase in temperature or an increase in ionic strength of the solution. The position of this equilibrium also depends on ligand structure [208]. In general, a lack of flexibility or unfavourable steric interactions involving the axial sites give rise to a higher percentage of the yellow form.

The Ni-N bond distance for square planar complexes is less than that for octahedral complexes; being *ca.* 1.9 and 2.1 Å for the two geometries respectively [206]. Since linear ligands such as 2,3,2-tet are more flexible, they can rearrange their donor nitrogens closer to the metal atom during the formation of a square planar complex. Cyclic ligands on the other hand experience mechanical resistance to reduction in the M-N distance. This observation led to the conclusion by Fabbrizzi and co-workers that the blue-yellow conversion depends on ligand structure and steric effects rather than cyclic effects [208]. The nickel complexes they investigated, 2,3,2-tet and cyclam formed 22% and 71% of the yellow species respectively in 0.1 M NaClO₄ at 25°C, compared with [Ni(1-N-methyl-cyclam)]²⁺ which is 78% yellow [204]. This is also illustrated by the linear nickel(II)-tetramine complexes [Ni(diaminoethane)₂]²⁺ (100% blue), [Ni(C,C-dimethyldiaminoethane)₂]²⁺ (a 50% mixture of blue and yellow) and [Ni(C,C,C',C'-tetramethyldiaminoethane)₂]²⁺ (100% yellow) [208].

In the case of macrocycles with pendant amines, such as diam, the position of the equilibrium may also be changed by adjusting the pH of the solution. For example, when an excess of concentrated perchloric acid was added to a violet solution of h-[Ni(diam)]²⁺, a yellow solution formed, from which a dark orange solid, h-[Ni(diamH₂)]-(ClO₄)₄ crystallized. Protonation of the pendant arms and

the presence of an excess of non-coordinating perchlorate anion induced the formation of the square complex and stabilized singlet state nickel(II).

The existence of blue and yellow forms of $[\text{Ni}(\text{cyclam})]^{2+}$ and $a\text{-}[\text{Ni}(\text{diamH}_2)]^{2+}$ and the absence of significant amounts of the yellow form of $b\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ in aqueous solution is apparent from their electronic spectra (discussed later; page 138).

In general, blue-yellow equilibria are fast; measurable only by fast kinetic techniques such as T-jump and photochemical perturbation methods [243-245]. For example, the first order rate constant for interconversion of planar and octahedral $[\text{Ni}(\text{II})(2,3,2\text{-tet})]^{2+}$ is $3.33 \times 10^6 \text{ s}^{-1}$ in water at 23°C [244]. The relatively slow rates of the yellow $\rightarrow$ purple conversion of $a\text{-}[\text{Ni}(\text{diamH}_2)]^{2+}$ in acid, base, neutral aqueous and salt solutions (between 2.0×10^{-2} and $5.0 \times 10^{-5} \text{ s}^{-1}$) suggests that it is not a square planar-octahedral conversion in the conventional sense; it is probably a *trans*-I to *trans*-III inversion process. (The assignment of nitrogen configurations *trans*-I and *trans*-III respectively to *a*- and *b*- isomers will be discussed in the Structures section on page 141). For this reason, the measured rates of disappearance of the $a\text{-}[\text{Ni}(\text{diamH}_2)]^{2+}$ cation in various aqueous solutions can not be compared with blue-yellow rates of other systems.

Inversion of Nitrogen Configuration

It has been suggested that all metal complexes of cyclam in which the metal and nitrogen atoms are co-planar assume the *trans*-III structure upon equilibration in basic media. (This explains the rapidity of *a*- $\rightarrow$ *b*- conversion in basic media). However, it can not be assumed that the four nitrogens retain the same configuration throughout

the steps leading to complex formation [254]. In fact, it is likely that nitrogen inversions take place *via* the conjugate base during metal complex formation [255].

trans-I-*trans*-III inversions have been observed in many systems [107, 254, 256]. Some of these cases were unexpected; for example, when the nitrogen donors were tertiary [254]. Even more surprising was the finding of Moore [107] that *trans*-I and *trans*-III isomers of tetra-N-methyl-cyclam interconvert *reversibly*. This requires the dissociation of the tertiary amine prior to inversion. In such isomerization reactions, the role of the pendant group or solvent molecules is to displace the tertiary amine donor and/or occupy the vacated coordination site during the inversion process [254]. Reversible inversion was not observed in the diam system.

It has been assumed that the *trans*-I-*trans*-III conversion is a stepwise process [254]. The intermediate detected by Moore [107] by nuclear magnetic resonance and kinetic methods was of *trans*-II configuration. Alcock and co-workers have isolated and characterized such an intermediate with one of the nitrogens uncoordinated for a copper(II) tetraazamacrocyclic [168].

Previous Investigations of Nitrogen Configurations of Cyclam Type Complexes

Hancock and co-workers in their molecular mechanics and crystallographic study of hole size in tetraazamacrocyclics made the following general conclusions [98]. (a) *trans*-I forms are much more flexible than *trans*-III forms; they accommodate octahedral coordination geometry with difficulty and tend to cause the metal ion to lift out of the N_4 plane. (b) For cyclam type complexes, the *trans*-III is the most stable configuration except when the M-N length is high (>2.29 Å) or low

(<1.90 Å) (c) Because of Van der Waals repulsions, ligands axially coordinated to planar *trans*-III forms experience considerable steric hindrance. (d) Folded cyclam type complexes (*cis*-V) will be favoured for octahedral metal ions with M-N distance above 2.09 Å. (e) The ideal bond length of Ni(II) and other metal ions can vary in response to gross distortion of coordination geometry, such as the tetragonal distortion in [Ni(cyclam)Cl₂].

Billo and co-workers have calculated the relative strain energies for planar and octahedral conformers of Ni(II) cyclam complexes, as shown in table 18 [89(a)].

Table 18: Relative Strain Energies for Square Planar and *trans*-Octahedral Diaquo Nickel(II) Complexes of Cyclam¹

Configuration	Planar	Octahedral
<i>trans</i> -I	0.32	2.35
<i>trans</i> -II	1.30	2.91
<i>trans</i> -III	0.00	0.00
<i>trans</i> -IV	7.74	8.21
<i>trans</i> -V	2.36	4.20

¹ = Energies in Kcal mol⁻¹

The strain energy of the octahedral *trans*-I form is 2.35 Kcal mol⁻¹ more than that of the octahedral *trans*-III, whereas the planar *trans*-I and III forms have a small energy difference of 0.32 Kcal mol⁻¹.

The flexibility of the *trans*-I ligand enables it to adopt the shorter Ni-N bond length of the low spin form with minimal change in total strain energy. In contrast, the strain energy of the *trans*-III species significantly increases during high to low spin conversion. It has been shown that the best-fit metal-nitrogen bond length for *trans*-I complexes is 2.01 Å, in comparison with 2.07 Å for *trans*-III complexes [89(a), 98]. (The ideal metal-donor

distances for low and high spin Ni(II) are ca. 1.9 and 2.1 Å respectively).

The ease of formation of the yellow square planar species by $a\text{-[Ni(diamH}_2\text{)]}^{4+}$ in solution suggests that it has a *trans*-I structure. In addition, the strain energy calculations of Billo indicate that the second least strained configuration for planar and *trans* octahedral nickel complexes of cyclam is *trans*-I. For these reasons, it is likely that the *a*- isomer has a *trans*-I configuration.

Electronic Spectra

Electronic spectral data can be used to distinguish between the possible geometries of the nickel complexes.

The spectra of aqueous $b\text{-[Ni(diamH}_2\text{)]}^{4+}$ salts have four absorption bands at ca. 1160, 665, 510 and 340 nm. These bands can be assigned to ${}^3E_g \leftarrow {}^3B_{1g}$, ${}^3B_{2g} \leftarrow {}^3B_{1g}$, $({}^3E_g, {}^3A_{2g}) \leftarrow {}^3B_{1g}$ and ${}^3T_{1g}(P) \leftarrow {}^3B_{1g}$ transitions of tetragonally distorted octahedral $b\text{-[Ni(diamH}_2\text{)(H}_2\text{O)}_2]^{4+}$ [257, 258]. Bands assignable to square planar singlet ground state Ni(II) could not be detected in aqueous or sodium perchlorate solutions of the *b*-isomer.

The spectrum of freshly dissolved $a\text{-[Ni(diamH}_2\text{)]}^{4+}$ has a band at 453 nm which is assignable to the ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition of square planar nickel(II) [257]. The bands at 326 and 692 nm arise from the formation of tetragonally distorted, triplet state $[Ni(diamH_2)(H_2O)_2]^{4+}$ in solution. The molar absorptivities (ϵ) of the yellow band at 453 nm in water, 2 mol dm⁻³ sodium chloride and 2 mol dm⁻³ hydrochloric acid at 50°C are 23, 31 and 55 mol⁻¹ dm³ cm⁻¹ respectively, indicating different blue-yellow equilibrium positions. (The limiting spectrum of yellow cyclam type complexes in saturated sodium perchlorate is ca. 60 mol⁻¹ dm³ cm⁻¹). The high energy band at 191 nm

is assigned to charge transfer or parity allowed transitions of the ligand.

In comparison, $[\text{Ni}(\text{cyclam})]^{2+}$ has bands at *ca.* 445 (yellow), 335 (blue) and 667 nm (blue) [208].

The band at *ca.* 485-500 nm in many of the nickel complexes of diam is a result of the combination of the ($^3\text{E}_g, ^3\text{A}_{2g}$) $\leftarrow$ $^3\text{B}_{1g}$ transition of tetragonal Ni(II) and the $^1\text{B}_{1g}\leftarrow$ $^1\text{A}_{1g}$ transition of square planar Ni(II) [259].

The electronic spectra aqueous solutions of $\text{b-}[\text{Ni}(\text{diam})]\text{X}_2$ and $\text{b-}[\text{Ni}(\text{diamH}_2)]\text{X}_4$ ($\text{X} = \text{ClO}_4$ or Cl) have bands at 315, 485 and 340, 510 nm respectively, suggesting relatively strong metal ion-pendant amine interaction in the former case. The band at 485 nm in $[\text{Ni}(\text{diam})(\text{NCS})_2]$ is indicative of relatively strong metal ion-thiocyanate (or metal ion-pendant amine) interaction.

The similarity of the spectra of *b-* complexes with chloride, perchlorate and tetrachlorozincate in water (and analogously for the *a-* complexes) indicates an absence of metal ion-anion interactions in solution. In contrast, the spectrum of $\text{b-}[\text{Ni}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_2$ is different from those of other $\text{b-}[\text{Ni}(\text{diamH}_2)]^{4+}$ complexes, with bands at *ca.* 326, 497 and 340, 510 nm respectively. This is possibly indicative of some axial interaction between the metal ion and thiocyanate, even in solution. (The pendant arm protonation constants which are discussed on page 183 support this).

Molar absorptivities for *cis*- NiN_4X_2 complexes are generally higher than those of *trans*- NiN_4X_2 equivalents. The similar order of magnitude of ϵ for the *a-* and *b-* isomers ($< 20 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) suggests that they both have a *trans* type structure.

Table 19 contains electronic spectral data of selected cyclam type complexes of nickel(II).

Table 19: Electronic Spectra of Selected Nickel(II) Complexes

Complex	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	
[Ni(cyclam)]Cl ₂	1163, 678, 658, 515, 367, 343	1
[Ni(cyclam)](ClO ₄) ₂	650(<1), 448(59), 330(<1)	2
<i>trans</i> I-[Ni(TMC)](ClO ₄) ₂	654(32), 510(70), 391(112)	2
<i>trans</i> III-[Ni(TMC)](ClO ₄) ₂	494(27), 367(10)	2
a-[Ni(diam)](Cl) ₂	974, 925, 685, 586, 494, 328	
b-[Ni(diam)]Cl ₂	860, 790, 485, 315	
[Ni(cyclam)(NCS) ₂]	325(16), 510(10) (chloroform)	3
b-[Ni(diamH ₂)(NCS) ₂] ²⁺	325(16), 497(11.5)	

TMC = 1, 4, 8, 11-tetra-*N*-methylcyclam
 1 = [103], 2 = [256], 3 = [257]

Magnetic Properties

The magnetic moments of selected nickel complexes are given in Table 20.

Table 20: Magnetic Moments of Selected Nickel Complexes at 25°C

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}$	
a-[Ni(diam)]Cl ₂	3.12	
b-[Ni(diamH ₂)Cl ₂]Cl ₂	3.03	
a-[Ni(diamH ₂)](ClO ₄) ₄	0.30	
[Ni(cyclam)Cl ₂]	3.09	[103]
[Ni(2, 3, 2-tet)](ClO ₄) ₂	0.35	[253]
[Ni(2, 3, 2-tet)Cl ₂]H ₂ O	3.10	[236]
[Ni(2, 3, 2-tet)(en)]Cl. 2H ₂ O	3.16	[236]
[Ni(12, 14-Me ₂ cyclam)X ₂]		[257]
X = Cl, Br, NO ₃ , SCN	2.86-3.07	
X = I, PF ₆	0.5-0.6	

The effective magnetic moments for the paramagnetic nickel complexes of 2, 3, 2-tet, cyclam and diam are between

3.03 and 3.16 μ_B . This is lower than those of "normal" octahedral or weakly distorted Ni(II) complexes, which have magnetic moments of around 3.2 μ_B at room temperature. The difference has been attributed to increased tetragonal distortion.

Infrared Spectra

The infrared spectrum of *b*-[Ni(diam)](NCS)₂ has a band at 2014 cm^{-1} assignable to $\nu(\text{CN})$ of coordinated thiocyanate (Ni-NCS) [221]. The absence of splitting is indicative of a *trans*-III complex, which has very similar axial sites. In contrast, there are two bands in this region in the infrared spectrum of *a*-[Ni(diam)-(NCS)₂]; at 2005 and 2050 cm^{-1} , also assigned to $\nu(\text{CN})$ of coordinated thiocyanate (Ni-NCS). The splitting suggests that the two axial sites are different and confirms that the *a*-isomer is not *trans*-III. Two bands are also observed for *cis* NiN_4X_2 complexes. However, a *cis* structure for *a*-[Ni(diam)(NCS)₂] was ruled out because of the similarity of molar absorptivities of the *a*- and *b*- isomers.

The infrared spectrum of *b*-[Ni(diamH₂)](NCS)₄ has bands at 2054 and 2094 cm^{-1} assignable to coordinated (Ni-NCS) and ionic thiocyanate respectively.

Structures

The prepared nickel(II) complexes of diam have pendant arms axially coordinated when isolated from neutral solutions for *a*- or neutral/basic solutions for *b*-, in the absence of competing ligands such as thiocyanate. From acidic solutions, complexes with protonated pendant amines are isolated. These complexes have a square planar geometry for the *a*- isomers and square planar or

tetragonally distorted octahedral with anions or solvent molecules occupying the axial sites for the b- isomer.

The X-ray crystal structures of b-[Ni(diam)](ClO₄)₂, b-[Ni(diam)(NCS)₂] and b-[Ni(diamH₂)](ClO₄)₄ have been determined [172p]. The average equatorial and axial Ni-N lengths of these compounds are listed in table 21. Figure 22 shows the structure of [Ni(diam)](ClO₄)₂ and selected Ni-N bond lengths.

Table 21: The Average Equatorial and Axial Ni-N lengths of Some b- Nickel Complexes of Diam

Compound	Equatorial	Axial
b-[Ni(diam)](ClO ₄) ₂	2.071	2.126
b-[Ni(diam)(SCN) ₂]	2.066	2.128
b-[Ni(diamH ₂)](ClO ₄) ₄	1.96(5)	- 1

1 = unrefined

The b-[Ni(diam)]²⁺ cation was found to be tetragonally distorted with mean Ni-N distances of 2.069 (equatorial) and 2.127 Å (axial). The axial distance is similar for pendant amine and isothiocyanato (M-NCS) coordination in [Ni(diam)(NCS)₂]. The equatorial distances are similar to those of *trans*-[Ni(cyclam)X₂] type complexes, 2.05-2.08 Å, which typically have tetragonal distortions and long axial bonds. The axial bond lengths are similar to the Ni-N distances of [Ni(en)₃]²⁺ complexes (ca. 2.13 Å) [172]. The structure of the a- isomer has not yet been determined.

The structural studies of [Ni(cyclam)Cl₂] [260] and b-[Ni(diam)]Cl₂ have shown that they both have the *trans*-III configuration. The ease with which the chloride, perchlorate, thiocyanate and tetrachlorozincate compounds of b-[Ni(diam)]²⁺ and b-[Ni(diamH₂)]⁴⁺ interconvert indicates that they all have the same (*trans*-III) nitrogen configu-

Figure 22: Structure of $b\text{-}[\text{Ni}(\text{diam})](\text{ClO}_4)_2$

Selected bond lengths:

Ni-N₁ = 2.075 Å

Ni-N₂ = 2.069 Å

Ni-N₃ = 2.071 Å

Ni-N₄ = 2.068 Å

Ni-N₅ = 2.124 Å

Ni-N₆ = 2.127 Å

ration. Minor spectral and structural differences of these compounds are attributable to changes in the steric relationship between the cation and the coordinated and free anion, changes in ligand conformation and the level of tetragonal distortion [7].

Similarly, the ease of interconversion of compounds of the $a\text{-}[\text{Ni}(\text{diam})]^{2+}$ cation suggests that they too have the same ligand configuration. Earlier, it was established that the $a\text{-}$ isomer is not of *cis* NiN_4X_2 type; the solution properties of the $a\text{-}$ compounds and Previous Investigations of Nitrogen Configurations of Cyclam Type Complexes (page 136) strongly suggest that $a\text{-}$ compounds have a *trans*-I geometry.

Evidence for the Existence of the "c- isomer"

The rotary evaporated filtrate of the hydrogenated $[\text{Ni}(\text{dini})]\text{Cl}_2$ solution from which the $a\text{-}$ and $b\text{-}$ isomers of $[\text{Ni}(\text{diam})]^{2+}$ had been removed was dark brown, sticky and hygroscopic. This material was designated crude isomer $c\text{-}[\text{Ni}(\text{diamH}_2)]\text{Cl}_4 \cdot \text{XH}_2\text{O}$. The high solubility of the $c\text{-}$ isomer in water, alcohol and propan-2-ol permitted its separation from the $a\text{-}$ and $b\text{-}$ isomers.

Crystalline isomer $c\text{-}$ was obtained by the addition of sodium thiocyanate or perchloric acid to the sticky brown material dissolved in a minimum volume of water or methanol. Crystals of $c\text{-}[\text{Ni}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ were dark brown and lustrous and could be recrystallized up to five times from hot water or dilute acid without change in appearance or electronic and infrared spectra. The brownish orange perchlorate salt, $c\text{-}[\text{Ni}(\text{diamH}_2)]\text{-}(\text{ClO}_4)_4$ could also be recrystallized many times without change in appearance or spectra. The infrared spectra of compounds of the $c\text{-}$ isomer were different from the spectra of analogous $a\text{-}$ and $b\text{-}$ compounds.

When $c\text{-[Ni(diamH}_2\text{)(NCS)}_2\text{](SCN)}_2$ was boiled with activated charcoal, the dark brown colour was lost and a pinkish purple compound similar in colour to the analogous $a\text{-}$ and $b\text{-}$ complexes was isolated. However, the infrared spectra of the brown and purple thiocyanate compounds of the $c\text{-}$ isomer were almost identical, suggesting that the dark brown colour was due to a strongly coloured impurity.

The protonation constants of $c\text{-[Ni(diamH}_2\text{)]X}_4$ ($X = \text{ClO}_4^-$ and SCN^-) calculated from potentiometric measurements were also distinctly different from those of the $b\text{-}$ analogues.

When $c\text{-[Ni(diamH}_2\text{)]}^{4+}$ was heated in concentrated hydrochloric acid at *ca.* 140°C for about 18 hours, the brown solution turned a greenish brown colour and a white solid was isolated. When propan-2-ol was added to this filtrate, a small amount of brownish cream precipitate was isolated. The infrared spectra indicated that the white solid was the usual *meso*-(diamH_6) Cl_6 . However, the brownish cream precipitate from the filtrate was found to be different with a complex and characteristic infrared spectrum. Like the $c\text{-[Ni(diamH}_2\text{)]}^{4+}$, this " $c\text{-}$ ligand" was highly soluble. The yield was too low for further analysis. The isolation of the *C-meso* ligand from the acid solution of the $c\text{-}$ isomer suggests that the crystalline compounds of $c\text{-[Ni(diamH}_2\text{)]}^{4+}$ were mixtures of $b\text{-}$ and $c\text{-}$ or that most of the $c\text{-}$ isomer converted to the $b\text{-}$ form in concentrated acid at high temperatures.

It is difficult to guess the structure of the $c\text{-}$ isomer because of the limited availability of data; it could be the *rac* isomer, a partially reduced or an entirely different condensation product; however, the elemental analysis suggests that it is an isomer of *diam*.

Electronic Spectral Data

The electronic spectra of the c- complexes were distinctly different from those of a- and b- complexes prepared under identical conditions. The electronic spectral data of a-, b- and c-[Ni(diamH₂)](ClO₄)₄ and b- and c-[Ni(diamH₂)(NCS)₂](SCN)₂ are given in table 22. (The c- compounds were recrystallized five times from dilute acid).

Table 22: Electronic Spectral Data of Thiocyanate and Perchlorate Compounds of a-, b- and c- isomers in Water at 25°C

Complex	$\lambda_{\max}/\text{nm}$ ($\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$)
a-[Ni(diamH ₂)](ClO ₄) ₄	192, 326(7), 453(9), 692(2), 910(2), 990(2)
b-[Ni(diamH ₂)](ClO ₄) ₄	335(10), 506(6), 666(3) 1069(1), 1158(1), 1260(0.5)
c-[Ni(diamH ₂)](ClO ₄) ₄	194, 330, 460, 640 (50°C)
b-[Ni(diamH ₂)(NCS) ₂](SCN) ₂	214, 326(16), 497(11.5)
c-[Ni(diamH ₂)(NCS) ₂](SCN) ₂	215, 321(90), 489(29.5)

The data in table 22 show that the three isomers are distinctly different. The main differences are the presence of the singlet state nickel(II) band at ca. 450 nm in the a- and c- spectra (perchlorate salt) and its absence from the b- spectrum, and the differences in position of the band at ca. 665 nm. The higher values of ϵ in the c- spectrum (thiocyanate salt) could be due to the interference from the high intensity charge transfer band in the ultraviolet region.

Magnetic Properties

The effective magnetic moment of c-[Ni(diamH₂)-(NCS)₂](SCN)₂ was 3.14 μ_B .

Infrared Spectra

The positions of all the main bands in the infrared spectra of a-, b- and c- complexes are different.

The frequencies of $\nu(\text{NH})$ and $\delta(\text{N-H})$ are listed in table 23. The bands of c-[Ni(diamH₂)(NCS)₂](SCN)₂ at 2054 and 2014 cm⁻¹ are assignable to ionic and coordinated thiocyanate (Ni-NCS) respectively.

Table 23: The Frequencies of $\nu(\text{N-H})$ and $\delta(\text{N-H})$ of a-, b- and c-[Ni(diamH₂)]⁴⁺

Complex	$\nu(\text{N-H})$	$\delta(\text{N-H})$
a-[Ni(diamH ₂)](ClO ₄) ₄	3210, 3280	1620, 1540
b-[Ni(diamH ₂)](ClO ₄) ₄	3230, 3410	1610, 1550
c-[Ni(diamH ₂)](ClO ₄) ₄	3080, 3200	1600, 1500
b-[Ni(diamH ₂)(NCS) ₂](SCN) ₂	3030, 3080, 3200, 3230	1615, 1490
c-[Ni(diamH ₂)(NCS) ₂](SCN) ₂	3200	1620, 1585 1510

Structures

An attempt to determine the crystal structure of c-[Ni(diamH₂)](ClO₄) was unsuccessful because the chosen crystal turned out to be one of the b- isomer. (This too supports the theory that crystalline c- isomer contains some b- form).

COPPER(II)

The following copper(II) complexes of diam were synthesized and characterized by elemental analysis, magnetic susceptibility measurements, electronic and infrared spectroscopy; $[\text{Cu}(\text{diamH}_2)]\text{Cl}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, $[\text{Cu}(\text{diam})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 1$ and $6\text{H}_2\text{O}$, $[\text{Cu}(\text{diamH}_2)]\text{Cl}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 2$ and $2\frac{1}{2}\text{H}_2\text{O}$ and $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$. The pendant arm protonation constants of selected copper complexes of diam which were calculated from potentiometric titration curves will be discussed separately (page 181).

Compounds of the cations $[\text{Cu}(\text{diam})]^{2+}$ and $[\text{Cu}(\text{diamH}_2)]^{2+}$ have been reported, with crystal structures [60, 72]. The *C-rac* and *C-meso* forms of $[\text{Cu}(\text{diamH}_2)]^{2+}$ were prepared by the zinc/acid reduction of the condensation product $[\text{Cu}(\text{dini})]^{2+}$. The *C-meso* form was found to be the major product [60]. $[\text{Cu}(\text{diam})]^{2+}$ has also been prepared via an unusual cleavage and macrocyclization reaction [72]. Reduction of [2-methyl-2-nitro-N,N'-bis(pyridin-2-ylmethyl)propane-1,3-diamine]copper(II) with zinc in acid and subsequent recomplexation yielded $[\text{Cu}(\text{diam})](\text{ClO}_4)_2$ as the major product [72]. The single crystal X-ray structure of purple $[\text{Cu}(\text{diam})](\text{ClO}_4)_2$ has shown that the complex is *C-meso-trans*-III and centrosymmetric. The unprotonated pendant amines were on opposite sides of the macrocyclic plane with perchlorate oxygens occupying the axial sites with a Cu-O distance of 2.59 Å. The observed Cu-N distances were 2.022(6) and 1.996(7) Å. Electron spin resonance and electronic spectroscopy defined a square planar geometry in solution with weak axial interactions [72]. The crystal structure of blue *C-meso*- $[\text{Cu}(\text{diamH}_2)]-(\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ was also centrosymmetric and had axial perchlorates, the Cu-O length being 2.523(7) Å. Cu-N

distances were 2.021(5) Å and 2.027(6) Å. The coordination geometry of the copper-diam complexes is very similar to that of $[\text{Cu}(\text{cyclam})](\text{ClO}_4)_2$, which is also centrosymmetric with Cu-N distances of 2.02(4), and 2.02(3) Å and Cu-O of 2.57(4) Å [22a].

It should be noted that the $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ prepared by Lawrance and co-workers was reported as being blue whereas the compound of the same formula prepared in this work was red.

During the course of this work, these cations were prepared by reaction of the isolated C-*meso* ligand, diam with copper(II) chloride or perchlorate. This reaction was rapid, even in 4 mol dm⁻³ hydrochloric acid solutions. Many hydrates of the salts were isolated (with between one and six moles of water per mole of compound). The chloride salts of the protonated and non-protonated cation and the mixed chloride perchlorate salt of the protonated cation were purple. The perchlorate salt of the protonated cation, prepared under concentrated perchloric acid conditions, $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 1$ or $6\text{H}_2\text{O}$ was red.

When $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ was recrystallized from aqueous sodium hydroxide or concentrated aqueous ammonia, a dark ruby coloured complex of the formula $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 2$ or $2\frac{1}{2}\text{H}_2\text{O}$ was obtained. The same compound was prepared by reaction of diam and copper(II) perchlorate in water.

When red $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ was recrystallized from dilute ammonia (pH ca. 9), a mixture of products was obtained. A purple crystalline compound of the formula $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ separated first, and on standing the ruby coloured compound mentioned earlier crystallized from the filtrate. The purple $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ could be heated at 120°C for a prolonged period without change. These purple crystals were also obtained when red

$[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ was recrystallized from aqueous sodium bicarbonate. The presence of just two basic groups in the purple salt was indicated by potentiometric titration results, excluding the possibility of coordinated ammonia or hydroxide. The infrared spectrum of this compound has an unidentified band at *ca.* 1685 cm^{-1} , which is too high for $\delta(\text{N-H})$. The third species was a purple ammine which (sometimes) crystallized from ammoniacal solutions; these crystals probably have coordinated ammonia, which was lost on exposure to the atmosphere, to reform the red (anhydrous?) perchlorate compound.

Electronic Spectra

The Cu(II) ion in an elongated tetragonal octahedral ligand field has a D_{4h} symmetry. The e_g and t_{2g} levels of the 2D free ion term will further split in to B_{1g} , A_{1g} and B_{2g} , E_g levels respectively. Thus, three spin allowed transitions are expected in the visible and near infrared region. These have been assigned to the $^2A_{1g} \leftarrow ^2B_{1g}$, $^2B_{2g} \leftarrow ^2B_{1g}$ and $^2E_g \leftarrow ^2B_{1g}$ transitions in order of increasing energy [261]. Since these transitions occur within the same band envelope with little or no resolution [262], the band at *ca.* 520 nm in the diam complexes is assignable to a combination of these transitions.

The electronic spectral studies of Hathaway have shown that tetragonal or octahedral CuN_6 chromophores have $d-d$ transitions in the region 645-540 nm and those with square planar CuN_4 chromophores have transitions around 555-500 nm [262]. Maxima of the copper complexes prepared during the course of this research (around 520 nm) arise from the CuN_4 chromophore. A similar observation has been made by Lawrance and co-workers for the *rac* and *meso* isomers of $\text{Cu}(\text{diamH}_2)^{4+}$ and the linear analogue (1,9-diammonio-5-methyl-5-nitro-3,7-diazanonane)copper(II),

confirmed by electron spin resonance studies [60]. There is no evidence of coordinating pendant arms, at least in aqueous solution, since spectra in acidic, basic and neutral solutions are similar [60]. In addition, the structural studies of $[\text{Cu}(\text{diam})]^{2+}$ and $[\text{Cu}(\text{diamH}_2)]^{4+}$ show that the axial sites are occupied by the perchlorate oxygens and not by the pendant amines [72]. The pendant amine must approach fairly close to the metal ion before they can axially coordinate [60]. Considering the preference of Cu(II) for elongated axial bonding due to Jahn-Teller effects, it is not surprising that the pendant amines are not coordinated.

The the main electronic spectral bands of selected copper complexes is given in table 24.

The Solvent and Anion Dependency of the Electronic Spectra of Copper(II)-Diam complexes

Electronic spectra of copper complexes of diam are solvent and anion dependant. The shift of the band to longer wavelengths in coordinating solvents such as water and dimethylsulphoxide or in the presence of coordinating anions such as chloride is indicative of axial interactions with the solvent or anion [11]. Electronic spectral data for selected copper(II)-diam complexes, and $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$, in various media are given in tables 25 and 26 respectively.

The results in tables 25 and 26 suggest the following; when chloride ions or DMSO occupy the axial sites of $[\text{Cu}(\text{diamH}_2)]^{4+}$, a λ_{max} of ca. 530 nm and purple solids and solutions are obtained. Water molecules in the axial sites give rise to λ_{max} of ca. 520 nm and purple solids and solutions. When the axial sites are weakly occupied by anions such as sulphate, perchlorate, hydroxide, or nitrate, a λ_{max} of ca. 508-518 nm and

reddish solids and/or solutions are obtained. In non-coordinating solvents such as acetone, axial interactions are weakest; a λ_{max} of 500 nm and a red solution is obtained. Thus, the order of strength of axial interactions with copper(II) appears to be;

Table 24: The Electronic Spectra of Copper(II) Complexes

Complex	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	
[Cu(tet b) blue] ²⁺	833(269), 680(172)	1
[Cu(tet a) blue] ²⁺	649(213)	1
[Cu(tet b) red] ²⁺	524(174)	1
[Cu(tet a) red] ²⁺	510(135)	1
[Cu(2,3,2-tet)] ²⁺	518(51)	1
Cu ²⁺ (aq)	794(11)	1
[Cu(cyclam)](ClO ₄) ₂ (DMF)	520(85)	2
	(water) 503	3
^a [Cu(meni)](ClO ₄) ₂	509(80), 248(4800)	4
^b [Cu(meamH)](ClO ₄) ₃	509(79), 250(5650)	4
^c [Cu(dini)](ClO ₄) ₂	512(69.8), 251(3400)	5
<i>meso</i> -[Cu(diamH ₂)](ClO ₄) ₄	516(69.6), 249(8050) (pH 5)	5
<i>rac</i> -[Cu(diamH ₂)](ClO ₄) ₄	512(70.4), 249(7250) (pH 5)	5
<i>meso</i> -[Cu(diam)](ClO ₄) ₂	516(70), 249(8000)	6
^a meni = 6-methyl-6-nitro-cyclam		
^b meamH = 6-ammonio-6-methyl-cyclam		
^c dini = 6,13-dimethyl-6,13-dinitro-cyclam		
1 = [263(a)], 2 = [263(b)], 3 = [214] 4 = [22a], 5 = [60],		
6 = [72]		

NOTE: [Cu(tet b)blue]²⁺ is in a folded rather than planar coordination, giving rise to 2 *d-d* bands. In the other copper(II) complexes, the ligand is in a planar or distorted planar configuration giving rise to a single absorption maximum.

Since the molar absorptivity of all the Cu(II)-diam complexes are similar (*ca.* $70 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), the nitrogen configuration of these compounds is possibly the same; *trans*-III.

Table 25: Electronic Spectral Data of Selected Cu-diam Complexes in Water ($\emptyset$ refers to $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$)

Complex	Colour		λ_{max}
	(solid)	(solution)	
$[\text{Cu}(\text{diamH}_2)]\text{Cl}_4$	purple	purple	527
$[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_2\text{Cl}_2$ ($\emptyset$ rec in 0.2 M HCl)	purple	purple	524
$[\text{Cu}(\text{diam})](\text{ClO}_4)_2$ ($\emptyset$ rec in strong NH_3 , $\text{pH} > 12$)	ruby	reddish	508
$[\text{Cu}(\text{diam})](\text{ClO}_4)_2$ ($\emptyset$ rec in NH_3 ; $\text{pH} \approx 9$)	purple	purple	523
$[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ ($\emptyset$ in water)	red	purple	520

Table 26: Electronic Spectra of $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ ($\emptyset$) in Various Media

Solvent	λ_{max}
dimethylsulphoxide	531
1M HCl	528
<i>ca.</i> 1M NaCl	528
water	520
<i>ca.</i> 2M Na_2SO_4	518
<i>ca.</i> 1M NaClO_4	515
2M HClO_4	512
1M NaOH	513
2M NaNO_3	508
acetone	500

Magnetic Properties

The effective magnetic moments of the copper(II)-diam complexes are in the range 1.81-1.85 μ_B , typical of copper(II) complexes in the absence of antiferromagnetic coupling. The slight increase above the spin only value of 1.73 μ_B is due to spin-orbit coupling between an orbitally degenerate excited state and the ground state [262].

Infrared Spectra

Significant infrared bands of selected copper complexes are shown in table 27.

Table 27: Infrared Spectra of Selected Copper Complexes

Compound	Main IR bands/cm ⁻¹		
a [Cu(meamH)](ClO ₄) ₃	1614, 1550	δ (NH)	1
	1627(w)	δ (NH)	
b [Cu(meni)](ClO ₄) ₂	1350, 1550	ν (NO ₂)	
[Cu(C-meso-5, 12-Me ₂ cyclam)]-(ClO ₄) ₂	3220, 3180	ν (NH)	
	1100, 628	(ClO ₄ ⁻)	2
[Cu(diamH ₂)](ClO ₄) ₄	3150, 3240	ν (NH)	
	1610, 1535, 1520	δ (NH)	
	1050, 610	(ClO ₄ ⁻)	

a meni = 6-methyl-6-nitro-cyclam

b meamH = 6-ammonio-6-methyl-cyclam

1 = [22a] 2 = [259]

The unsplit perchlorate bands at 1050 and 610 cm⁻¹ confirm the presence of ionic (and the absence of coordinated) perchlorate in (red) [Cu(diamH₂)](ClO₄)₄.

Structures

The crystal structures of $[\text{Cu}(\text{diamH}_2)]^{4+}$ and $[\text{Cu}(\text{diam})]^{2+}$ which have been determined [60,72] were discussed earlier. Although there is some evidence to suggest that all the copper complexes of diam prepared in this work have the same (*trans*-III) configuration (similar values of molar absorptivity), there is also evidence to believe that some of the compounds are non-*trans*-III. For example, distinctly different pendant amine protonation constants were obtained for $[\text{Cu}(\text{diam})]^{2+}$ when protonated and non-protonated salts were used. The values of $\log K$ being 5.28/4.29 for $[\text{Cu}(\text{diam})](\text{ClO}_4)_2$ and 6.68/ 5.70 for $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$. (See page 181). Since it has been suggested that all (planar) nitrogen atoms ~~atoms~~ assume a *trans*-III configuration when equilibrated in basic solutions [254], the "anomalous" compound is probably the red $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ made under concentrated perchloric acid conditions. (However, $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ equilibrated in acid/titrated with base *and* equilibrated in base/titrated with acid gave identical results, as did the nonprotonated salt, $[\text{Cu}(\text{diam})](\text{ClO}_4)_2$. In addition, acid dissociation kinetics of $[\text{Cu}(\text{diamH}_2)]^{4+}$ were very slow, which is typical of *trans*-III complexes (discussed on page 191). These observations suggest that both compounds are *trans*-III).

COBALT(II) AND (III)

The following cobalt(II) and cobalt(III) complexes of diam were synthesized and characterized by elemental analysis, magnetic susceptibility measurements, electronic, infrared, ^{13}C and ^1H nuclear magnetic resonance spectroscopy; $[\text{Co}(\text{diam})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, $[\text{Co}(\text{diam})](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $[\text{Co}(\text{diam})](\text{ClO}_4)\text{Cl}_2$, $[\text{Co}(\text{diam})]_8\text{Cl}_{14}(\text{CO}_3)_5 \cdot 56\text{H}_2\text{O}$, *trans*- $[\text{Co}(\text{diamH}_2)\text{Cl}_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, *trans*- $[\text{Co}(\text{diamH}_2)\text{Cl}_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, *cis*- $[\text{Co}(\text{diamH}_2)(\text{C}_2\text{O}_4)](\text{C}_2\text{O}_4)\text{Cl} \cdot 5\text{H}_2\text{O}$, *trans*- $[\text{Co}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, $[\text{Co}(\text{diamH})\text{Cl}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{diamH}_2)\text{Cl}_2](\text{diamH}_2)_7\text{Cl}_{17} \cdot 28\frac{1}{2}\text{HCl} \cdot 17\text{H}_2\text{O}$, $[(\text{H}_2\text{O})\text{Co}(\text{diam})\text{Co}-\text{O}_2-\text{Co}(\text{diam})(\text{H}_2\text{O})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{diam})(\text{OH})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{II})(\text{diam})](\text{O}_2)\text{Cl}(\text{CoCl}_4)_\frac{1}{4} \cdot 4\frac{1}{2}\text{H}_2\text{O}$ (or $[\text{Co}(\text{II})(\text{diam})]\text{Cl}(\text{CoCl}_4)_\frac{1}{4} \cdot 6\text{H}_2\text{O}$), $[\text{Co}(\text{diam})]\text{Br}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $[\text{Co}(\text{II})(\text{diamH}_2)]\text{Br}_4 \cdot 1$ and $2\frac{1}{2}\text{H}_2\text{O}$, $[\text{Co}(\text{II})(\text{diam})](\text{O}_2)\text{Br}(\text{CoBr}_4)_\frac{1}{4} \cdot 3\text{H}_2\text{O}$ (or $[\text{Co}(\text{II})(\text{diam})]\text{Br}(\text{CoBr}_4)_\frac{1}{4} \cdot 4\text{H}_2\text{O}$) and $\text{Co}(\text{diam})(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$. In addition, a compound which is probably *cis*- $[\text{Co}(\text{diamH}_2)(\text{en})]\text{Cl}_5 \cdot \text{XH}_2\text{O}$ was synthesized and characterized only by infrared spectroscopy.

These cobalt complexes were prepared by reaction of diam with a cobalt(II) salt under aqueous and aerial conditions, unless otherwise stated. By varying the conditions of reaction such as anion, temperature, pH and rate of crystallization a variety of cobalt complexes of diam were obtained.

Under basic conditions (or in the presence of perchloric acid), the yellow octahedrally coordinated cation $[\text{Co}(\text{diam})]^{3+}$ was formed and perchlorate, chloride, bromide, mixed chloride perchlorate and mixed chloride carbonate salts were prepared. This cation was unaffected by prolonged heating in solution with acid, base, cyanide, thiocyanate, nitrite, oxalate or diaminoethane.

From the reaction of cobalt(II) chloride with diam

and concentrated hydrochloric acid under hot aqueous or ethanolic conditions, green *trans*-[Co(diamH₂)Cl₂]Cl₃ was isolated. This compound remained unchanged in hot aqueous or acidic solutions, but under basic conditions is rapidly converted to the yellow hexacoordinated [Co(diam)]³⁺ cation. *Trans*-[Co(diamH₂)Cl₂]Cl₃ was more resistant to hydrolysis in water or acidic solutions than the equivalent *trans*-[Co(en)₂Cl₂]⁺ and *trans*-[Co(cyclam)Cl₂]⁺ cations, probably because of the high charge on the cation [Co(diamH₂)(H₂O)₂]⁵⁺ when water molecules are coordinated. The reaction of this compound with thiocyanate yielded brownish violet *trans*-[Co(diamH₂)(NCS)₂](SCN)₃. The reaction with oxalate and diaminoethane yielded pink *cis*-[Co(diamH₂)(C₂O₄)]Cl(C₂O₄) and a reddish brown compound which could be *cis*-[Co(diamH₂)(en)]Cl₅ respectively. The electronic and infrared spectra of these complexes suggest that they have a folded *cis* configuration. (If the diaminoethane compound does indeed have a *cis* geometry, the charge on the [Co(diamH₂)(en)]⁵⁺ cation is high). Similar *cis* complexes of cyclam have been prepared [264-267].

In general, substitution reactions of the *trans* complexes with monodentate ligands occur with retention of configuration [268]. However, when *trans* complexes are reacted with bidentate ligands, folded *cis* complexes may be obtained.

From the filtrate of the green *trans*-dichloro compound preparation, red crystals of [Co(diamH)Cl]Cl₃ were obtained in low yield (ca. 10%). The same compound was prepared in much higher yield by heating orange [Co(diam)(OH)](ClO₄)₂ (discussed below) in concentrated hydrochloric acid (ca. 75%). ¹H nuclear magnetic resonance data suggest that these compounds have a single pendant amine coordinated and the other uncoordi-

nated. When heated in base, the yellow hexacoordinated $[\text{Co}(\text{diam})]^{3+}$ cation was obtained.

When cobalt perchlorate was reacted with diam in water^{at} room temperature, dark brown, dimeric, diamagnetic, μ -peroxo species, $[(\text{H}_2\text{O})(\text{diam})\text{Co}(\text{III})-\text{O}_2-\text{Co}(\text{III})(\text{diam})-(\text{H}_2\text{O})](\text{ClO}_4)_4$. H_2O was obtained. This compound has a peroxo bridge between two $\text{Co}(\text{III})$ atoms co-ordinated to diam in a *trans* configuration. The presence of the peroxo group was confirmed by decolourization of acidified permanganate.

Atmospheric oxygen absorbing capabilities of ammoniacal solutions of cobalt(II) salts have been thoroughly investigated [269]. Peroxo complexes of cyclam analogous to the above described compound were reported by Bosnich and co-workers [270]. These have been used as intermediates in the syntheses of *trans*- $[\text{Co}(\text{III})(\text{cyclam})\text{XY}]^{n+}$ type complexes.

The electronic spectrum of the $\text{Co}(\text{III})$ μ -peroxo complex of diam in water was poorly resolved because of the intense charge transfer band which gives the peroxo complexes their characteristic brown colour. The band at ca. 420 nm (450 nm for the cyclam analogue) has been assigned to the *d-d* transition $^1\text{A}_2 \leftarrow ^1\text{A}_1$ [270]. (Other bands are masked by the strong charge transfer band).

The infrared spectrum of the μ -peroxo complex does not contain bands assignable to the peroxo group. Bosnich and co-workers have suggested that the O-O stretch is infrared inactive due to the C_{2h} local symmetry of the $\text{Co}-\text{O}_2-\text{Co}$ group [270].

When the μ -peroxo complex was heated in water or perchloric acid, the yellow $[\text{Co}(\text{diam})]^{3+}$ cation was obtained. Unlike the cyclam analogue, the $\text{Co}(\text{III})$ μ -peroxo complex of diam was found to be an unsuitable intermediate for the preparation of *trans*- $\text{Co}(\text{III})$ complexes of diam

because of the high stability of the yellow hexamine cation (even in strong acids). For example, the reaction between the peroxo species and concentrated hydrochloric acid gave a mixture of green *trans*-[Co(diamH₂)Cl₂]Cl₃ and yellow [Co(diam)]Cl₃. These observations provide further proof for the instability of the *trans*-diaquo cation. (Since the reaction with acid yielded some *trans*-dichloro product, the assigned *trans*-diaquo structure of the μ -peroxo species is confirmed).

The reaction between diam and cobalt(II) perchlorate in hot water (without the addition of acid or base), resulted in an orange complex, [Co(diam)(OH)](ClO₄)₂ · H₂O. When heated in base, dimethylsulphoxide or water for prolonged periods, this converted to the yellow [Co(diam)]³⁺ cation. Heating the orange salt in concentrated hydrochloric acid resulted in the red monoprotinated cation, [Co(diamH)Cl]³⁺. The [Co(diam)(OH)]²⁺ cation could not be folded with bidentate ligands such as diaminoethane.

All Co(III) complexes of diam are low spin, with magnetic moments of around 0.6 μ_B , as expected from a d⁶ ion in a strong octahedral field.

Unusual Cobalt Compounds of Diam

During the preparation of cobalt complexes of diam, several unusual compounds which can not be positively identified without crystal structure determination were isolated. In the electronic spectral data discussed, the molar absorptivities in mol⁻¹ dm³ cm⁻¹ are given in parentheses, after the absorption maxima.

(a) [Co(diamH₂)Cl₂](diamH₂)₇Cl₁₇ · 28HCl · 17H₂O

When excess propan-2-ol was added to a solution of cobalt(II) chloride, diam and concentrated hydrochloric acid, a very pale green compound for which analytical

results fit the formula $[\text{Co}(\text{diamH}_2)\text{Cl}_2](\text{diamH}_2)_7\text{Cl}_{17} \cdot 28\frac{1}{2}\text{HCl} \cdot 17\text{H}_2\text{O}$ was isolated (yield was *ca.* 35%). This formula suggests that the green *trans*- $[\text{Co}(\text{diamH}_2)\text{Cl}_2]^{3+}$ cation and many diprotonated diam molecules occur as a complex salt. This compound had a complex infrared spectrum and its electronic spectrum contained four bands of the green *trans*-dichloro complex at 230 (13900), 378 (42), 438 (32) and 620 (25.5) nm as well as two additional bands at 249 (14150) and 311 (1630) nm. When this compound was recrystallized, a slightly darker green compound was obtained, (with accompanying changes in the infrared spectrum), suggesting that some of the diam molecules have dissociated from the cobalt compound. (The infrared spectrum of the darker green compound was also different from that of *trans*- $[\text{Co}(\text{diamH}_2)\text{Cl}_2]\text{Cl}_3$). (This darker green compound was characterized only by infrared spectroscopy).

(b) $[\text{Co}(\text{II})(\text{diam})]\text{Cl}(\text{CoCl}_4)_\frac{1}{2} \cdot 6\text{H}_2\text{O}$ or $[\text{Co}(\text{II})(\text{diam})](\text{O}_2)\text{Cl}(\text{CoCl}_4)_\frac{1}{2} \cdot 4\frac{1}{2}\text{H}_2\text{O}$ and $[\text{Co}(\text{II})(\text{diam})]\text{Br}(\text{CoBr}_4)_\frac{1}{2} \cdot 4\text{H}_2\text{O}$ or $[\text{Co}(\text{diam})](\text{O}_2)\text{Br}(\text{CoBr}_4)_\frac{1}{2} \cdot 3\text{H}_2\text{O}$

The reaction of diam with chloride and bromide salts of cobalt(II) under the same conditions used to prepare the brown Co(III) μ -peroxo perchlorate complex gave rise to paramagnetic, reddish brown crystals that fit the formulae $[\text{Co}(\text{II})(\text{diam})]\text{Cl}(\text{CoCl}_4)_\frac{1}{2} \cdot 6\text{H}_2\text{O}$ or $[\text{Co}(\text{II})(\text{diam})](\text{O}_2)\text{Cl}(\text{CoCl}_4)_\frac{1}{2} \cdot 4\frac{1}{2}\text{H}_2\text{O}$ and $[\text{Co}(\text{II})(\text{diam})]\text{Br}(\text{CoBr}_4)_\frac{1}{2} \cdot 4\text{H}_2\text{O}$ or $[\text{Co}(\text{diam})](\text{O}_2)\text{Br}(\text{CoBr}_4)_\frac{1}{2} \cdot 3\text{H}_2\text{O}$ respectively. (The yield was around 40%). These compounds did not decolourize acidic permanganate, indicating the absence of the peroxo group. The formulae of best fit are those with dioxygen; however, there is no proof for this. Since these complexes are quite stable and can be heated as the solid (at 120°C) for days and in solution for hours with no apparent

change, the presence of dioxygen is doubtful. (However, prolonged heating in solution yielded the yellow $[\text{Co}(\text{III})-(\text{diam})]^{3+}$ cation). Although triplicate atomic absorption results confirmed the presence of $1\frac{1}{2}$ moles of cobalt per mole of compound, the presence of the CoCl_4^{2-} (or CoBr_4^{2-}) anion(s) is questionable because of the colour of the compounds; reddish brown instead of the expected blue colour.

The band at 485 (67) nm in the visible spectrum of the aqueous tetrachlorocobaltate compound are assigned to the ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ transition of $\text{Co}(\text{II})$ in an octahedral environment [271]. The transition that gives rise to the band at 354 (92) nm is uncertain. The charge transfer band occurs at 217 (13700) nm.

The magnetic moment of these complexes (4.01 and 4.06 μ_B for the chloride and bromide salts respectively) are lower than expected for high spin octahedral complexes of $\text{Co}(\text{II})$, typically, 4.7-5.2 μ_B at room temperature. Generally, these values are much higher than expected from the spin only formula (3.87 μ_B) because of high orbital contribution [271]. It should be noted that solid monomeric dioxygen complexes of $\text{Co}(\text{II})$ are generally diamagnetic [272, 273].

It is not obvious why these cobalt(II) compounds are isolated in the presence of halide ions and the cobalt (III) μ -peroxo compound in the presence of perchlorate. Perhaps the coordination of a halide reduces the charge on the cation which favours the electron transfer. When the preparation was carried out in the presence of both chloride and perchlorate, only the $[\text{Co}(\text{diam})]^{3+}$ cation was obtained. (The chloride salt of the $\text{Co}(\text{II})$ -dioxygen complex of diam was recently successfully recrystallized as the perchlorate salt, as yet not analyzed. This was also reddish brown in colour and paramagnetic and had an

infrared spectrum similar to the parent species, apart from the perchlorate band, indicating that only the anion(s) had been changed).

(c) [Co(II)(diamH₂)]Br₄ · 1 or 2½H₂O

During an attempt to prepare *trans*-[Co(III)(diamH₂)-Br₂]Br₃ from heated or unheated aqueous or ethanolic solutions of diam and cobalt(II) bromide, acidified with concentrated hydrobromic acid, an olive yellow compound of the formula [Co(II)(diamH₂)]Br₄ · 1 or 2½H₂O was isolated in high yield. This had electronic spectral bands at 544 (21, sh), 374 (463) and 228 (10100) nm and an effective magnetic moment of 2.04 μ_B, suggesting it is low spin with a square planar geometry. Its nuclear magnetic resonance results were unusual and are discussed on page 169. Axial coordination of bromides is perhaps disfavoured because of greater steric repulsion between the relatively large bromide and the methyl groups and hydrogens. When [Co(II)-(diamH₂)]Br₄ was heated in water or base, the electronic spectrum of this solution indicated the presence of the [Co(III)(diam)]³⁺ cation. Heating the olive yellow compound in hydrochloric acid resulted in the formation of the green *trans*-[Co(III)(diamH₂)Cl₂]³⁺ cation in solution.

(d) Co(diam)(ClO₄)₃ · H₂O

when diam, cobalt(II) perchlorate and perchloric acid (in a 1:1:2 mole ratio) were stirred under nitrogen for four days and then sodium perchlorate and propan-2-ol added, a shiny grey precipitate of the formula Co(diam)-(ClO₄)₃ · H₂O was obtained in high yield. This was diamagnetic, had electronic spectral bands at 390 (800, sh), 304 (6600) and 220(12900) nm and was yellowish in solution. The infrared spectrum suggests that it has a *trans*

geometry. Heating this compound in water for prolonged periods resulted in the formation of the $[\text{Co}(\text{diam})]^{3+}$ cation.

Electronic Spectra

Two spin allowed $d-d$ transitions are expected for octahedral low spin Co(III) complexes, assigned as ${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$ and ${}^1\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$. These bands for $[\text{Co}(\text{diam})]^{3+}$ are at ca. 449 and 325 nm respectively.

The X-ray crystal structure of $[\text{Co}(\text{diam})]^{3+}$ shows that the Co-N bonds are unusually short [172]. (This is discussed further in the Structures section; page 169). The short M-N distances are reflected in the electronic spectrum of $[\text{Co}(\text{diam})]^{3+}$; the bands have shifted to higher energies compared to analogous *tris*-diaminoethane and *sar* complexes. Molar absorptivities are also lower. It has been shown that a complex with longer than average Co-N bond length has electronic spectral maxima at lower energies (longer wavelengths) with larger molar absorptivities [172, 274]. The short Co-N lengths could be forced by the requirements for pendant arm coordination (*i.e.* causing metal ion "compression"). Alternatively, the short bond lengths could indicate that the intra-ligand repulsions in this system are less than the combined inter- and intra-ligand repulsions in other hexaaza Co(III) systems, thus permitting the adoption of more nearly optimal Co-N distances (*i.e.* the Co-N bonds in other systems are "stretched"). This type of high energy shift has been observed in other coordinated pendant arm systems [179].

When the symmetry is lowered to D_{4h} , the terms (${}^1\text{T}_{1g}$ and ${}^1\text{T}_{2g}$) are split and three bands are usually observed. They are ${}^1\text{E}_g^a \leftarrow {}^1\text{A}_{1g}$, ${}^1\text{A}_{2g} \leftarrow {}^1\text{A}_{1g}$ and $({}^1\text{E}_g^b + {}^1\text{B}_{2g}) \leftarrow {}^1\text{A}_{1g}$ [275]. These transitions for *trans*- $[\text{Co}(\text{diamH}_2)\text{Cl}_2]\text{Cl}_3$ occur

at 620, 440 and 379 nm respectively. The analogous cyclam complex has bands at 617, 458 and 387 nm. The band of *trans*-[Co(diamH₂)(NCS)₂](SCN)₃ at 533 nm is assignable to a combination of the first two transitions. For the cyclam analogue, this band occurs at 521 nm [275]. The bands around 200 nm are assigned to charge transfer processes.

Table 28 lists the electronic spectral bands of selected cobalt(III) complexes.

Table 28: Electronic Spectra of Cobalt(III) Complexes of Selected Ligands

Complex	$\lambda_{MAX}/nm(\epsilon/mol^{-1} dm^3 cm^{-1})$	
[Co(diam)] ³⁺	449(70), 329(69)	
[Co(en) ₃] ³⁺	468, 340	1
[Co(sar)] ³⁺	471, 343	1
[Co(NH ₃) ₆] ³⁺	475, 339	2
<i>trans</i> -[Co(NH ₃) ₄ Cl ₂] ⁺	629, 476, 401	2
<i>trans</i> -[Co(cyclam)Cl ₂] ⁺	617(35), 458(24), 387(56)	3
<i>trans</i> -[Co(cyclam)Cl ₂] ⁺	637(32), 441(42), 383	4
<i>trans</i> -[Co(diamH ₂)Cl ₂] ³⁺	620(33), 440(34), 379(50)	
<i>trans</i> -[Co(cyclam)(NCS) ₂] ⁺	521(267)	3
<i>trans</i> -[Co(diamH ₂)(NCS) ₂] ³⁺	533(367)	
[Co(NH ₃) ₅ (H ₂ O)] ³⁺	493, 330	2
[Co(NH ₃) ₅ Cl] ²⁺	534, 468, 364	2
[Co(diamH)Cl]Cl ₃	520(73), 445(45), 354(100)	
<i>cis</i> -[Co(cyclam)(H ₂ O) ₂] ³⁺	506(110), 367(99)	5
<i>cis</i> -[Co(cyclam)(OH) ₂] ⁺	532(120), 374(112)	5
<i>cis</i> -[Co(en)(cyclam)Cl ₂] ⁺	493(145), 353(141)	6
<i>cis</i> -[Co(cyclam)Cl ₂] ⁺	558(105)	5
<i>cis</i> -[Co(cyclam)(NCS) ₂] ⁺	510(392)	5

1=[172], 2=[276], 3=[275], 4=[277], 5=[266], 6=[278]

Infrared Spectra

Poon [268] has shown that *cis* and *trans* isomers of

$[\text{Co}(\text{cyclam})\text{X}_2]^+$ can be identified by the position and number of infrared bands in the CH_2 rocking region ($800\text{--}910\text{ cm}^{-1}$). In general, *cis* complexes have five or more bands spread fairly evenly between 800 and 910 cm^{-1} and *trans* complexes have two bands close to 900 cm^{-1} and one band close to 800 cm^{-1} . The intensities are weaker for *cis* complexes. Table 29 lists the infrared bands in the $800\text{--}910\text{ cm}^{-1}$ region for cobalt complexes of diam. The spectral data suggest that in the absence of bidentate ligands, cobalt(III) complexes of diam adopt a *trans* configuration, as observed.

Table 29: Infrared Bands in the $800\text{--}910\text{ cm}^{-1}$ Region for the Cobalt Complexes of Diam

<u>Complex</u>	<u>Ir bands/cm^{-1}</u>
$[\text{Co}(\text{diam})]\text{X}_3$	800, 830, 855
<i>trans</i> - $[\text{Co}(\text{diamH}_2)\text{Cl}_2]\text{Cl}_3$	875, 900, 910
<i>trans</i> - $[\text{Co}(\text{diamH}_2)(\text{NCS})_2](\text{SCN})_3$	845, 878, 900
<i>trans</i> - $[\text{Co}(\text{diamH})\text{Cl}]\text{Cl}_3$	850, 880, 890
<i>trans</i> - $\text{Co}[(\text{diamH}_2)\text{Cl}_2](\text{diamH}_2)_7\text{Cl}_{17}$	800, 850, 875
<i>trans</i> - $[\text{Co}(\text{diam})(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$	800, 840, 882
<i>trans</i> - $[(\text{H}_2\text{O})(\text{diam})\text{Co}-\mu\text{-O}_2\text{-Co}(\text{diam})(\text{H}_2\text{O})](\text{ClO}_4)_4$	800, 845, 888
$\text{Co}(\text{Diam})(\text{ClO}_4)_3$ (grey)	800, 840, 890
<i>cis</i> - $[\text{Co}(\text{diamH}_2)(\text{en})]\text{Cl}_5$	810, 840, 860, 890, 905
<i>cis</i> - $[\text{Co}(\text{diamH}_2)(\text{C}_2\text{O}_4)](\text{C}_2\text{O}_4)\text{Cl}$	825, 845, 875, 885, 908

^1H and ^{13}C Nuclear Magnetic Resonance Spectra

$[\text{Co}(\text{diam})]\text{X}_3$ complexes

The complexes $[\text{Co}(\text{diam})]^{3+}$ with perchlorate, chloride, bromide and mixed chloride perchlorate and carbonate chloride have similar ^1H and ^{13}C spectra. All protons are deshielded compared with those of uncoordina-

ted diam and all carbon atoms with the exception of the methyl group carbons are deshielded. The deshielding is caused by the introduction of the (electron attracting) cobalt(III) cation. The shielding of the methyl carbons may be an indication of unfavourable steric interaction between the cobalt ion or hydrogens of the macrocyclic ring and the methyl groups, as a result of pendant arm coordination.

Multiplets are observed for a and b protons. (The atom designation in figure 20 is used throughout). All other resonances are singlets. The methyl protons of coordinated diam are always axially oriented. The relatively simple spectra are indicative of the symmetrical environment of the *trans*-III configuration.

The central value of multiplets of these compounds are given in Table 30(a). Also given as a comparison are the ^{13}C spectral data for $[\text{Co}(\text{sar})\text{XY}]^{\text{n}+}$ complexes prepared by Sargeson and co-workers [65], in table 30(b). $[\text{Co}(\text{sar})]^{3+}$ is shown in figure 23.

Table 30(a): ^1H and ^{13}C Data for $[\text{Co}(\text{diam})]\text{X}_3$

$[\text{Co}(\text{diam})]\text{X}_3$

<u>^1H Data</u>	<u>^{13}C Data</u>
3.92 (8 b H's)	65.58 (c C's)
3.22 (8 a H's)	60.73 (b C's)
1.81 (6 CH_3 H's)	54.24 (a C's)
	19.55 (CH_3 C's)

Table 30(b): ^{13}C Data for Selected Sar Complexes. ^{13}C Spectra data for $\text{Co}(\text{sar})\text{XY}^{\text{n}+}$ [65, 66]

	X- <u>C</u> , Y- <u>C</u>	N- <u>CH</u> ₂ - <u>CH</u> ₂ -N	<u>/CH</u> ₂ - X- <u>CH</u> ₂ - , Y- <u>CH</u> ₂ - <u>\CH</u> ₂ -	<u>/CH</u> ₂ - <u>\CH</u> ₂ -	<u>CH</u> ₃ -
(1)	39.7	56.4		51.1	-
(2)	44.8 57.7	56.6	55.9	52.90	22.70
(3)	57.1	55.9		51.8	-
(4)	57.1	55.8		55.8	
(5)	45.6	-	-	-	-

NOTE (1) = X = Y = H
 (2) = X = CH₃ Y = NH₃⁺
 (3) = X = Y = NH₃⁺
 (4) = X = Y = NH₂
 (5) = Co(en)₃

Figure 23: X = Y = H; [Co(sar)]³⁺

The carbon atoms b and c of [Co(diam)]³⁺ are deshielded compared with the equivalent carbons of the sar complexes. This could be indicative of greater strain in the sar complexes at these positions. On the other hand, the a and methyl carbons of [Co(diam)]³⁺ are slightly

shielded with respect to the equivalent atoms of the sar complexes. The upfield occurrence (low δ) of the methyl carbons in the diam complex is probably a result of the steric repulsion between the relatively bulky methyl and pendant amine groups. (Since the methyl group in the analogous sar complex is axially oriented and does not have bulky groups in its vicinity as in the diam complexes, it occurs at a higher value of δ). The higher field occurrence of the $\text{NH-CH}_2\text{-CH}_2\text{-NH}$ carbons in the sar complexes can be attributed to the deshielding effect due to the presence of the extra diaminoethane chain.

^1H and ^{13}C Spectra of Some Cobalt Complexes of Diam

The ^1H and ^{13}C spectral data of various cobalt complexes are given in Table 31. (The central values of multiplets are reported). Most compounds have a single methyl resonance indicating a symmetrical environment of a *trans*-III type structure.

Two methyl resonances are observed in the ^1H and ^{13}C spectra of $[\text{Co}(\text{diamH})]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, compound (3) and $[\text{Co}(\text{diam})(\text{OH})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, compound (5) in table 31. This indicates that the two six membered chelate rings are in different environments, which can be attributed to single pendant arm coordination. Because of unfavourable steric interaction between the the methyl group and the central metal/hydrogens, the ^1H methyl resonance of (3) at 1.82 ppm can be assigned to the methyl group on the chelate ring containing the coordinated pendant amine. The resonance at 2.21 ppm is assignable to the methyl group on the chelate ring containing the free protonated amine. Similarly, the ^{13}C methyl resonances of (5) at 19.58 and 28.06 ppm can be assigned to the methyl groups on the chelate rings that contain the coordinated and free pendant amines respectively.

Table 31: ^1H and ^{13}C Spectra of Cobalt Complexes of Diam

Complex	^1H	assignment	^{13}C	assignment
(1) <i>trans</i> -[Co(diamH ₂)Cl ₂]- Cl ₃ · 2H ₂ O	3.57	b	58.10	c
	3.17	a	54.92	b
	1.98	<u>CH</u> ₃	53.58	a
			23.29	<u>CH</u> ₃
(2) [Co(diamH ₂)Cl ₂]- (diamH ₂) ₇ Cl ₁₇ · 28 $\frac{1}{4}$ HCl · 17H ₂ O	3.40	b	55.24	c
	3.20	a	53.77	b
	1.66	<u>CH</u> ₃	47.56	a
			20.73	<u>CH</u> ₃
(3) [Co(diamH)Cl]Cl ₃ · 2H ₂ O	3.80	b		
	3.27	a		
	2.21	<u>CH</u> ₃	-	-
	1.82	<u>CH</u> ₃		
(4) [Co(II)(diamH ₂)]Br ₄ · 2 $\frac{1}{4}$ H ₂ O	3.70	a/b	64.03	c
	2.11	<u>CH</u> ₃	60.55	b
	2.01	<u>CH</u> ₃	53.54	a
			28.86	<u>CH</u> ₃
			26.43	<u>CH</u> ₃
(5) [Co(diam)(OH)](ClO ₄) ₂ · H ₂ O			63.57	c
			60.77	b
		-	52.28	a
			19.58	<u>CH</u> ₃
			28.06	<u>CH</u> ₃
(6) [Co(II)diam](O ₂)Cl (CoCl ₄) $\frac{1}{2}$ · 4 $\frac{1}{4}$ H ₂ O or [Co(II)(diam)]Cl(CoCl ₄) $\frac{1}{2}$ · 6H ₂ O (T)	3.48(b)	a/b	60.56	c
	1.74(b)	<u>CH</u> ₃	54.07	b
			52.36	a
			19.29	<u>CH</u> ₃

The ^1H and ^{13}C spectra of $[\text{Co}(\text{II})(\text{diamH}_2)]\text{Br}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, compound (4) in table 31 are unusual. The simplicity of these spectra is uncharacteristic of paramagnetic compounds. Also, the chemical shifts of the ^{13}C resonances of (4) are higher than those of the other compounds in table 31. (These observations suggest that the diam is coordinated to a diamagnetic cobalt(III) ion, with paramagnetic cobalt(II) present). ^1H and ^{13}C spectra of (4) contain two resonances assignable to the methyl groups, indicating an unsymmetrical environment.

Splitting is observed in the resonances assigned to a and b protons. H-H coupling via four single bonds commonly found in cyclic and polycyclic systems increase the complexity of the spectra [227]. This type of coupling give rise to coupling constants of 1 Hz or more. All other peaks are singlets.

Structures

The crystal structure of $[\text{Co}(\text{diam})]^{3+}$ has been reported [172]. The cobalt(III) ion was in octahedral coordination, with the pendant arms occupying the axial sites. The equatorial (macrocycle) and axial (pendant) Co-N distances were similar; 1.938(1) Å and 1.946(2) Å respectively. These lengths are shorter than the values reported for analogous cobalt(III) complexes of cyclam (ranging from 1.987(7) to 2.016 Å) and diaminoethane (ca. 1.964 Å). These could be the shortest values reported for a precisely determined cobalt(III) structure [172].

The crystal structure of $[\text{Co}(\text{diam})]^{3+}$ shows that it has the most strain free *trans*-III nitrogen configuration. It is likely that all the *trans* complexes of diam are *trans*-III. The two (possibly) *cis* complexes of diam with oxalate and diaminoethane are likely to have the relatively strain free folded, *cis*-V configuration.

CHROMIUM(III)

The following chromium(III) complexes of diam were synthesized and characterized by elemental analysis, magnetic measurements, electronic and infrared spectroscopy; $[\text{Cr}(\text{diam})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, $[\text{Cr}(\text{diam})](\text{ClO}_4)\text{Cl}_2$, $[\text{Cr}(\text{diamH})(\text{H}_2\text{O})]\text{Cl}_4 \cdot 3\text{H}_2\text{O}$ and $[\text{Cr}(\text{diamH})(\text{H}_2\text{O})\text{Cl}(\text{ClO}_4)_3] \cdot 2\frac{1}{2}$ and $3\frac{1}{2}\text{H}_2\text{O}$.

The yellow hexamine $[\text{Cr}(\text{diam})]\text{Cl}_3$ was prepared by heating diam with anhydrous chromium(III) chloride in dimethylsulphoxide. This was recrystallized from hot water or unheated dilute hydrochloric acid. The mixed perchlorate chloride salt of $[\text{Cr}(\text{diam})]^{3+}$ was prepared by recrystallizing $[\text{Cr}(\text{diam})]\text{Cl}_3$ from dilute, unheated perchloric acid.

When $[\text{Cr}(\text{diam})]\text{Cl}_3$ was recrystallized from hot dilute hydrochloric or perchloric acid, orange monoprotonated $[\text{Cr}(\text{diamH})]\text{X}_4$ was obtained. (This reaction also took place at room temperature within days). This is in contrast with the behaviour of the analogous $[\text{Co}(\text{diam})]^{3+}$ cation which remained unchanged when heated in acid. The electronic spectral data (discussed below) showed that the axial site vacated by the uncoordinated pendant arm in the orange monoprotonated complex is occupied by a water molecule rather than a chloride ion. Complexes with two protonated pendant arms were not obtained, even in the presence of concentrated acid. (If this could be brought about, it is unlikely that the compound would be a diaquo species, because of the high resultant charge on the $[\text{Cr}(\text{diamH}_2)(\text{H}_2\text{O})_2]^{5+}$ cation). When the orange pentamine complexes were heated in basic solution, they readily converted to the yellow hexamine.

The tendency of chromium(III) complexes of cyclam to adopt a *cis* configuration is in marked contrast to the behaviour for cobalt(III), where a *trans* configuration is

usually adopted [279]. On the other hand, tet a (*meso*-1,7-CTH) gives a variety of *trans* complexes with chromium whereas tet b (*rac*-1,7-CTH) tends to produce complexes of *cis* configuration. This is because tet b can readily fold to give *cis*-octahedral compounds whereas tet a tends to adopt a planar coordination of the nitrogens because of unfavourable steric interaction between the axial methyl groups and the ligands occupying the axial positions [280]. In the case of $[\text{Cr}(\text{diam})]^{3+}$ and $[\text{Cr}(\text{diamH})]^{4+}$, the presence of potentially axial-coordinating pendant amines and the C-*meso* disposition of the methyl groups favour *trans* configurations.

Electronic Spectra

By comparing the electronic spectra of nonprotonated and monoprotonated chromium(III) complexes of diam and analogous *trans* chromium(III) cyclam complexes prepared by Kane-Maguire and co-workers [281], a *trans* configuration can be assigned to the Cr-diam compounds. In addition, the similarity between *trans*- $[\text{Cr}(\text{cyclam})(\text{NH}_3)(\text{H}_2\text{O})]^{3+}$ and the monoprotonated chromium complex of diam (339, 409 and 477 nm compared with 340, 406 and 480 nm respectively) suggests that the free axial position of the diam complex is occupied by a water molecule rather than a chloride. The electronic spectral values of various chromium(III) complexes of linear, cyclic and polycyclic amine/ammine ligands are given in table 32.

Three ligand field bands can be expected from a d^3 ion in an octahedral field. The bands of chromium(III) complexes of diam at ca. 490, 420 and 340 nm can be assigned to ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$, ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_{2g}$ transitions respectively. As observed with typical *trans* isomers of chromium(III)-ammine/amine compounds [280], the molar absorptivities of the chromium complexes

of diam are low; less than $50 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. (The *cis* isomers are known to have much higher molar absorptivities; generally between 70 and $200 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

Table 32: Electronic Spectra of Selected Chromium(III) Complexes

Complex	$\lambda_{\text{max}} (\epsilon / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$	
$[\text{Cr}(\text{diam})]\text{Cl}_3$	335(44), 429(50), 500(16, sh)	
$[\text{Cr}(\text{diamH})(\text{H}_2\text{O})]^{4+}$	340(34, sh), 406(43, b), 480(26, sh)	
<i>trans</i> - $[\text{Cr}(\text{cyclam})(\text{NH}_3)_2]^{3+}$	334(50), 420(36), 445(32, sh)	1
<i>trans</i> - $[\text{Cr}(\text{en})_2(\text{NH}_3)_2]^{3+}$	347(37), 454(47)	1
<i>trans</i> - $[\text{Cr}(\text{cyclam})(\text{NH}_3)(\text{H}_2\text{O})]^{3+}$	339(41), 409(28), 477(23)	1
<i>trans</i> - $[\text{Cr}(\text{cyclam})\text{Cl}_2]^+$	572(19.9), 407(35), 365(41)	2
<i>cis</i> - $[\text{Cr}(\text{cyclam})\text{Cl}_2]^+$	529(111), 404(106)	2
$[\text{Cr}(\text{III})\text{diamsar}]^{3+}$	346(109), 447(208), 456(203), 642, 647(0.6), 663(0.5), 685(0.8)	3
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	351(33), 463(39)	1
$[\text{Cr}(\text{en})_3]^{3+}$	350(61), 456(76)	1

1 = [281] 2 = [280] 3 = [69]

The energy of the lowest energy (longest wavelength) *d-d* band is proportional to the ligand field strength [282] (*i.e.* higher the energy, shorter the wavelength, higher the ligand field strength). The lowest energy bands of $[\text{Cr}(\text{diam})]^{3+}$ and *trans*- $[\text{Cr}(\text{diamH})(\text{H}_2\text{O})]^{4+}$ occur at 500 and 480 nm respectively. The analogous cyclam complexes, *trans*- $[\text{Cr}(\text{Cyclam})(\text{NH}_3)_2]^{3+}$ and *trans*- $[\text{Cr}(\text{cyclam})(\text{NH}_3)(\text{H}_2\text{O})]^{3+}$ have lowest energy bands at 445 and 477 nm respectively. The low energy shift of $[\text{Cr}(\text{diam})]^{3+}$ complex suggests that its ligand field strength is less than that of the analogous cyclam complex. This is probably caused by longer Cr-N bonds in the chromium(III)-diam system and also explains why the

pendant arms can be dissociated easily in acidic solutions. This behaviour is in contrast with that observed for $[\text{Co}(\text{diam})]^{3+}$; this cation was found to contain short Co-N bonds, its electronic spectrum showed a high energy shift and it remained unchanged in hot acidic solutions [172]. The comparison with the chromium system suggests that the short bonds and the high energy shift in the cobalt system is because of a lower level of repulsion resulting in near optimal Co-N lengths (higher ligand field strength) rather than the alternative reasoning of metal ion compression. The similarity of the low energy bands of monoprotonated *trans*- $[\text{Cr}(\text{diamH})(\text{H}_2\text{O})]^{4+}$ and its cyclam analogue (480 and 477 nm respectively) is indicative of similar levels of ligand field strengths and strain in the two systems.

Magnetic Properties

The effective magnetic moments of the chromium(III) complexes of diam (3.86-3.94 μ_B) are close to the spin-only value for three unpaired electrons (3.87 μ_B).

Infrared Spectra

Further support for the *trans* assignment can be found in the CH_2 rocking frequency region (800-950 cm^{-1}) of the infrared spectra of the chromium complexes. It is known that *cis* complexes with a C_{2v} point group have four or five main bands in this region whereas *trans* (D_{4h}) compounds have only two or three [268, 283-285]. The diam complexes of chromium show three major bands in this region; at ca. 820, 840 and 895 cm^{-1} , confirming the assigned *trans* configuration.

Structures

It is most likely that all the chromium(III) complexes of diam have the *trans*-III nitrogen configuration. (The same was assumed for the *trans*-chromium(III) complexes of tet a [280]).

PALLADIUM(II)

The following palladium(II) complexes of diam were synthesized and characterized by elemental analysis, magnetic measurements, electronic and infrared spectroscopy; $[\text{Pd}(\text{diamH}_2)]\text{Cl}_3(\text{PdCl}_4)\frac{1}{2} \cdot 2\frac{1}{2}\text{H}_2\text{O}$, $[\text{Pd}(\text{diam})]_2(\text{PdCl}_4)\frac{1}{2}\text{Cl}_3$, $[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ and $[\text{Pd}(\text{diam})](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$. The pendant arm protonation constants for $[\text{Pd}(\text{diam})]^2$ will be discussed separately (page 182).

The reaction between PdCl_4^{2-} and diam in hot aqueous solution yielded golden brown $[\text{Pd}(\text{diamH}_2)]\text{Cl}_3(\text{PdCl}_4)\frac{1}{2} \cdot 2\frac{1}{2}\text{H}_2\text{O}$. When this was recrystallized from aqueous ammonia, pale yellow crystals of $[\text{Pd}(\text{diam})]_2(\text{PdCl}_4)\frac{1}{2}\text{Cl}_3$ were obtained. When $[\text{Pd}(\text{diamH}_2)](\text{PdCl}_4)\frac{1}{2}\text{Cl}_3$ was recrystallized in aqueous perchloric acid, the ivory coloured salt $[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4$ was obtained. The non protonated perchlorate salt, $[\text{Pd}(\text{diam})](\text{ClO}_4)_2$ was prepared by recrystallizing the the latter from dilute aqueous ammonia.

Electronic Spectra

The electronic spectra of the protonated palladium salts are listed in table 33.

Table 33: Electronic Spectra of Selected Palladium-diam Complexes

Complex	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)
$\text{Pd}(\text{diamH}_2)]\text{Cl}_3(\text{PdCl}_4)\frac{1}{2}$	391(640), 195(sh, 18600)
$[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4$	276(479), 200(20900)

The band at 276 nm of $[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4$ is assigned to the ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$ transition of square planar, (low spin) d^8 Pd(II) complexes [286]. In $\text{Pd}(\text{diamH}_2)]\text{Cl}_3(\text{PdCl}_4)\frac{1}{2}$, this transition is masked by the tetrachloro-palladate anion which has high intensity bands at ca. 435,

333 and 278 nm. The charge transfer band of $[\text{Pd}(\text{diamH}_2)]^{4+}$ occurs at ca. 200 nm. The molar absorptivities are large in spite of the Laporte selection rule because of extensive mixing of the metal d and ligand orbitals and their proximity to the charge transfer bands [286].

Magnetic Properties

These compounds are of square planar geometry and are low spin. $[\text{Pd}(\text{diamH}_2)](\text{ClO}_4)_4$ had a magnetic moment of 0.41 μ_B .

Infrared Spectra

The infrared spectra of the perchlorate compounds contained unsplit bands at ca. 1080 and 615 cm^{-1} assignable to ionic perchlorate.

Structures

It is likely that the prepared palladium complexes have a *trans*-III nitrogen configuration, as observed with analogous cyclam complexes [287]. However, recently, Shröder and co-workers reported the single crystal X-ray structures of $[\text{Pd}(\text{II})(\text{tbc})]^{2+}$ (tbc=1, 4, 8, 11-tetrabenzyl-cyclam) and $[\text{Pd}(\text{tmc})]^{2+}$ (tmc=1, 4, 8, 11-tetramethyl-cyclam) cations [289, 290]. Both cations showed a square planar stereochemistry with a *trans*-I nitrogen configuration.

RHODIUM(III)

The following rhodium(III) complexes of diam were synthesized and characterized by elemental analysis, electronic, infrared and nuclear magnetic resonance spectroscopy; $[\text{Rh}(\text{diam})]_2\text{Cl}_5(\text{ClO}_4) \cdot 7\text{H}_2\text{O}$ and $[\text{Rh}(\text{diam})]_3(\text{ClO}_4)_5(\text{ZnCl}_4)_2 \cdot 3\text{H}_2\text{O}$.

The yellow octahedral $[\text{Rh}(\text{diam})]^{3+}$ cation was formed when diam and rhodium(III) chloride were refluxed in water or methanol.

Electronic Spectra

The electronic spectral bands of selected complexes of rhodium are listed in table 34.

Table 34: Electronic Spectra of Selected Rhodium Complexes

Complex	λ_{max} ($\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	
$[\text{Rh}(\text{NH}_3)]_6^{3+}$	306, 256	1
$[\text{Rh}(\text{diam})]^{3+}$	340(sh), 207(30460)	
<i>cis</i> - $[\text{Rh}(\text{cyclam})\text{Cl}_2]$	354(223), 299(308), 207(33900)	2
<i>trans</i> - $[\text{Rh}(\text{cyclam})\text{Cl}_2]$	408(78) 310(80), 242(3300) 204(37100)	2

1 = [291] 2 = [292]

The band at 340 nm in the electronic spectrum of $[\text{Rh}(\text{diam})]^{3+}$ is assignable to a combination of the transitions ${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$ and ${}^1\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$. The high energy band at 207 nm is assigned to charge transfer or parity allowed transitions of the ligand.

Infrared Spectra

The number of bands in the CH_2 rocking region of the infrared spectra of rhodium compounds of cyclam type ligands can be used to differentiate between *cis* and *trans*

geometries [292]. The CH_2 rocking modes appear as single and double bands for *trans* and *cis* complexes respectively. The single CH_2 band at 840 cm^{-1} in $[\text{Rh}(\text{diam})]^{3+}$ is indicative of a *trans* configuration. (However, the infrared spectral bands of rhodium compounds of diam were quite broad and additional bands may have been masked). The unsplit bands at 1085 and 620 cm^{-1} were assignable to ionic perchlorate.

^1H Nuclear Magnetic Resonance Spectra

The ^1H nuclear magnetic resonance spectral data for the diam complex of rhodium were inconclusive because of poor resolution. The only information that could be obtained was the axial orientation of the methyl groups.

Structures

Many *cis* and *trans* complexes of $[\text{Rh}(\text{cyclam})]^{3+}$ have been prepared [292, 230]. Generally, the geometry of these complexes can be deduced from the nuclear magnetic resonance, electronic and infrared spectral data [292, 230]. However, it is not certain whether $[\text{Rh}(\text{diam})]^{3+}$ has the macrocycle in *trans*-planar or *cis* folded configuration because of the poor resolution in the ^1H resonance data, broadening of infrared bands and the lack of comparable electronic spectral data. If the $[\text{Rh}(\text{diam})]^{3+}$ cation does have a *trans* geometry, coordination of the pendant amines is likely.

ZINC(II)

A zinc complex of diam which best fits the formula $[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot 2\text{H}_2\text{O}$ was prepared by the reaction of diam and zinc chloride in aqueous solution. The complex was characterized by elemental analysis, infrared and nuclear magnetic resonance spectroscopy. It was highly insoluble in water and rapidly hydrolysed in dilute acid.

Infrared Spectra

The infrared spectrum of $[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot 2\text{H}_2\text{O}$ contains a band at 3590 cm^{-1} assignable to free OH.

Nuclear Magnetic Resonance Spectra

The ^1H and ^{13}C spectra of $[\text{Zn}(\text{diam})](\text{OH})(\text{Zn}_2\text{Cl}_5) \cdot 2\text{H}_2\text{O}$ contained single axially oriented methyl resonances at 1.72 and 23.92 ppm respectively.

Structures

Five or six coordinate zinc complexes of cyclic tetramines bound to four nitrogens in a planar arrangement often have the zinc coordinated out of plane [293-296]. This out of plane displacement causes quite large inequalities in the axial bond lengths [293]. The reasons for the adoption of this type of structure can not be explained by simple cation-"ligand-hole size" arguments. Ito and co-workers [293] have suggested that subtle inter- and intra-molecular forces are responsible for these out of plane structures.

The nuclear magnetic resonance data suggest that the zinc complex of diam could not have this type of structure. The ^1H and ^{13}C spectral data indicate that the two six membered chelate rings of the macrocycle are equivalent, suggesting a *trans*-III configuration, with the zinc coordinated in plane.

CADMIUM(II) AND LEAD(II)

The cadmium(II) complex $\text{Cd}(\text{diam})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and the lead(II) complexes that best fit the formulae $[\text{Pb}(\text{diamH}_3)](\text{CH}_3\text{COO})_3(\text{ClO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ and $[\text{Pb}(\text{diamH}_3)](\text{diamH}_3)_4(\text{NO}_3)_{17} \cdot 8\text{H}_2\text{O}$ were prepared by the reaction of diam with cadmium chloride and lead acetate or nitrate respectively in aqueous solution. Acetic acid was added to neutralize the ligand during the preparation of the lead complex to avoid the formation of lead hydroxide. These complexes were characterized by elemental analysis and infrared spectroscopy. These salts undergo rapid hydrolysis in acidic solutions.

Infrared Spectra

The infrared spectrum of $[\text{Pb}(\text{diamH}_3)](\text{CH}_3\text{COO})_3(\text{ClO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ has bands assignable to protonated amine and acetate stretches at 1560 cm^{-1} , additional acetate bands at 1320 and 1335 cm^{-1} , and unsplit ionic perchlorate bands at 1070 and 615 cm^{-1} . The spectrum of $[\text{Pb}(\text{diamH}_3)](\text{diamH}_3)_4(\text{NO}_3)_{17} \cdot 8\text{H}_2\text{O}$ contains bands at 1390 , 850 and 720 cm^{-1} assignable to ionic nitrate.

Structures

Complexes of cyclam with larger metal ions such as lead(II), mercury(II) and cadmium(II) which have ionic radii of 1.20 , 1.10 and $0.97\text{ \AA}$ respectively have been investigated [85, 96, 297, 298]. Planar coordination of cyclam type ligands requires an optimum M-N distance of $2.07\text{ \AA}$ [91]. This distance corresponds to a metal ionic radius of $0.65\text{--}0.7\text{ \AA}$. (Small deviations from this range can be accommodated by the flexibility of the macrocycle). In general, planar coordinated first row transition metal ions produce a *trans*-III configuration. With large

ions, the structures adopted are a compromise between the strain free *trans* geometry and cavity overcrowding [298]. The very large lead(II) ion tends to adopt a folded *cis* octahedral type structure with cyclam whereas the smaller mercury(II) and cadmium(II) prefer a *trans*-I structure, rather than the more common *trans*-III. The former has the advantage of allowing the metal ion to sit above the N_4 plane, thus minimizing the level of constriction.

It is possible that the diam complex of cadmium is of *trans*-I configuration. The lead complexes on the other hand could be folded. This is particularly feasible since both lead complexes of diam have three out of the six potentially coordinating nitrogens protonated. The C, H, N, Cl and Pb analyses of $[Pb(diamH_3)](diamH_3)_4(NO_3)_{17} \cdot 8H_2O$ suggest that it has a rather unusual structure.

PROTONATION CONSTANTS

The pendant amine protonation constants of diam, b- and c-[Ni(diam)]²⁺, b- and c-[Ni(diam)(NCS)₂]²⁺, [Cu(diam)]²⁺ and [Pd(diam)]²⁺ were calculated from potentiometric titration results using the Gilbert Herron Method [215]. The following salts were used; (diam). 3½H₂O, (diamH₆)Cl₆. 2H₂O, b-[Ni(diam)]Cl₂. 6H₂O, b-[Ni(diamH₂)-(H₂O)₂]Cl₄. 2H₂O, b-[Ni(diamH₂)](ClO₄)₄. 6H₂O, b-[Ni(diamH₂)NCS)₂](SCN)₂. ½H₂O, c-[Ni(diamH₂)(NCS)₂](SCN)₂. 3H₂O, c-[Ni(diamH₂)](ClO₄)₄, [Cu(diam)](ClO₄)₂. 2H₂O (ruby coloured), [Cu(diamH₂)](ClO₄)₄. H₂O and [Pd(diamH₂)](ClO₄)₄. 5½H₂O.

The accurately weighed salts were dissolved in 0.1 mol dm⁻³ sodium perchlorate solution to which a known volume of standard hydrochloric acid was added. These solutions were equilibrated at 25°C, protected from the atmosphere by a stream of nitrogen and potentiometrically titrated with carbonate free standard sodium hydroxide.

Protonation Constants of Amine Ligands

The following general conclusions concerning protonation constants of linear and cyclic tetramines have been drawn [299]. All amines exhibit higher basicity for the first two protonation steps than for the following steps. Basicity of the first two steps of macrocycles is higher than those of the related linear tetramines. This has been attributed to the formation of intramolecular hydrogen bonds N...H-N⁺ in cyclic amines and the binding of protonated nitrogens to water molecules through hydrogen bridges O...H-N⁺ in linear tetramines. Third and fourth protonation (or basicity) constants of tetraazamacrocycles are lower than those of analogous linear species because of the proximity of the NH₂⁺ groups resulting in strong

electrostatic repulsions in the former case.

Diam exhibited two high and two low protonation constants ($\log K$); 11.20/9.70 and 6.2/5.30 respectively. The high and low values are (probably) assignable to the protonation of the pendant amines and two diagonally opposite nitrogens in the diam macrocycle respectively. The last two values of $\log K$ (arising from the protonation of the remaining nitrogens) were too low (<2) to be determined, presumably because of large electrostatic repulsions.

Table 35 lists the protonation constants of selected cyclic and linear amines.

Table 35: Protonation Constants of Selected Cyclic and Linear Amines at 25°C

Ligand	I/Mol dm ⁻³	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	
cyclam	0.5 (KNO ₃)	11.59	10.62	1.61	2.42	[299]
tet a	0.1 (NaNO ₃)	11.9	10.6	2.4	2.1	[300]
[12]aneN ₄	0.5 (KNO ₃)	10.97	9.87	<2	<2	[302]
[13]aneN ₄	0.5 (KNO ₃)	11.19	10.12	<2	<2	[302]
2,3,2-tet	0.5 (KNO ₃)	10.30	9.57	7.18	5.66	[301]
trien	0.5 (KNO ₃)	10.02	9.39	7.00	4.00	[302]
¹ aetc	0.5 (KNO ₃)	10.39	9.63	8.10	3.16	[156]
diam	0.1 (NaClO ₄)	11.20	9.7	6.2	5.30	
¹ aetc = 1-(2-aminoethyl)-4,8,11-trimethyl-cyclam						

Protonation Constants of the Metal Complexes of Diam

Because of the tendency of palladium complexes to adopt a square planar geometry with uncoordinated pendant arms, the pendant arm protonation constants of [Pd(diam)]²⁺ were expected to be higher than those for the other metal complexes studied. The values obtained, 6.08 and 5.10 were higher than those of "normal" complexes of copper and nickel. (The meaning of "normal" will be explained below).

The b-nickel complexes were expected to give the lowest protonation constants because of their tendency to adopt an octahedral geometry with coordinated pendant arms. The titration results for b-[Ni(diam)]Cl₂, b-[Ni(diamH₂)]Cl₄ and b-[Ni(diamH₂)](ClO₄)₄ gave similar log K values of 4.50 and 3.95. (Similar values are expected since they all form [Ni(diamH₂)(H₂O)₂]⁴⁺ in acidic solution with little axial interaction between the central nickel and anions). However, b-[Ni(diamH₂)(NCS)₂](SCN)₂ gave log K values of 5.08 and 4.88. The difference can be attributed to the presence of the thiocyanate anions which compete with the pendant arms for axial coordination. This was confirmed by repeating the titration of b-[Ni(diamH₂)]Cl₄ in the presence of four moles of thiocyanate, which gave protonation constants identical to b-[Ni(diamH₂)(NCS)₂](SCN)₂. Support for axial interaction between the nickel centre and the thiocyanate can be found in the electronic spectra of these compounds (discussed earlier; page 138). (The acid dissociation constant of thiocyanic acid is 0.85 at 25°C [303]. Since this value is high, the large protonation constants of the thiocyanate compounds cannot be attributed to thiocyanic acid formation).

The pendant amine protonation constants measured for b- and c-[Ni(diamH₂)](ClO₄)₄ and [Ni(diamH₂)(NCS)₂](SCN)₂ are listed in table 36.

Table 36: The Protonation Constants of Perchlorate and Thiocyanate Salts of b- and c- [Ni(diam)]⁴⁺

<u>Salt Used</u>	<u>log K₁</u>	<u>log K₂</u>
b-[Ni(diamH ₂)(NCS) ₂](SCN) ₂	5.08	4.88
c-[Ni(diamH ₂)(NCS) ₂](SCN) ₂	6.17	4.91
b-[Ni(diamH ₂)](ClO ₄) ₄	4.50	3.91
c-[Ni(diamH ₂)](ClO ₄) ₄	5.73	3.94

It should be noted that the $\log K_1$ values of analogous b- and c- isomers are quite different (the c- value is about 1.1 units higher than the b- value) whereas the $\log K_2$ values are very similar. This can be attributed to the apparent tendency of the c- complexes to form square planar species in solution, as observed in the electronic spectra of c-[Ni(diamH₂)]⁴⁺ salts. The thiocyanate effect is also observed in the c- system. This data provide evidence for the existence of the c- isomer.

The copper complexes were expected to have protonation constants higher than those of nickel complexes because of the tendency of copper to form square planar or tetragonally distorted complexes with weakly bound axial perchlorates and uncoordinated pendant arms. However, they were expected to be below the palladium values because of the even weaker tendency of palladium to form tetragonal compounds. The protonation constants for [Cu(diam)](ClO₄)₂, 5.28 and 4.29 conformed with this expectation. However, the protonation constants for [Cu(diamH₂)](ClO₄)₄ (6.68 and 5.70) were unexpectedly high; significantly higher than those of the palladium complexes. This suggests that the two copper complexes are two different isomers; it is possible that the latter is a *trans*-I complex. This would explain its tendency to adopt a square planar geometry (perhaps with extremely weak axial perchlorate interactions). On the contrary, when [Cu(diamH₂)](ClO₄)₄ was equilibrated in base and titrated with acid, a titration curve identical to the acid equilibrated, base titrated results was obtained. Since it has been suggested that planar coordinated metal complexes of cyclam-type ligands assume the *trans*-III configuration upon equilibration in basic media [254], the possibility of [Cu(diamH₂)](ClO₄)₄ having a planar, non-*trans*-III configuration is remote. (The acid equilibrated, base titrated and base equili-

brated, acid titrated results for $[\text{Cu}(\text{diam})](\text{ClO}_4)_2$ were also the same).

For the "normal" b- nickel complexes (which do not contain competing ligands such as thiocyanate), the "normal" copper complex (which is of known geometry; *trans*-III) and the palladium complex, the order of tendency to form square planar compounds is $\text{Pd} > \text{Cu} > \text{Ni}$, as expected.

KINETICS

Isomerization and Hydrolysis of $a\text{-[Ni(diamH}_2\text{)]}^{4+}$

The compounds of $[\text{Ni(diamH}_2\text{)}]^{4+}$ are stable as the solids, however, in solution the a - isomer changes to the b - form. In aqueous, neutral salt or dilute hydrochloric acid solution, $a\text{-[Ni(diamH}_2\text{)]}^{4+}$ occurs mainly as the yellow singlet ground state nickel(II) species while the b - isomer occurs as the pink, triplet ground state diaquo species. Hence, the inversion reaction produces a significant change in the electronic spectrum. In basic solutions, both, a - and $b\text{-[Ni(diam)]}^{2+}$ occur as the pink triplet state nickel(II) species with similar electronic spectra. However, the addition of a small volume of concentrated hydrochloric acid (ca. pH 1) results in the reformation of yellow singlet state $a\text{-[Ni(diamH}_2\text{)]}^{4+}$ but not the analogous b - form. Hence, the rate of the $a \rightarrow b$ - conversion in acidic, basic and salt solutions be followed spectrophotometrically.

The isomerization reaction in basic, neutral salt and acidic solutions at 50°C was monitored at 453 nm, the band maximum for singlet ground state $a\text{-[Ni(diamH}_2\text{)]}^{4+}$.

In base, this reaction is rapid, as is typical of such inversion reactions which proceed by an internal conjugate base mechanism, in which the hydroxide ion deprotonates an amine and generates an intermediate that rearranges rapidly [203]. The observed rate constant for the inversion reaction in 0.1 mol dm⁻³ sodium hydroxide was $2.0(3) \times 10^{-2} \text{ s}^{-1}$.

The rate of this reaction in 2 mol dm⁻³ sodium chloride and 2 mol dm⁻³ sodium nitrate were $5.0(5) \times 10^{-5}$ and $5.6(5) \times 10^{-5} \text{ s}^{-1}$ respectively, indicating no appreciable specific salt effect.

The reaction rates in 0.1-2.0 mol dm⁻³ hydrochloric

acid were also measured, maintaining the ionic strength at 2 mol dm^{-3} with sodium chloride. The rate was found to be dependant on acid concentration. The plot of the observed first order rate constant versus acid concentration (Figure 21) shows an approximately linear relationship between 0.1 and 1 mol dm^{-3} with curvature indicating saturation kinetics beyond 1.0 mol dm^{-3} . The rate in 0.1 mol dm^{-3} acid ($2.80 \times 10^{-5} \text{ s}^{-1}$) was less than in the sodium chloride solution because of the appreciable base catalyzed reaction in this solution.

Billo has studied the ~~the~~ isomerization of *cis*- $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ to *trans*- $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ over the pH range 1-10 [203]. The reaction was acid catalyzed between pH 1-3, and base catalyzed between pH 4-10. The rate law for isomerization was;

$$K_{\text{obs}} = K_0 + K_{\text{H}}[\text{H}_3\text{O}^+] + K_{\text{OH}}[\text{OH}^-].$$

The rate constants were $K_0 = 1.5 \times 10^{-8} \text{ s}^{-1}$, $K_{\text{H}} = 5.8 \times 10^{-6} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $K_{\text{OH}} = 560 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 25°C and $I = 0.10 \text{ mol dm}^{-3} \text{ NaClO}_4$. Hay and Akbar Ali have studied the conversion of blue *cis*- $[\text{Ni}([13] \text{ aneN}_4)(\text{OH}_2)_2]^{2+}$ to yellow planar $[\text{Ni}([13] \text{ aneN}_4)]^{2+}$ which was also base catalysed [304]. The reaction was first order in hydroxide and first order in the complex with the rate law;

$$\text{rate} = K_{\text{OH}}^- [\text{Complex}] [\text{OH}^-].$$

At 25°C and $I = 0.10 \text{ mol dm}^{-3} \text{ NaClO}_4$, the value of K_{OH}^- was $2.4 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. For $\alpha\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$, there is also a novel acid catalyzed inversion reaction which follows the acid limiting dependence;

$$K_{\text{obs}} = A[\text{H}^+]/(1+B[\text{H}^+]),$$

$$\text{with } A = 3.8(5) \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \text{ and}$$

$$B = 0.7(2) \text{ mol}^{-1} \text{ dm}^3.$$

This type of acid dependence has been observed for the acid hydrolysis reactions of a number of azamacrocyclic complexes of nickel(II) and copper(II) [212, 213, 305-308].

The dissociation kinetics have been interpreted by two mechanisms. The first mechanism involves a rapid pre-equilibrium protonation step with an equilibrium constant B (1) followed by rate determining dissociation of the protonated complex with a rate constant A/B (2);

The second mechanism involves reaction *via* a "more reactive species", formed reversibly from the starting material (rate constants for forward and reverse reactions are K_1 and K_{-1} respectively) which reacts with H^+ (with rate constant K_2), where $A = K_1K_2/K_{-1}$, and $B = K_2/K_{-1}$.

The inversion of $\alpha\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ could proceed *via* the same protonated intermediate, since the chirality of the nitrogen centre is lost upon protonation. However, the equilibrium constant (B) of $0.7 \text{ mol}^{-1} \text{ dm}^3$ would require 60% of the complex to be in the protonated form in 2 mol dm^{-3} hydrochloric acid. Also, this species would be expected to have a triplet ground state NiN_3O_3 chromophore or less likely, a singlet ground state NiN_3O chromophore, which would show a large bathochromic shift relative to the spectrum of $\alpha\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$. Since there is no significant difference in the electronic spectrum of ~~in~~ $\alpha\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ in 2 mol dm^{-3} hydrochloric acid and 2 mol dm^{-3} sodium chloride, this mechanism must be excluded.

The alternative mechanism does not suffer this problem. The proposed intermediate could have a spectrum very similar to the starting material, if for example, it was an isomeric form, such as configuration II, formed by acid independent inversion of one nitrogen centre. Protonation on the "adjacent" (across the six-membered chelate

ring) nitrogen would destroy the chirality of this centre, and deprotonation would reform the intermediate, or yield configuration III, $b\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$.

The protonated species could also undergo dissociation, and in fact, a parallel slow dissociation reaction of $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ in acid was observed. (The $b\text{-}$ isomer is extremely resistant to acid hydrolysis). Aqueous or acidic solutions of $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ gave precipitates with ammoniacal dimethylglyoxime. The rate of this reaction was determined, making use of the fact that reaction of copper(II) is rapid in 2 mol dm^{-3} acid, while reaction with nickel(II) is extremely slow under these conditions. A solution of $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ in 2.0 mol dm^{-3} hydrochloric acid at 50°C , containing copper(II) was monitored at the band maximum of $[\text{Cu}(\text{diamH}_2)]\text{Cl}_4$, 527 nm and the rate of appearance of this species was determined. The observed first order rate constant was $1.8(2) \times 10^{-7} \text{ s}^{-1}$.

Billo has suggested that dissociation of $[\text{Ni}(\text{cyclam})]^{2+}$ probably involves folding to give a *cis*-V complex [202]. The dissociation of $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ could occur *via* a similar mechanism. The relatively rapid hydrolysis rate of the *trans*-I $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ can be explained by its flexibility which may result in facile folding to the *cis*-V configuration. In contrast, the acid dissociation behaviour of *trans*-III $b\text{-}[\text{Ni}(\text{diamH}_2)]^{2+}$ is similar to that of the planar cyclam complex- SLOW; remaining unchanged in concentrated hydrochloric acid at room temperature for prolonged periods and unmeasurably slow in 2 mol dm^{-3} hydrochloric acid at 70°C .

The disappearance rate of the singlet ground state $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ is thus given by the overall expression which includes base and acid catalyzed inversion, and acid catalyzed hydrolysis.

In basic solutions, the rate = $0.2[\text{OH}^-][[\text{Ni}(\text{diam})^{2+}] \text{ s}^{-1}$,

and in acidic solutions, the rate is the sum of the isomerization and dissociation terms and can be described by the equation;

$$\text{rate} = 3.8(5) \times 10^{-4} [\text{H}^+] [\text{Ni}(\text{diamH}_2)^{4+}] / (1 + 0.7(2) [\text{H}^+])$$

$$+ 1.8(2) \times 10^{-7} [\text{H}^+] [\text{Ni}(\text{diamH}_2)^{4+}]$$

assuming linear dependence on $[\text{OH}^-]$ for the base catalysis, and on $[\text{H}^+]$ for the acid hydrolysis respectively.

The Rate of Disappearance of $a\text{-}[\text{Ni}(\text{diam})]\text{Cl}_2$ in Water at 25°C

The rate of disappearance of the lilac coloured, octahedral $a\text{-}[\text{Ni}(\text{diam})]^{2+}$ cation in water at 25°C was monitored spectrophotometrically. The decrease in intensity of the triplet state nickel(II) band of the $a\text{-}$ isomer at 586 nm was used to calculate the observed first order rate constant, which was $2.3(5) \times 10^{-5} \text{ s}^{-1}$. (The $b\text{-}[\text{Ni}(\text{diam})]^{2+}$ cation does not have bands near 586 nm). In comparison, the rate constant for the disappearance of singlet state, square planar $a\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ in 2 mol dm^{-3} sodium chloride at 50°C was $5.0 \times 10^{-5} \text{ s}^{-1}$. Considering the lower temperature for the reaction of octahedral $a\text{-}[\text{Ni}(\text{diam})]^{2+}$, it appears that the isomerization intermediate forms more readily for the non-protonated $a\text{-}$ isomer, which may also have coordinated pendant arms.

Acid Hydrolysis Kinetics

An interesting property of azamacrocyclic ligands is the resistance to substitution shown by complexes of normally labile metal ions such as nickel(II) and copper(II). Acid hydrolysis reactions of amine complexes of these ions are usually rapid, but the reactions for cyclic amines can be extremely slow, for example, the acid dissociation constant of square planar $[\text{Ni}(\text{cyclam})]^{2+}$ in 1 mol dm⁻³ perchloric acid at 25°C is $8 \times 10^{-10} \text{ s}^{-1}$ with a half life of around 30 years [202,214]. The reaction rates depend on macrocyclic ring size, (in general, reactions are slowest for fourteen membered "cyclam" type rings), the presence of substituents, unsaturation and other structural features. The rate can also vary with nitrogen configuration; for example, metastable *cis*-V $[\text{Ni}(\text{cyclam})-(\text{H}_2\text{O})_2]^{2+}$ reacts three orders of magnitude faster than the stable *trans*-III isomer mentioned above, with a dissociation rate constant of $3 \times 10^{-6} \text{ sec}^{-1}$ [202,214]. For tetra-N-methylcyclam, the *trans*-I nickel(II) complex is acid labile and the *trans*-III isomer is extremely acid stable [152]. In general, copper(II)-amine complexes react much faster than analogous nickel complexes. However, the dissociation of copper complexes of cyclam-type macrocycles can be extremely slow; for example, $[\text{Cu}(\text{cyclam})]^{2+}$ dissociates extremely slowly, even at 6 mol dm⁻³ acid at 25°C [211]. Chung and co-workers have studied the isomerization and acid dissociation kinetics of blue tet a and tet b and red tet b (isomers of 5,5,7,12,12,14-hexamethylcyclam) [300,309,310]. These complexes were found to dissociate at different rates *via* consecutive and reversible steps and the cleavage of the second Cu-N bond has been proposed as the rate determining step [309]. Hay and co-workers have studied the acid dissociation rates of $[\text{Ni}(\text{II})([17]\text{aneN}_4)]^{2+}$ and $[\text{Cu}(\text{II})([18]\text{aneN}_4)]^{2+}$ cations in

perchloric acid at 25°C ($I = 1.0 \text{ mol dm}^{-3}$) [214]. Acid limiting kinetics were displayed by the dissociation of the copper complex beyond about 0.15 mol dm^{-3} acid whereas the nickel complex displayed linear behaviour over the entire acidity range studied ($0.015\text{--}0.50 \text{ mol dm}^{-3}$). The dissociation of $[\text{Ni(II)}([\text{17}] \text{aneN}_4)]^{2+}$ was 10^{10} fold faster than that of $[\text{Ni(cyclam)}]^{2+}$. Acid dissociation reactions of penta- and hexaazamacrocycles have also been studied [311]. Reaction rates of triazamacrocycles are also faster than those of tetraazamacrocyclic systems. Murphy and Zompa studied the acid dissociation of the nickel(II) complexes of $[\text{9}] \text{aneN}_3$ and $[\text{12}] \text{ane-1,5,9-N}_3$, which displayed linear acid dependence over the hydrogen ion concentration range studied ($0.2\text{--}5.0 \text{ mol dm}^{-3}$). Riedo and Kaden found that the copper complexes of these ligands and of $[\text{10}] \text{aneN}_3$ dissociated at much faster rates than the nickel complexes with a linear dependence on acid [312]. Graham and Weatherburn also studied a variety of triazamacrocyclic complexes of copper and observed acid independent behavior for some complexes at high acid concentrations [307, 313].

Experiments were set up to measure the rates of acid hydrolysis of the diam complexes, to establish any effect arising from the pendant arms. The rate for the nickel complex, $\text{b-}[\text{Ni(diamH}_2)]^{4+}$ was found to be extremely slow at 70°C in 2 mol dm^{-3} hydrochloric acid and this study was abandoned (although acid demetallation occurs in concentrated hydrochloric acid at 140°C within 48 hours).

and 527 nm (the band maxima of the copper(II) complex in perchloric and hydrochloric acid respectively) were recorded. A small decrease in absorbance was found; ca. 2% over the year at 50°C and ca. 14% at 70°C. Assuming that this represented the first part of the demetallation reaction, pseudo first order rate constants were calculated. For the infinity value, the absorbance of the same concentration of copper complex demetallated in concentrated hydrochloric acid (at 70°C, in two days) was used. The calculated rate constants were to a first approximation independent of the particular acid or its concentration, with rate constants of $(1 \pm 0.05) \times 10^{-9}$ and $(8 \pm 1) \times 10^{-9} \text{ s}^{-1}$ at 50 and 70°C respectively.

Subsequent studies raise questions about the nature of the reaction being followed. It was found that the copper(II) ion reacts rapidly with diam in acid up to 4 mol dm⁻³. The nickel ion also reacts under these conditions, but very slowly. These results suggest extreme thermodynamic stability for the diam complexes. It is possible that the reaction being monitored was the approach to an equilibrium which had most of the copper (II) coordinated (in which case the calculated rates are in error because of the assumed infinity values). Alternatively, some reaction of the complex other than simple hydrolysis may be occurring, possibly deamination of the pendant arm(s), oxidative dehydrogenation, with consequent shift of the band maximum, or subsequent hydrolysis. For the 70°C reactions, a new band in the spectrum gradually appeared near 360 nm. (This band was not observed at 50°C). Time precluded additional studies such as of the complexation reactions under acidic conditions, which might have answered these questions.

The uncertainties in the dissociation kinetics of the copper complex are rather large, particularly in the

70°C measurements (with a percentage error of 12.5%). The main contributors to this large uncertainty were as follows: (a) low solubility of $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4$ in perchloric acid (hydrochloric acid was not used as the main medium because of possible complications arising from specific chloride effects), (b) possible leakage (teflon screw tops were used to minimize this), (c) contamination from reusing the sample (d) long reaction time and high temperatures (which increase the possibility of side reactions). The uncertainties could be minimized by sealing the solutions in disposable sealed ampoules, maintaining lower temperatures (disadvantage; even longer reaction times). Using the chloride salt and hydrochloric acid will minimize solubility problems.

The acid dissociation reaction of the metastable cation $\alpha\text{-}[\text{Ni}(\text{diamH}_2)]^{4+}$ (of possible configuration I), in parallel with the isomerization reaction to configuration III, is described on page 188.

CONCLUSION

Successful methods for the preparation of compounds of *meso*-(6, 13-dimethyl-6, 13-diamino-1, 4, 8, 11-tetraaza-cyclotetradecane) were developed. These generally had a *trans*-III nitrogen configuration, with two, one or none of the labile pendant arms coordinated. For labile metal ions, coordination of the pendant arms was controlled by pH variation.

The following further investigations are desirable;

- (a) Confirm the nitrogen configuration of the *a*- isomer of the nickel complex of diam (thought to be *trans*-I) and determine its crystal structure.
- (b) Determine the nitrogen configuration and structure of the *c*- isomer of the nickel complex of diam.
- (c) Confirm the *cis*-V configuration assigned to the $[\text{Co}(\text{diamH}_2)(\text{C}_2\text{O}_4)]^{3+}$ cation and attempt to prepare and characterize other *cis* derivatives.
- (d) Establish the crystal structures of the prepared "unusual" cobalt compounds of diam.
- (e) Determine the structures of the non-protonated copper complexes of diam, $[\text{Cu}(\text{diam})(\text{ClO}_4)_2 \cdot \text{XH}_2\text{O}]$, the properties of which suggest that they are not just different hydrates of the same compound.
- (f) Measure the pendant arm protonation constants ($\log K$) of copper complexes of diam with anions other than perchlorate to explain the distinctly different $\log K$ values obtained for the salts $[\text{Cu}(\text{diam})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{diamH}_2)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$. (Structural studies may be required).
- (g) Study the behaviour of the copper complexes of diam in acidic solutions (such as complexation) to determine the nature of the reaction followed during the acid dissociation experiments.
- (h) Further studies of complexes of diam with larger metal ions such as lead(II), which appear to have unusual properties.

APPENDIX A: Abbreviations and trivial names

cyclam = 1, 4, 8, 11-tetraazacyclotetradecane

diam = 6, 13-diamino-6, 13-dimethyl-1, 4, 8, 11-tetraazacyclo-
tetradecane

dini = 6, 13-dimethyl-6, 13-dinitro-1, 4, 8, 11-tetraazacyclo-
tetradecane

en = diaminoethane

sar = 3, 6, 10, 13, 16, 19-hexaazabicyclo[6.6.6]eicosane

diamsar = 1, 8, -diamino-3, 6, 10, 13, 16, 19-hexaazabicyclo-
[6.6.6]eicosane

tet a = *meso*-1, 7-CTH

tet b = *rac*-1, 7-CTH

1, 7-CTH = 5, 5, 7, 12, 12, 14-hexamethylcyclam

2, 3, 2-tet = 1, 4, 8, 11-tetraazaundecane

[9]aneN₃ = 1, 4, 7-triazacyclononane

[12]aneN₄ = 1, 4, 7, 10-tetraazacyclododecane (cyclen)

REFERENCES

- [1] G.A. Melson, Ed., *Coordination Chemistry of Macrocyclic Compounds*, Plenum Press, New York, 1979.
- [2] R.P. Linstead and M. Whalley, *J. Chem. Soc.*, 1952, 4839 (1952).
- [3] G.E. Ficken and R.P. Linstead, *J. Chem. Soc.*, 1952, 4846 (1952).
- [4] J.A. Elvidge and R.P. Linstead, *J. Chem. Soc.*, 1952, 5008 (1952).
- [5] J.A. Elvidge and J.H. Golden, *J. Chem. Soc.*, 1957, 700, (1952).
- [6] J. Van Alphen, *Rec. Trav. Chim. Pays-Bas.*, 55, 835 (1936)
- [7] B. Bosnich, C.K. Poon and M.L. Tobe, *Inorg. Chem.*, 4, 1102 (1965)
- [8] B. Bosnich, M.L. Tobe and G.A. Webb, *Inorg. Chem.*, 4, 1109 (1965)
- [9] N.F. Curtis, *J. Chem. Soc.*, 1960, 4409 (1960)
- [10] N.F. Curtis and D.A. House, *Chem. Ind.*, 42, 1708 (1961)
- [11] N.F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968)
- [12] M.C. Thompson and D.H. Busch, *Chem. Eng. News*, (Sept. 17) 57 (1962)
- [13] M.C. Thompson and D.H. Busch, *J. Am. Chem. Soc.*, 86, 3651 (1964)
- [14] G.A. Melson and D.H. Busch, *Proc. Chem. Soc.*, 1963, 223 (1963)
- [15] D.H. Busch, *Rec. Chem. Prog.*, 25, 107 (1964)
- [16] G.N. Schrauzer, *Chem. Ber.*, 95, 1438 (1962)
- [17] F. Umland and D. Thierig, *Angew. Chem.*, 74, 388 (1962)
- [18] C.J. Pederson, *J. Am. Chem. Soc.*, 89, 2495, 7017 (1967)
- [19] B. Dietrich, J. M. Lehn and J.P. Sauvage, *Tetrahedron Lett.*, 1969, 2885, 2889 (1969)
- [20] J. M. Lehn, J. Simon and J. Wagner, *Nouv. J. Chim.*, 1, 77 (1977)

- [21] (a) I.I. Creaser, J.M. Harrowfield, A.J. Herlt, A.M. Sargeson, J. Springborg, R.J. Geue, M.R. Snow, *J. Am. Chem. Soc.*, **99**, 3181 (1977)
(b) I.I. Creaser, R.J. Geue, J.M. Harrowfield, A.J. Herlt, A.M. Sargeson, M.R. Snow, J. Springborg, *J. Am. Chem. Soc.*, **104**, 6016 (1982)
- [22] (a) G.A. Lawrance, M. Rossignoli, B.W. Skelton, A. White, *Aust. J. Chem.*, **40**, 1441, (1987)
(b) A.M. Sargeson, *Chem. Br.*, **15**, 23 (1979)
- [23] L.F. Lindoy and D.H. Busch, *Preparative Inorganic Reactions*, (W. Jolly, Ed.), **6**, 1, Interscience, New York (1971)
- [24] D.K. Cabbiness and D.W. Margerum, *J. Am. Chem. Soc.*, **91**, 6540 (1969)
- [25] J.M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975)
- [26] D.H. Busch, K. Farmery, V. Goedken, V. Katovic, A.C. Melnyk, C.R. Sperati and N. Tokel, *Adv. Chem. Ser.*, **100**, 44 (1971)
- [27] V.L. Goedken, P.H. Merrell and D.H. Busch, *J. Am. Chem. Soc.*, **94**, 3397 (1972)
- [28] J.C. Dabrowiak, P.H. Merrell and D.H. Busch, *Inorg. Chem.*, **11**, 1979 (1972)
- [29] D.H. Busch, *Helv. Chim. Acta*, **50**, 174 (1967)
- [30] D.H. Busch, *Science*, **171**, 241 (1971)
- [31] J.J. Christensen, J.O. Hill and R.M. Izatt, *Science*, **174**, 459 (1971)
- [32] C.J. Pedersen and H.K. Frensdorff, *Angew. Chem. Int. Ed. Engl.*, **11**, 16 (1972)
- [33] D.S.C. Black and A.J. Hartshorn, *Coord. Chem. Rev.*, **9**, 219 (1972-1973)
- [34] J.M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973)
- [35] J.J. Christensen, D.J. Eatough and R.M. Izatt, *Chem. Rev.*, **74**, 351 (1974)
- [36] L.F. Lindoy, *Chem. Soc. Rev.*, **5**, 421 (1975)
- [37] G.R. Newkome, J.D. Sauer, J.M. Roper and D.C. Hager, *Chem. Rev.*, **77**, 513 (1977)
- [38] R.H. Holm and T.J. Truex, *J. Am. Chem. Soc.*, **93**, 285 (1971)

- [39] T.J. Truex and R.H. Holm, *J. Am. Chem. Soc.*, **94**, 4529 (1972)
- [40] S.C. Tang, G.N. Weinstein and R.H. Holm, *J. Am. Chem. Soc.*, **95**, 613 (1973)
- [41] S.C. Tang, S. Koch, G.N. Weinstein, R.W. Lane and R.H. Holm, *Inorg. Chem.*, **12**, 2589 (1973)
- [42] S. Koch, R.H. Holm and R.B. Frankel, *J. Am. Chem. Soc.*, **97**, 6714 (1975)
- [43] C.L. Honeybourne, *Inorg. Nucl. Chem. Lett.*, **11**, 191 (1975)
- [44] M.d.S. Healy, A.J. Rest, *Adv. Inorg. Chem. Radiochem.*, **21**, 1 (1978)
- [45] D. Anastasi, Condensation Reactions of Copper(II) and Nickel(II) with Formaldehyde and Various Nucleophiles, B.Sc (Hons) Project, Victoria University (1983)
- [46] W. Rosen and D.H. Busch, *J. Am. Chem. Soc.*, **91**, 4694 (1969)
- [47] K. Travis and D.H. Busch, *Inorg. Chem.*, **13**, 2591 (1974)
- [48] J.E. Richman and T.J. Atkins, *J. Am. Chem. Soc.*, **96**, 2268 (1974)
- [49] E.K. Barefield, *Inorg. Chem.*, **11**, 2273 (1972)
- [50] E.K. Barefield, F. Wagner, A.W. Herlinger and A.R. Dahl, *Inorg. Synth.*, **16**, 220 (1976)
- [51] E.G. Jäger, *Z. Chem.*, **4**, 437 (1964)
- [52] L. Woolf and E.G. Jäger, *Z. Anorg. Allgem. Chem.*, **346**, 76 (1966)
- [53] E.G. Jäger, *Z. Chem.*, **8**, 30 (1968)
- [54] E.G. Jäger, *Z. Chem.*, **8**, 392 (1968)
- [55] E.G. Jäger, *Z. Chem.*, **8**, 470 (1968)
- [56] E.G. Jäger, *Z. Anorg. Allgem. Chem.*, **364**, 177 (1969)
- [57] P. Bamfield, *J. Chem. Soc. (A)*, **1969**, 2021 (1969)
- [58] C.M. Kerwin and G.A. Melson, *Inorg. Chem.*, **12**, 2410 (1973)
- [59] D.B. Bonfoey and G.A. Melson, *Inorg. Chem.*, **14**, 309 (1975)

- [60] P. Comba, N.F. Curtis, G.A. Lawrance, A.M. Sargeson, B.W. Skelton and A.H. White, *Inorg. Chem.*, **25**, 4260, (1986)
- [61] M.C. Thompson and D.H. Busch, *J. Am. Chem. Soc.*, **84**, 1762 (1962)
- [62] M.C. Thompson and D.H. Busch, *J. Am. Chem. Soc.*, **86**, 213 (1964)
- [63] N.W. Alcock and P.A. Tasker, *J. Chem. Soc. Chem. Commun.*, **1972**, 1239 (1972)
- [64] A.J. Herlt, A.M. Sargeson, J. Springborg, D. Taylor, R.J. Geue and M.R. Snow, *J. Chem. Soc. Chem. Commun.*, **1976**, 285 (1976)
- [65] R.J. Geue, T.W. Hambley, J.M. Harrowfield, A.M. Sargeson and M.R. Snow, *J. Am. Chem. Soc.*, **106**, 5478 (1984)
- [66] H.A. Boucher, G.A. Lawrance, P.A. Lay, A.M. Sargeson, A.M. Bond, D.F. Sangster and J.C. Sullivan, *J. Am. Chem. Soc.*, **105**, 4652 (1983)
- [67] J. M. Harrowfield, A.J. Herlt, P.A. Lay, A.M. Sargeson, A.M. Bond, W.A. Mulac and J.C. Sullivan, *J. Am. Chem. Soc.*, **105**, 5503 (1983)
- [68] A.M. Sargeson, *Pure Appl. Chem.*, **56**, 1603 (1984)
- [69] P. Comba, I.I. Creaser, L.R. Gahan, J.M. Harrowfield, G.A. Lawrance, L.L. Martin, A.W.H. Mou, A.M. Sargeson, W.H.F. Sasse and M.R. Snow, *Inorg. Chem.*, **25**, 384 (1986)
- [70] M.D. Suh, W. Shin, D. Kim, S. Kim, *Inorg. Chem.*, **23**, 618 (1984)
- [71] P. Comba, A.M. Sargeson, L.M. Engelhardt, J.M. Harrowfield, A.H. White, E. Horn and M.R. Snow, *Inorg. Chem.*, **24**, 2325 (1985)
- [72] G.A. Lawrance, B.W. Skelton, A.H. White and P. Comba, *Aust. J. Chem.*, **39**, 1101 (1986)
- [73] C.J. Hipp, L.F. Lindoy and D.H. Busch, *Inorg. Chem.*, **11**, 1988 (1972)
- [74] F. Wagner, M.T. Mocella, M.J. D'Aniello, A.H.J. Wang and E.K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974)
- [75] D.C. Olson and J. Vasilevskis, *Inorg. Chem.*, **8**, 1611 (1969)
- [76] D.C. Olson and J. Vasilevskis, *Inorg. Chem.*, **10**, 463 (1971)

- [77] D.C. Olson and J. Vasilevskis, *Inorg. Chem.*, **11**, 980 (1972)
- [78] D.P. Rillema, J.F. Endicott and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971)
- [79] J.C. Dabrowiak, F.V. Lovecchio, V.L. Goedken and D.H. Busch, *J. Am. Chem. Soc.*, **94**, 5502 (1972)
- [80] V.L. Goedken and D.H. Busch, *J. Am. Chem. Soc.*, **94**, 7355 (1972)
- [81] F.V. Lovecchio, E.S. Gore and D.H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974)
- [82] A.M. Tait, M.Z. Hoffman and E. Hayon, *Inorg. Chem.*, **15**, 934 (1976)
- [83] A.M. Tait, M.Z. Hoffman and E. Hayon, *J. Am. Chem. Soc.*, **98**, 86 (1976)
- [84] A.M. Tait, M.Z. Hoffman and E. Hayon, *Int. J. Radiat. Phys. Chem.*, **8**, 691 (1976)
- [85] R.L. Deming, A.L. Allred, A.R. Dahl, A.W. Herlinger and M.O. Kestner, *J. Am. Chem. Soc.*, **98**, 4132 (1976)
- [86] E.K. Barefield and M.T. Mocella, *Inorg. Chem.*, **12**, 2829 (1973)
- [87] M.O. Kestner and A.L. Allred, *J. Am. Chem. Soc.*, **94**, 7189 (1972)
- [88] R.S. Cahn, C. Ingold and V. Prelog, *Angew. Chem. Int. Ed. Engl.*, **5**, 385 (1966)
- [89] (a) P.J. Connolly and E.J. Billo, *Inorg. Chem.*, **26**, 3224 (1987)
(b) E.K. Barefield, A. Bianchi, E.J. Billo, P.J. Connolly, P. Paoletti, J.S. Summers, and D.G. Van Derveer, *Inorg. Chem.*, **25**, 4197 (1986)
- [90] (a) A.M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966)
(b) J.K. Beattie, *Acc. Chem. Res.*, **4**, 253 (1971)
(c) C.J. Hawkins, *Absolute Configurations of Metal Complexes*, Wiley-Interscience, New York (1971)
(d) F.A. Journak and K.N. Raymond, *Inorg. Chem.*, **11**, 3149 (1972)
(e) S.R. Niketic, K. Rasmusson, F. Woldbye and S. Lifson, *Acta Chem. Scand.*, **A30**, 497 (1976)
- [91] L.Y. Martin, L.J. De Hayes, L.J. Zompa and D.H. Busch, *J. Am. Chem. Soc.*, **96**, 4046 (1974)
- [92] T. Ito, M. Kato and H. Ito, *Bull. Chem. Soc. Jpn.*, **57**, 1556 (1984)

- [93] T. Ito, M. Kato, H. Ito, *Bull. Chem. Soc. Jpn.*, **57**, 2641 (1984)
- [94] A. McPherson, M.G. Rossman, D.W. Margerum and M.R. James, *J. Coord. Chem.*, **1**, 73 (1971)
- [95] (a) D.J. Roger, V.H. Schievelbein, A.R. Kalyanaraman and J.A. Bertrand, *Inorg. Chim. Acta*, **6**, 307 (1972)
 (b) F. Hanic, F. Pavelick and D. Cjespesova, *Kristallografiya*, **17**, 10 (1972)
- [96] M. Kodama and E.J. Kimura, *J. Chem. Soc. Dalton Trans.*, **1977**, 2269 (1977)
- [97] V.J. Thöm, G.D. Hosken, R.D. Hancock, *Inorg. Chem.*, **24**, 3378 (1985)
- [98] V.J. Thöm, C.C. Fox, J.C.A. Boeyens, R.D. Hancock, *J. Am. Chem. Soc.*, **106**, 5947 (1984)
- [99] V.J. Thöm and R.D. Hancock, *J. Chem. Soc. Dalton Trans.*, **1985**, 1877 (1985)
- [100] B.J. Hathaway, and A.A.G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970)
- [101] J. Gazo, R. Boca, E. Jona, M. Kabesova, L. Macaskova and J. Sima, *Coord. Chem. Rev.*, **43**, 87 (1982)
- [102] M. Sugimoto, J. Fujita, H. Ito, K. Toriumi and T. Ito, *Inorg. Chem.*, **22**, 955 (1983)
- [103] L.Y. Martin, C.R. Sperati and D.H. Busch, *J. Am. Chem. Soc.*, **99**, 2968 (1977)
- [104] J.R. Gollogly and C.J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969)
- [105] (a) P.O. Whimp, M.F. Bailey and N.F. Curtis, *J. Chem. Soc. (A)*, **1970**, 1956 (1970)
 (b) L.G. Warner and D.H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969)
- [106] E.K. Barefield and F. Wagner, *Inorg. Chem.*, **12**, 2435 (1973)
- [107] P. Moore, J. Sachinidis and G.R. Willey, *J. Chem. Soc. Chem. Commun.*, **1983**, 522 (1983)
- [108] (a) J.H. Coates, D.A. Hadi, S.F. Lincoln, *Aust. J. Chem.*, **35**, 903 (1982)
 (b) J.H. Coates, D.A. Hadi, T.W. Hambley, S.F. Lincoln and J.R. Rogers, *Cryst. Struct. Commun.*, **11**, 815 (1982)
 (c) J.H. Coates, D.A. Hadi, S.F. Lincoln H.W. Dodgen and J.P. Hunt, *Inorg. Chem.*, **20**, 707 (1981)

- [108] (d) M. Kodama and E. Kimura, *J. Chem. Soc. Dalton Trans.*, 1981, 694 (1981)
- (e) N.F. Curtis and G.W. Reader, *J. Chem. Soc. (A)*, 1971, 1771 (1971)
- (f) N.F. Curtis and G.W. Reader, *J. Chem. Soc. Dalton Trans.*, 1972, 1453 (1972)
- [109] T.A. Kaden, *Top. Curr. Chem.*, 121, 157 (1984)
- [110] H. Stetter and W. Frank, *Angew. Chem.*, 88, 760 (1976)
- [111] H. Stetter, W. Frank and R. Mertens, *Tetrahedron*, 37, 767 (1981)
- [112] R. Delgado, J.J. Frausto Dasilva, *Talanta*, 29, 815 (1982)
- [113] F. Weigl and K. Raymond, *J. Am. Chem. Soc.*, 101, 2728 (1979)
- [114] K.V. Damu, M.S. Saikjee, J.P. Michael, A.S. Howard and R.D. Hancock, *Inorg. Chem.*, 25, 3879 (1986)
- [115] F.R. Muller and H. Handel, *Tetrahedron Lett.*, 23, 2769 (1982)
- [116] V. Louvet, P. Apriou and H. Handel., *Tetrahedron Lett.*, 23, 2445 (1982)
- [117] E. Kimura, *Pure and Appl. Chem.*, 58, 1461 (1986)
- [118] Y. Iitaka, T. Koike and E. Kimura, *Inorg. Chem.*, 25, 402 (1986)
- [119] L. Fabbrizzi, *Comments Inorg. Chem.*, 4, 33 (1985)
- [120] A. Bencini, L. Fabbrizzi and A. Poggi, *Inorg. Chem.*, 20, 2544 (1981)
- [121] P.S. Pallavicini, A. Perotti, A. Poggi, B. Seghi and L. Fabbrizzi, *J. Am. Chem. Soc.*, 109, 5139 (1987)
- [122] J.P. Collman, T.R. Halpert and K.S. Suslick, *Metal Ion Activation of Dioxygen*, (T.G. Spiro, Ed.), Wiley, New York (1980)
- [123] (a) C.K. Chang, T.G. Traylor, *Proc. Nat. Acad. Sc. USA*, 70, 2647 (1973)
- (b) C.K. Chang, T.G. Traylor, *J. Am. Chem. Soc.*, 95, 5810, 8475 and 8477 (1973)
- [124] P.H. Smith and K. N. Raymond, *Inorg. Chem.*, 24, 3469 (1985)
- [125] D.E. Fenton and G. Rossi, *Inorg. Chim. Acta*, 98, L29, (1985)

- [126] (a) C.W.G. Ansell and P.R. Raithby, *J. Chem. Soc. Dalton Trans.*, 1983, 177 (1983)
 (b) E.C. Constable, L.Y. Chung, J. Lewis and P.R. Raithby, *J. Chem. Soc. Chem. Commun.*, 1985, 1058 (1985)
- [127] C.A. Chang and M.E. Rowland., *Inorg. Chem.*, 22, 3866 (1983)
- [128] C.A. Chang and V.O. Ochaya, *Inorg. Chem.*, 25, 355 (1986)
- [129] Y. Sun, A.E. Martell and R.J. Motekaitis, *Inorg. Chem.*, 25, 4780 (1986)
- [130] T. Arishma, K. Hamada, S. Takamoto, *Nippon Kagaku Kaishi*, 1973, 1119 (1973)
- [131] M. Takahashi and S. Takamoto, *Bull. Chem. Soc. Jpn.*, 50, 3413 (1977)
- [132] M.J. van der Merwe, J.C.A. Boeyens and R.D. Hancock, *Inorg. Chem.*, 24, 1208 (1985)
- [133] M.J. van der Merwe, J.C.A. Boeyens and R.D. Hancock, *Inorg. Chem.*, 22, 3489 (1983)
- [134] K. Wieghardt, U. Bossek, P. Chaudhuri, W. Herrmann, B.C. Menke and J. Weiss, *Inorg. Chem.*, 21, 4308 (1982)
- [135] K. Wieghardt, U. Bossek, M. Guttman and J.Z. Weiss, *Naturforsch., B: Anorg. Chem., Org. Chem.*, 38 B, 81 (1983)
- [136] B.A. Sayer, J.P. Michael, R.D. Hancock, *Inorg. Chim. Acta*, 77, L63 (1983)
- [137] L.R. Gahan, G.A. Lawrance and A.M. Sargeson, *Aust. J. Chem.*, 35, 1119 (1982)
- [138] A. Hammershoi, A.M. Sargeson, *Inorg. Chem.*, 22, 3554 (1983)
- [139] M.I. Kabachnik, T. Ya. Medved, M. Yu. Polikarpov, B.K. Shcherbakov, F.I. Bel'skii, E.I. Matrosov and M.P. Pasechnik, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1984, 835 (1984)
- [140] M. Yu. Polikarpov, B.K. Shcherbakov, F.I. Bel'skii, T. Ya. Medved and M.I. Kabachnik, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1982, 1669 (1982)
- [141] M.A. Konstantinovskaya, E.I. Sinyavskaya, K.B. Yatsimirskii, B.K. Shcherbakov, M. Yu. Polikarpov, T. Ya. Medved and M.I. Kabachnik, *Zh. Neorg. Khim.*, 30, 2571 (1985)

- [142] K.B. Yatsimirskii, M.I. Kabachnik, E.I. Sinyavskaya, T. Ya. Medved, M. Yu. Polikarpov and B.K. Shcherbakov, *Zh. Neorg. Khim.*, 29, 884 (1984)
- [143] K.B. Yatsimirskii, E.I. Sinyavskaya, L.V. Tsimbal, T. Ya. Medved, B.K. Shcherbakov, M. Yu. Polikarpov and M.I. Kabachnik, *Zh. Neorg. Khim.*, 29, 888 (1984)
- [144] C.F.G.C. Geraldies, M.C. Alpoim, M.P.M. Marques, A.D. Sherry and M. Singh, *Inorg. Chem.*, 24, 3876 (1985)
- [145] L. Christiansen, D.N. Hendrickson, H. Toftlund, S.R. Wilson and C. Xie, *Inorg. Chem.*, 25, 2813 (1986)
- [146] K. Wieghardt, E. Schöffmann, B. Nuber and J. Weiss, *Inorg. Chem.*, 25, 4877 (1986)
- [147] W.P. Cacheris, S.K. Nickle and A.D. Sherry, *Inorg. Chem.*, 26, 958 (1987)
- [148] H. Häflinger and T. A. Kaden, *Helv. Chim. Acta*, 62, 683 (1979)
- [149] S. Bußen, J. Dale, P. Groth and J. Krane, *J. Chem. Soc. Chem. Commun.*, 1977, 1172 (1977)
- [150] K.P. Wainwright, *J. Chem. Soc. Dalton Trans.*, 1980, 2117 (1980)
- [151] W. Schibler and T.A. Kaden, *J. Chem. Soc. Chem. Commun.*, 1981, 603 (1981)
- [152] F. Wagner and E.K. Barefield, *Inorg. Chem.*, 15, 408 (1976)
- [153] T.J. Lotz and T.A. Kaden, *Helv. Chim. Acta*, 61, 1376 (1978)
- [154] (a) M. Hediger and T.A. Kaden, *J. Chem. Soc. Chem. Commun.*, 1978 14 (1978)
(b) M. Hediger and T.A. Kaden, *Helv. Chim. Acta*, 66, 861 (1983)
- [155] L. Horner and H. Neumann, *Chem. Ber.*, 98, 3462 (1965)
- [156] A.K. Basak and T.A. Kaden, *Helv. Chim. Acta*, 66, 2086 (1983)
- [157] N.W. Alcock, R.G. Kingston, P. Moore and C. Pierpoint, *J. Chem. Soc. Dalton Trans.*, 1984, 1937 (1984)
- [158] N.W. Alcock, P. Moore and C. Pierpoint, *J. Chem. Soc. Dalton Trans.*, 1984, 2371 (1984)
- [159] N.W. Alcock, H.A.A. Omar, P. Moore and C. Pierpoint, *J. Chem. Soc. Dalton Trans.*, 1985, 219 (1985)

- [160] R.W. Hay and D.M. Clark, *Inorg. Chim. Acta*, 83, L23 (1984)
- [161] T.J. Lotz and T.A. Kaden, *J. Chem. Soc. Chem. Commun.*, 1977, 15 (1977)
- [162] K.P. Wainwright, *J. Chem. Soc. Dalton Trans.*, 1983, 1149 (1983)
- [163] E.K. Barefield, K.A. Foster, G.A. Freeman and K.D. Hodges, *Inorg. Chem.*, 25, 4663 (1986)
- [164] J.F. Desreux and M.F. Loncin, *Inorg. Chem.*, 25, 69 (1986)
- [165] H. Hope, M. Viggiano, B. Moezzi and P.P. Power, *Inorg. Chem.*, 23, 2550 (1984)
- [166] I. Murase, M. Mikuriya, H. Sonoda, Y. Fukuda and S. Kida, *J. Chem. Soc. Dalton Trans.*, 1986, 953 (1986)
- [167] A. Evers, R.D. Hancock and I. Murase, *Inorg. Chem.*, 25, 2160 (1986)
- [168] N. W. Alcock, P. Moore and H.A.A. Omar, *J. Chem. Soc. Chem. Commun.*, 1985, 1058 (1985)
- [169] N.W. Alcock, E.H. Curzon, P. moore, H.A.A. Omar and C. Pierpoint, *J. Chem. Soc. Dalton Trans.*, 1985, 1361 (1985)
- [170] N.W. Alcock, K.P. Balakrishnan, P. Moore and H.A.A. Omar, *J. Chem. Soc. Dalton Trans.*, 1987, 545 (1987)
- [171] M. Mikuriya, S. Kida and I. Murase, *J. Chem. Soc. Dalton Trans.*, 1987, 1261 (1987)
- [172] N.F. Curtis, G.J. Gainsford, T.W. Hambley, G.A. Lawrance, K.R. Morgan and A. Siriwardena, *J. Chem. Soc. Chem. Commun.*, 1987, 295 (1987)
- [172]_p Personal communication; G.J. Gainsford
- [173] M. Mikuriya, S. Kida and I. Murase, *Bull. Chem. Soc. Jpn.*, 60, 1355 (1987)
- [174] N.W. Alcock, K.P. Balakrishnan and P. Moore, *J. Chem. Soc. Chem. Commun.*, 1985, 1731 (1985)
- [175] A. Riesen, M. Zehnder and T.A. Kaden, *J. Chem. Soc. Chem. Commun.*, 1985, 1336 (1985)
- [176] I. Tabushi, Y. Taniguchi and H. Kato, *Tetrahedron Lett.*, 12, 1049 (1977)
- [177] E. Kimura, T. Koike, H. Nada and Y. Iitaka, *J. Chem. Soc. Chem. Commun.*, 1986, 1322 (1986)

- [178] E. Kimura, Y. Yamaoka, M. Morioka and T. Koike, *Inorg. Chem.*, **25**, 3883 (1986)
- [179] E. Kimura, T. Koike, K. Uenishi, M. Hediger, M. Kuramoto, S. Joko, Y. Arai, M. Kodama and Y. Iitaka, *Inorg. Chem.*, **26**, 2975 (1987)
- [180] R.W. Hay, M. P. Pujari, K. Hideg and O.H. Hankovszky, *Transition Met. Chem.*, **10**, 188 (1985)
- [181] E. Kimura, T. Toike, R. Machida, R. Nagai and M. Kodama, *Inorg. Chem.*, **23**, 4181 (1984)
- [182] B. Korybut-Daszkiewicz, *J. Chem. Soc. Chem. Commun.*, **1985**, 192 (1985)
- [183] D.A. House, M. Harnett, W.T. Robinson and M.C. Couldwell, *J. Chem. Soc. Chem. Commun.*, **1984**, 979, (1984)
- [184] E. Kimura, T. Koike, K. Uneshi and R.B. Davidson, *J. Chem. Soc. Chem. Commun.*, **1986**, 1110, (1986)
- [185] E. Kimura, M. Shionoya, T. Mita and Y. Iitaka, *J. Chem. Soc. Chem. Commun.*, **1987**, 1712, (1987)
- [186] T.J. Reid, M.R.N. Murthy, A. Sicignano, N. Tanaka, W.D.L. Musick and M.G. Rossman, *Proc. Nat. Acad. Sci. USA*, **78** 4767 (1981)
- [187] P.D. Pulsinelli, M.F. Perutz and R.L. Nagel, *Proc. Nat. Acad. Sci. USA*, **70**, 3870 (1973)
- [188] I. Murase, K. Hamada and S. Kida, *Inorg. Chim. Acta*, **54**, 471 (1981)
- [189] E.K. Barefield, D. Chueng, D. van Derveer and F. Wagner, *J. Chem. Soc. Chem. Commun.*, **1981**, 302 (1981)
- [190] A. Buttafava, L. Fabbrizzi, A. Perotti and B. Seghi, *J. Chem. Soc. Chem. Commun.*, **1982**, 1166 (1982)
- [191] (a) L. Fabbrizzi, L. Montagna, A. Poggi, T.A. Kaden and L.C. Siegfried, *Inorg. Chem.*, **25**, 2671 (1986)
 (b) L. Fabbrizzi, L. Montagna, A. Poggi, T.A. Kaden and L.C. Siegfried, *J. Chem. Soc. Dalton Trans.*, **1987**, 2631 (1987)
- [192] M. Ciampolini, M. Micheloni, N. Nardi, F. Vizza, A. Buttafava, L. Fabbrizzi and A. Perotti, *J. Chem. Soc. Chem. Commun.*, **1984**, 998 (1984)
- [193] M.P. Suh, W. Shin, H. Kim and C.H.Koo, *Inorg. Chem.*, **26**, 1846 (1987)

- [194] I. Murase, K. Hamada, S. Ueno and S. Kida, *Synth. React. Inorg. Metal-Org. Chem.*, **13**, 191 (1983)
- [195] L. Fabbrizzi, F. Forlini, A. Perotti and B. Seghi, *Inorg. Chem.*, **23**, 807 (1984)
- [196] E. Garcia-Espana, M. Micheloni, P. Paoletti and A. Bianchi, *Gazz. Chim. Ital.*, **1985**, 115 (1985)
- [197] R. Schneider, A. Riesen and T.A. Kaden, *Helv. Chim. Acta*, **69**, 53 (1986)
- [198] A. McAuley, S. Subramanian and T.W. Whitcombe, *J. Chem. Soc. Chem. Commun.*, **1987**, 539 (1987)
- [199] M.N. Hughes, *The Inorganic Chemistry of Biological Processes*, Wiley, New York, second edition (1980)
- [200] J.F. Desreux, E. Mercigny and M.F. Loucin, *Inorg. Chem.*, **20**, 987 (1981)
- [201] A.P. Leugger, L. Hertli and T.A. Kaden, *Helv. Chim. Acta*, **61**, 2296 (1978)
- [202] E.J. Billo, *Inorg. Chem.*, **23**, 236 (1984)
- [203] E.J. Billo, *Inorg. Chem.*, **20**, 4019 (1981)
- [204] M. Ciampollini, L. Fabbrizzi, M. Licchelli, A. Perotti, F. Pezzini and A. Poggi, *Inorg. Chem.*, **25**, 4131 (1986)
- [205] C. K. Jørgensen, *Acta. Chem. Scand.*, **11**, 399 (1957)
- [206] L. Fabbrizzi, *J. Chem. Soc. Dalton Trans.*, **1980**, 1857
- [207] L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, **18**, 438 (1979)
- [208] A. Anichini, L. Fabbrizzi, P. Paoletti and R.M. Clay, *Inorg. Chim. Acta*, **24**, L21 (1977)
- [209] S.P. Kasprzyk and R.G. Wilkins, *Inorg. Chem.*, **21**, 3349 (1982)
- [210] D.A. Buckingham, C.R. Clark and W.S. Webley, *J. Chem. Soc. Chem. Commun.*, **1981**, 192 (1981)
- [211] D.K. Cabbiness and D.W. Margerum, *J. Am. Chem. Soc.*, **92**, 2151 (1970)
- [212] R.W. Hay and R. Bembi, *Inorg. Chim. Acta*, **62**, 89 (1982)
- [213] R. Bembi, V.K. Bhardwarj, R. Singh, R. Singh, K. Tasneja and S. Aftab, *Inorg. Chem.*, **23**, 4153 (1984)

- [214] R.W. Hay, M.P. Pujari and R. Bembi, *Transition Met. Chem.*, **11**, 261 (1986)
- [215*] J.W.L. Martin and N.F. Curtis, *Aust. J. Chem.*, **29**, 1219 (1980)
- [215] Personal communication; D.C. Weatherburn
- [216] A. Kornerup and J.H. Wanscher, *Methuen Handbook of Colour*, Introduced and revised by D. Davey, third edition, Eyre Methuen, London (1978)
- [217] H.F. Bauer and W.C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960)
- [218] H.F. Bauer and W.C. Drinkard, *Inorg. Synth.*, **8**, 202 (1966)
- [219] R.P. Linstead, J.A. Elvidge and M. Whalley, *A Course in Modern Techniques of Organic Chemistry*, London Butterworths (1955)
- [220] R.O.C. Norman, *Principles of Organic Synthesis*, Methuen and Co. Ltd., 541 (1968)
- [221] *Spectroscopy Tables for Use in Organic Chemistry*, Department of Chemistry, Victoria University, Wellington
- [222] (a) S.J. Lippard, Ed., *Progress in Inorganic Chemistry* **29**, 203, C.J. O'Connor, *Magnetochemistry-Advances in Theory and Experimentation*, Interscience (John Wiley and Sons) (1982)
 (b) CHEM 262 Laboratory Manual, Chemistry Department, Victoria University, Wellington (1982)
- [223] J. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham (revised by), *Vogel's Textbook of Quantitative Inorganic Analysis*, Fourth Edition, Longman, London and New York (1979)
- [224] R.G. Bates, *Determination of pH Theory and Practice*, Second Edition, Wiley-Interscience, 96 (1973)
- [225] P. Comba, T.W. Hambley and G.A. Lawrance, *Helv. Chim. Acta*, **68**, 2332 (1985)
- [226] H. Dodziuk, R.A. Kolinski and B. Korybut-Daszkiewicz, *Spectrochim. Acta*, **29A**, 511 (1973)
- [227] E.D. Becker, *High Resolution NMR; Theory and Chemical Applications*, second edition, Academic Press (1980)
- [228] D.A. Buckingham and J.P. Stevens, *J. Chem. Soc.*, **1964**, 4583 (1964)

- [229] C.S. Lee, S.Y. Wu and C.S. Young, *Inorg. Chem.*, **23**, 1298 (1984)
- [230] N.A.P. Kane-Maguire, P.K. Miller and L.S. Trzupek, *Inorg. Chim. Acta*, **76**, L179 (1983)
- [231] P. Paoletti, L. Fabbrizzi and R. Barbucci, *Inorg. Chim. Acta. Rev.*, **7**, 43 (1973)
- [232] L. Fabbrizzi and P. Paoletti, *Gazz. Chim. Ital.*, **104**, 929 (1974)
- [233] J.D. Vitiello and E.J. Billo, *Inorg. Chem.*, **19**, 3477 (1980)
- [234] F.P. Hinz and D.W. Margerum, *Inorg. Chem.*, **13**, 2941 (1974)
- [235] E.K. Barefield and D.H. Busch, *Quart. Rev (London)*, **22**, 457 (1968)
- [236] N.F. Curtis and N.B. Milestone, *Aust. J. Chem.*, **27**, 1167 (1974)
- [237] J.W.L. Martin, J.H. Johnston and N.F. Curtis, *J. Chem. Soc. Dalton Trans.*, **1978**, 68 (1978)
- [238] (a) H.K.J. Powell and N.F. Curtis, *Aust. J Chem.*, **26**, 977 (1971)
(b) F. Basolo, Y.T. Chen and R.K. Murmann, *J. Am. Chem. Soc.*, **76**, 956 (1954)
- [239] L. Rusnak and L.B. Jordan, *Inorg. Chem.*, **10**, 2199 (1971)
- [240] R. Buxtorf, R. Steimann and T.A. Kaden, *Chimia*, **28**, 15 (1974)
- [241] J.H. Coates, D.A. Hadi, S.F. Lincoln, H.W. Dodgen and J.P. Hunt, *Inorg. Chem.*, **20**, 707 (1981)
- [242] L. Fabbrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, **19**, 535 (1980)
- [243] K.J. Ivin, R. Jamison and J.J. McGarvey, *J. Am. Chem. Soc.*, **94**, 1763 (1972)
- [244] C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **95**, 7177 (1973)
- [245] R.G. Wilkins, R. Yellin, D.W. Margerum and D.C. Weatherburn, *J. Am. Chem. Soc.*, **91**, 4326 (1969)
- [246] B. Bosnich, R.D. Gillard, E.D. McKenzie and G.A. Webb, *J. Chem. Soc. (A)*, **1966**, 1331 (1966)
- [247] J.K. Beattie, M.T. Kelso, W.E. Moody and P.A. Tregloan *Inorg. Chem.*, **24**, 415 (1985)

- [248] G.S. Vigee, C.L. Watkins and H.F. Bowen, *Inorg. Chim. Acta*, **35**, 255 (1979)
- [249] M. Sugimoto, M. Nonomiya, T. Ito and J. Fujita, *Inorg. Chem.*, **22**, 950 (1983)
- [250] L. Fabbrizzi, *Inorg. Chem.*, **16**, 2667 (1977)
- [251] L.G. Warner and D.H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969)
- [252] R. Barbucci, L. Fabbrizzi, P. Paoletti and A. Vacca, *J. Chem. Soc. Dalton Trans.*, **1973**, 1763 (1973)
- [253] R.J. Pell, H.W. Dodgen and J.P. Hunt, *Inorg. Chem.*, **22**, 529 (1983)
- [254] G.M. Freeman, E.K. Barefield and D.G. Van Derveer, *Inorg. Chem.*, **23**, 3092 (1984)
- [255] R.A. Bauer, W.F. Robinson and D.W. Margerum, *J. Chem. Soc. Chem. Commun.*, **1973**, 289 (1973)
- [256] N. Herron and P. Moore, *Inorg. Chim. Acta.*, **36**, 89 (1979)
- [257] M.S. Holtman and S.C. Cummings, *Inorg. Chem.*, **15**, 660 (1976)
- [258] A.B.P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968)
- [259] R.W. Hay and D.P. Piplani, *J. Chem. Soc. Dalton Trans.*, **1977**, 1956 (1977)
- [260] B. Bosnich, R. Mason, P.J. Pauling, G.B. Robertson and M.L. Tobe, *Chem. Commun.*, 97 (1965)
- [261] S. Chandra and K.K. Sharma, *Transition Met. Chem.*, **8**, 1 (1983)
- [262] (a) B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970)
(b) B.J. Hathaway and A.G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970)
- [263] (a) S.Y. Wu, C.S. Lee and C.S. Chung, *Inorg. Chem.*, **23**, 2548 (1984)
(b) A.W. Addison and E. Sinn, *Inorg. Chem.*, **22**, 1225 (1983)
- [264] C.K. Poon and M.L. Tobe, *Coord. Chem. Rev.*, **1**, 81 (1964)
- [265] C.K. Poon and M.L. Tobe, *J. Chem. Soc. (A)*, **1967**, 2069 (1967)
- [266] C.K. Poon and M.L. Tobe, *J. Chem. Soc. (A)*, **1964**, 1549 (1964)

- [267] K.S. Mok and C.K. Poon, *Inorg. Chem.*, **10**, 225 (1971)
- [268] C.K. Poon, *Inorg. Chim. Acta*, **5**, 322 (1971)
- [269] (a) J. A. Connor and E.A.V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, **6**, 361 (1964)
(b) L.H. Vogt, H.M. Faigenbaum and S.E. Wiberley, *Chem. Rev.*, **63**, 269 (1963)
- [270] B. Bosnich, C.K. Poon and M.L. Tobe, *Inorg. Chem.*, **5**, 1514 (1966)
- [271] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, fourth edition, John Wiley and Sons (1980)
- [272] C. Floriani and F. Calderazzo, *J. Chem. Soc. (A)*, **1969**, 946 (1969)
- [273] (a) A.L. Crumblis and F. Basolo, *J. Chem. Soc.*, **92**, 55 (1970)
(b) B.M. Hoffman, D.L. Diemente and F. Basolo, *J. Chem. Soc.*, **92**, 61 (1970)
- [274] U. Sakaguchi, K. Tomioka and H. Yoneda, *Chem. Lett.*, **1984**, 349 (1984)
- [275] Y. Hung, L.Y. Martin, S.C. Jackels, A.M Tait and D.H. Busch, *J. Am. Chem. Soc.*, **99**, 4029 (1977)
- [276] R.A.D. Wentworth and T.S. Piper, *Inorg. Chem.*, **4**, 709 (1965)
- [277] P.O. Whimp and N.F. Curtis, *J. Chem. Soc. (A)*, **1966**, 867 (1966)
- [278] M. Nonoyama and O. Hirai *Inorg. Chim. Acta*, **54**, L283 (1981)
- [279] J. Ferguson and M.L. Tobe, *Inorg. Chim. Acta*, **4**, 109 (1970)
- [280] D.A. House, R.W. Hay and M. Akbar Ali, *Inorg. Chim. Acta*, **72**, 239 (1983)
- [281] N.A.P. Kane-Maguire, K.C. Wallace and D.B. Miller, *Inorg. Chem.*, **24**, 597 (1985)
- [282] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, second edition, Elsevier, New York (1984)
- [283] C.K. Poon and K.C. Pun, *Inorg. Chem.*, **19**, 568 (1980)
- [284] D.A. House and C.S. Garner, *J. Am. Chem. Soc.*, **88**, 2156 (1966)

- [285] B.U. Nair, T. Ramasamy and D. Ramaswamy, *Inorg. Chem.*, **25**, 51 (1986)
- [286] B.N. Figgis, *Introduction to Ligand Fields*, John Wiley and Sons (1966)
- [287] M. Yamashita, H. Ito, K. Toriumi and T. Ito, *Inorg. Chem.*, **22**, 1566 (1983)
- [288] K. Toriumi, M. Yamashita, H. Ito and T. Ito, *Acta Crystallogr., Sect. C*, **42**, 963 (1986)
- [289] A.J. Blake, R.O. Gould, T. I. Hyde and M. Shröder, *J. Chem. Soc. Commun.*, **1987**, 1730 (1987)
- [290] A.J. Blake, R.O. Gould, T. I. Hyde and M. Shröder, *J. Chem. Soc. Commun.*, **1987**, 431 (1987)
- [291] C.J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw Hill (1962)
- [292] E.J. Bounsall and S.R. Koprach, *Can. J. Chem.*, **48**, 1481 (1970)
- [293] T. Ito, M. Kato and H. Ito, *Bull. Chem. Soc. Jpn.*, **57**, 2634 (1984)
- [294] M.D. Glick, G.H. Cohen and J.L. Hoard, *J. Am. Chem. Soc.*, **89**, 1996 (1967)
- [295] M. Kato and T. Ito, *Inorg. Chem.*, **24**, 509 (1985)
- [296] N.W. Alcock, N. Herron and P. Moore, *J. Chem. Soc. Dalton Trans.*, **1978**, 1282 (1978)
- [297] N.W. Alcock, N. Herron and P. Moore, *J. Chem. Soc. Dalton Trans.*, **1979**, 1486 (1979)
- [298] N.W. Alcock, E.H. Curzon, N. Herron and P. Moore, *J. Chem. Soc. Dalton Trans.*, **1979**, 1987 (1979)
- [299] M. Micheloni, A. Sabatini and P. Paoletti, *J. Chem. Soc. Perkin Trans. 2*, 828 (1978)
- [300] J.W. Chen, D.S. Wu and C.S. Chung *Inorg. Chem.*, **25**, 1940 (1986)
- [301] R.M. Clay, S. Corr, M. Micheloni and P. Paoletti, *Inorg. Chem.*, **24**, 3330 (1985)
- [302] A. Bianchi, L. Bologni, P. Dapporto, M. Micheloni and P. Paoletti, *Inorg. Chem.*, **23**, 1201 (1984)
- [303] Chemical Society Special Publications, **17** (1964)
- [304] R.W. Hay and M. Akbar Ali, *Inorg. Chim. Acta*, **103**, 23 (1985)

- [305] R.W. Hay and R. Bembi, *Inorg. Chim. Acta*, **65**, L227 (1982)
- [306] L.J. Murphy and L.J. Zompa, *Inorg. Chem.*, **18**, 3278 (1979)
- [307] P.G. Graham and D.C. Weatherburn, *Aust. J. Chem.*, **34**, 291 (1981)
- [308] (a) R.W. Hay, M.P. Pujari and F. McLaren, *Inorg. Chem.*, **23**, 3033 (1984)
(b) R.W. Hay, M.P. Pujari, W.T. Moodie, S. Craig, D.T. Richens, A. Perotti and L. Ungaretti, *J. Chem. Soc. Dalton Trans.*, **1987**, 2605 (1987)
- [309] B.F. Liang and C.S. Chung, *Inorg. Chem.*, **22**, 1017 (1983)
- [310] B.F. Liang and C.S. Chung, *Inorg. Chem.*, **20**, 2152 (1981)
- [311] R.W. Hay, R. Bembi, W.T. Moodie and P.R. Norman, *J. Chem. Soc. Dalton Trans.*, **1982**, 1088 (1982)
- [312] T.J. Riedo and T.A. Kaden, *Helv. Chim. Acta*, **62**, 1089 (1979)
- [313] P.G. Graham, Kinetic Studies of Transition Metal Complexes with Macrocyclic Ligands, PhD Thesis Victoria University (1982)