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THE REACTION OF NITROUS OXIDE WITH THE AQUOPENTA-AMMINERUTHENIUM(II) ION

Characterisation of penta-ammine(dinitrogen oxide)-ruthenium(II) complexes

A thesis presented for the
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CONTENTS

Tables (which are not included in the text), figures and references are at the end of the respective chapter.

SUMMARY

In the presence of an external reducing agent, nitrous oxide reacts with $[Ru(NH_3)_5(OH_2)]^{2+}$ to form the dinitrogen complexes, $[Ru(NH_3)_5N_2]^{2+}$ and $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$, which were isolated as the tetrafluoroborate salts. The reaction conditions can be controlled so that very little of the di-nuclear complex is formed. The dinitrogen complexes are also formed in the absence of an external reducing agent when concentrated solutions of $[Ru(NH_3)_5(OH_2)]^{2+}$ (10^{-2} M) are used. In this case $[Ru(NH_3)_5(OH_2)]^{2+}$ acts as the reducing agent. A preliminary kinetic investigation of the reaction indicated that a nitrous oxide complex is formed as an intermediate but spectral evidence for it could not be obtained. However, when dilute solutions of $[Ru(NH_3)_5(OH_2)]^{2+}$ (3×10^{-4} M) were exposed to nitrous oxide, Armor and Taube did observe a nitrous oxide complex, $[Ru(NH_3)_5(N_2O)]^{2+}$, but they could not isolate it.

From an understanding of the reaction between nitrous oxide and $[Ru(NH_3)_5(OH_2)]^{2+}$, and the results of Armor and Taube, it was possible to design reaction conditions which have enabled the nitrous oxide complex to be isolated. The bromide, iodide, tetrafluoroborate and hexafluorophosphate salts have been characterised as $[Ru(NH_3)_5(N_2O)]Br_2$, $[Ru(NH_3)_5(N_2O)]I_2$, $[Ru(NH_3)_5(N_2O)](BF_4)_2 \cdot H_2O$ and $[Ru(NH_3)_5(N_2O)](PF_6)_2 \cdot H_2O$ respectively. Complexes containing $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ have also been prepared.

A powder photograph of $[Ru(NH_3)_5(N_2O)]Br_2$ indicated that it has a

SUMMARY (cont'd)

structure similar to that of the dinitrogen complex, $[Ru(NH_3)_5N_2]Cl_2$, in which the nitrous oxide is linearly co-ordinated. A normal co-ordinate analysis of the infrared spectra of the co-ordinated nitrous oxide was made, and it indicated that the nitrous oxide is co-ordinated to the ruthenium atom through its oxygen atom.

The aquopenta-ammineruthenium(II) ion has also been isolated. Its bromide, iodide and hexafluorophosphate salts have been characterised as $[Ru(NH_3)_5(OH_2)]Br_2$, $[Ru(NH_3)_5(OH_2)]I_2$ and $[Ru(NH_3)_5(OH_2)](PF_6)_2 \cdot H_2O$ respectively. A tetrafluoroborate salt was also isolated, but it could not be characterised.

Also, two reactions were found which yielded the penta-amminecarbonyl-ruthenium(II) complex. In one reaction carbon dioxide was the source of the carbonyl group, and in the other it was abstracted from formamide.

STATEMENT

This thesis contains no material which has been accepted for any other degree in any University. To the best of my knowledge, the work described here is original and no part of it has been reported elsewhere by any other person, except where due reference is made in the text.

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ABBREVIATIONS

The following list of abbreviations will be used in this thesis.

monomer	$[RuA_5N_2]^{2+}$
dimer	$[A_5RuN_2RuA_5]^{4+}$
i	initially
f	finally
A	ammonia, NH_3
en	ethylenediamine, $NH_2CH_2CH_2NH_2$
trien	triethylenetetra-amine, $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
py	pyridine
dipy	2,2'-dipyridyl
diphos	1,2-bis(diphenylphosphino)ethane
$DMGH_2$	dimethylglyoxime
THF	tetrahydrofuran
Me	methyl, CH_3
Et	ethyl, C_2H_5
Ph	phenyl, C_6H_5

for the reducing agents:-

Zn/Hg	amalgamated zinc
$Pt(H_2)$	dihydrogen on platinum black

in reference to infrared spectra:-

s	strong	sh	shoulder
m	medium	br	broad
w	weak	a	region covered by the anion

CHAPTER 1

INTRODUCTION

Recently many workers have been interested in the chemistry of ruthenium and its complexes. There have been reviews on most aspects of of this work and so this chapter is intended to give only a general outline of this current work.

1:1. Early Work.—

Prior to 1960 the chemistry of ruthenium was not very extensive. Most of the reactions which were known used the metal as the starting material, and as it is not very reactive, vigorous reaction conditions were necessary. As a result, the initial products were oxo-complexes in which the ruthenium was in a high oxidation state (VI, VII or VIII). For example, the fusion of the metal with potassium nitrate and potassium hydroxide yielded potassium ruthenate, $K_2[Ru^{VI}O_4]$.

Oxidation of the ruthenate with chlorine or permanganate in acid gave ruthenium tetroxide, RuO_4. This could be converted to ruthenium trichloride which is a convenient starting material for complexes containing ruthenium in the lower oxidation states (IV, III and II). However, depending on the preparative method, the trichloride was sometimes heavily contaminated with the nitrosyl complex, $[Ru(NO)Cl_3]$, and this impurity caused great confusion in formulating the products from

the reactions of the trichloride. Even so, Glue and his co-workers characterised some ruthenium(II) and (III)-ammines and Charronat isolated oxalato-complexes of ruthenium (IV), (III) and (II). A recent monograph by Griffith[1] covers most of this early work.

After the work of these men there were very few new complexes reported until after 1960. Since then there has been a renewed interest in the chemistry of ruthenium, and now many ruthenium complexes are known. Representative complexes for each of its oxidation states are given in Table 1:1. The most common oxidation states are the +3 and +2 states.

The commercial availability of the convenient starting complexes, $RuCl_3$ and $[RuA_6]Cl_3$[†], is one reason why ruthenium(II) and (III) complexes are now being extensively studied. These studies have also been stimulated by the interesting properties shown by the complexes which have been prepared.

1:2. Kinetic Studies of Ruthenium(II) and (III) Complexes.—

Extensive kinetic data have been collected for reactions of chromium(III) (d^3 system), cobalt(III) (d^6 low spin) and rhodium(III) (d^6 low spin) complexes. The preparation of ruthenium(II) and (III) complexes has given the kineticists a new series of complexes to study. Ruthenium(II) is a d^6 low spin system the same as cobalt(III) and rhodium(III).

[†]A list of abbreviations used in this thesis is given on page vii.

Ruthenium(III), however, has an electronic configuration which is not very common. It is a d^5 low spin system and, except for a limited number of iron(III) complexes, the ruthenium(III) complexes are the only ones in which the metal has this electronic configuration and which can be studied in aqueous media.

Also the ruthenium(II) and (III) complexes are inert, and *cis*- and *trans*- isomers of several complexes have been isolated. These isomers have been used to follow the stereochemical changes in several reactions.[2,4]

Although only a few kinetic studies of ruthenium(II) complexes have been reported up to date,[3] there have been several substitution, redox and hydrolysis reactions of ruthenium(III) reported,[4-8] and the number of reactions investigated will no doubt increase in the next few years.

1:3. Homogeneous Catalysis by Ruthenium(II) and (III) Complexes.—

Examples of homogeneous catalysis by ruthenium complexes have been known since 1961 when Halpern *et al.* found that ruthenium(III) chlorides, in aqueous hydrochloric acid, catalysed the dihydrogen reduction of iron(III) and ruthenium(IV) substrates. These reactions have been investigated extensively and it has been found that the rate determining step is the heterolytic splitting of the dihydrogen to form a ruthenium(III)-hydride intermediate. Similar reactions have also been observed in non-aqueous solvents.

Ruthenium(II)-chloro species also are active hydrogenation agents. In aqueous hydrochloric acid, ruthenium(II)-chloro species (probably $RuCl_4^{2-}$) hydrogenate active olefins (*e.g.*, maleic, fumaric and acrylic acids). An acid solution of $[RuCl_4(dipy)]^{2-}$ will also hydrogenate maleic acid.

The phosphine complexes, $[RuCl_2(PPh_3)_4]$ and $[RuCl_2(PPh_3)_3]$ are even more active. They can reduce unactivated olefins and acetylenes under an atmosphere of dihydrogen. They are active at 25°C while the other systems mentioned are not appreciably active below 80°C.

The formation of hydride intermediates by the heterolytic splitting of the dihydrogen also occurs in the ruthenium(II) systems. Hydrogenation occurs by the insertion of the substrate into this metal-hydrogen bond. The hydride intermediate from the phosphine systems, $[RuHCl(PPh_3)_3]$, is the most active catalyst known for the hydrogenation of alk-1-enes.

Many other examples of homogeneous catalysis by ruthenium complexes are known (*e.g.*, isomerisation, polymerisation and decarbonylation). This field of homogeneous catalysis by ruthenium complexes has been extensively reviewed by James.[9] The current interest in homogeneous catalysis indicates that this property of ruthenium complexes will attract increasing interest in the future.

1:4. Penta-ammineruthenium(II) Complexes.—

The preparation of the first dinitrogen complex, $[RuA_5N_2]X_2$ (X = monovalent anion), by Allen and Senoff,[10] and the subsequent formation of $[RuA_5N_2]^{2+}$ and $[A_5RuN_2RuA_5]^{4+}$ from the reaction of $[RuA_5(OH_2)]^{2+}$ with dinitrogen[11,12] has caused much interest in penta-ammineruthenium(II) complexes.

The lability of the aquo-ligand in the aquopenta-ammineruthenium(II) ion, $[RuA_5(OH_2)]^{2+}$, has resulted in much work being done with this complex. It has been used to prepare many penta-ammineruthenium(II) complexes. Most of the complexes prepared contain π-acceptor ligands such as pyridine, substituted pyridines, organic nitriles and carbon monoxide. The usual preparative technique is to prepare $[RuA_5(OH_2)]^{2+}$ *"in situ"*, by the reduction of $[RuA_5Cl]Cl_2$, in the presence of excess of the ligand. These reactions have been reviewed by Ford.[3]

1:5. Outline of Research.—

A chronological order of the work for this thesis is given here because the course of the project was influenced by work published from other laboratories.

In the initial report by Harrison and Taube[11] on the reaction between $[RuA_5(OH_2)]^{2+}$ and dinitrogen, a strong absorption in the product at 262 nm was not characterised. As an introduction to Schlenk tube techniques this

reaction was studied, but before any detailed work could be done, the system was completely characterised.[12]

The kinetic study of the reaction by Itzkovitch and Page[13] indicated that co-ordinated and free dinitrogen had similar reactivity towards substitution of the aquo-ligand in $[RuA_5(OH_2)]^{2+}$. As nitrous oxide may be considered to be dinitrogen co-ordinated to an oxygen atom and it is known to be a competitive inhibitor of dinitrogen reduction by nitrogenase,[14] the reaction of nitrous oxide and $[RuA_5(OH_2)]^{2+}$ was studied.

The reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide in the presence of a reducing agent gave mainly the dinitrogen complex, $[RuA_5N_2]^{2+}$, with small amounts of the dimer, $[A_5RuN_2RuA_5]^{4+}$. A short note of this reaction has been published.[15] The dinitrogen complexes were also formed in the absence of an external reducing agent and it was shown that the ruthenium(II) complex, $[RuA_5(OH_2)]^{2+}$, was acting as the reducing agent in this case. Although no conclusive evidence could be obtained for it, the results indicated that a nitrous oxide intermediate, $[RuA_5(N_2O)]^{2+}$, was present in the reaction.

These results were presented in 1969 at "A Symposium on Nitrogen Fixation" held in Melbourne. At this symposium Taube reported his kinetic results for the reaction of nitrous oxide with dilute solutions of $[RuA_5(OH_2)]^{2+}$. The product of the reaction was $[RuA_5(N_2O)]^{2+}$ but it was very unstable and was not isolated. It decomposed in the absence of

nitrous oxide and was reduced in the presence of a reducing agent to the dinitrogen complex, $[RuA_5N_2]^{2+}$. The results of Taube[16] were used to design conditions which resulted in the isolation of the nitrous oxide complex. The infrared spectra of the complexes were recorded and an initial report has been published.[17]

Complexes containing isotopically labelled nitrous oxide were also prepared to confirm the assignments which had been made for co-ordinated nitrous oxide and to help distinguish between oxygen and nitrogen co-ordination by the nitrous oxide. However it was not possible from the infrared spectra to determine definitely how the nitrous oxide was co-ordinated and so a normal co-ordinate analysis of the system was made.

A powder photograph of the bromide salt had indicated that the nitrous oxide was linearly co-ordinated to the metal and so a linear four atom system was used as the model for the normal co-ordinate analysis. The calculations indicated that the nitrous oxide is co-ordinated through the oxygen atom.

It had been planned to prepare the isotopically labelled dinitrogen complexes using labelled nitrous oxide, but before this could be attempted Armor and Taube reported the isolation and infrared spectra of the labelled dinitrogen complexes.[18] From their results, Armor and Taube concluded that the nitrous oxide was co-ordinated through the *exo* nitrogen atom and then reduced to dinitrogen. The presence of both linkage isomers

(*i.e.* oxygen and nitrogen linked nitrous oxide) in the reaction solutions is suggested to be the reason for the disparity between the conclusions drawn from the experiments with the labelled nitrous oxide.

Since the completion of the preparations, Bottomley and Crawford have reported the preparation of the nitrous oxide complexes from the nitrosyl-penta-ammineruthenium(II) complex and hydroxylamine.[19]

In this thesis the kinetic investigation of the reaction between $[RuA_5(OH_2)]^{2+}$ (generated *in situ*) and nitrous oxide is reported in Chapter 2, and the isolation and characterisation of the nitrous oxide complexes from this reaction follows in Chapters 3 and 4. As $[RuA_5(OH_2)]^{2+}$, which is the starting complex for these reactions, had not been isolated and characterised before, this was done, and is reported in Chapter 5. During the work two reactions were found which yielded carbonylpenta-ammine-ruthenium(II) and they are given in Chapter 6.

TABLE 1:1

Complexes of ruthenium

oxidation state	
VIII	RuO_4, RuO_4py_2
VII	$K[RuO_4]$
VI	RuF_6, $RuOF_4$, $K_2[RuO_4]$
V	$K[RuF_6]$, $(RuF_5)_4$
IV	$K_2[RuCl_6]$, $K_4[Ru_2OCl_{10}]$, $[Ru(NO)Cl_3]$
III	$RuCl_3$, $K_3[RuCl_6]$, $[RuA_6]Cl_3$, $[RuA_5NO]Cl_2$, $[RuCl_2(PPh_3)_3]$, $[Ru(CO)Br_3(PPh_3)_3]$
II	$RuBr_2$, $K_2[RuCl_5NO]$, $[RuA_6]Cl_2$, $[Ru(CO)Cl_2]_n$, $[Ru(CO)Cl_2(PEt_2Ph)_3]$
I	$[Ru(NO)I_2(AsPh_2Me)_2]_2$, $[Ru(NO)Br_2]_n$, $[Ru(CO)Br]_n$
0	$[Ru(diphos)_2]$, $Ru(CO)_5$, $Ru_3(CO)_{12}$

CHAPTER 1

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CHAPTER 2

THE REACTION OF NITROUS OXIDE WITH THE AQUOPENTA-AMMINERUTHENIUM(II) ION

2:1. Introduction.—

Since 1930 when Bortels[1] showed that molybdenum is essential for the utilization of dinitrogen by fixing organisms, many workers have suggested that a transition metal atom, which is able to co-ordinate with the dinitrogen, is present in the active site of the enzyme nitrogenase. In the following years this suggestion resulted in many attempts, all unsuccessful, to isolate a dinitrogen complex. In 1965, the isolation of the first dinitrogen complex, $[RuA_5N_2]X_2$ ($X = Cl^-$, Br^-, I^-, BF_4^-, PF_6^-), by Allen and Senoff[2] ended many years of speculation as to the ability of dinitrogen to act as a ligand in a transition metal complex.

Following the isolation of this complex from the reaction of hydrazine and ruthenium trichloride,[2,3] other sources of co-ordinated dinitrogen have been found (*e.g.*, ammonia,[4] azide ion,[5,6] organic azides[7] and hydrazine derivatives[8]), but the most interesting source is dinitrogen itself because of the similarity of its reaction with the complexes to the biological process of nitrogen fixation.

There are several non-aqueous systems involving a powerful reducing agent and a transition metal complex which will reduce dinitrogen, and

ammonia can be detected when the reaction solutions are hydrolysed.[9-11] Yields of ammonia are generally low, although in some systems it is stoichiometric,[12-14] and recently catalytic reduction of dinitrogen to ammonia has been achieved by incorporating a proton source in the system.[15,16]

The reaction of dicyclopentadienyltitanium dichloride with ethylmagnesium halide in ether or tetrahydrofuran under dinitrogen has been studied extensively,[17-19] and for this and similar systems[20-22] it has been suggested that the metal, in a low oxidation state, reacts with dinitrogen to form a nitride intermediate[14,19,22,23] which is protonated by the proton source in the catalytic systems. Although it is not easy to isolate dinitrogen complexes from these systems,[23] there have been many dinitrogen complexes isolated from other reactions.

Since the isolation[2,3] of $[RuA_5N_2]X_2$ (X = mono-valent anion) there has been much interest in the preparation and properties of dinitrogen complexes and many have now been prepared.[24-27] Unfortunately it has not been possible to reduce the co-ordinated dinitrogen in the complexes.[28-30]

The complexes which have been isolated indicate that the σ-acceptor and π-donor properties of the co-ordination site for the dinitrogen are very critical in determining the stability of the complex. These requirements are so critical that series of stable dinitrogen complexes are not very common.[8, 31-33]

Phosphines have been found to be suitable co-ligands for dinitrogen and numerous phosphine-dinitrogen complexes are known. However these phosphine complexes are only soluble in non-aqueous media. The aquo-ammine complexes of ruthenium(II), $[RuA_5(OH_2)]^{2+}$, *cis*-$[RuA_4(OH_2)_2]^{2+}$ and *cis*-$[Ru(trien)(OH_2)_2]^{2+}$, react with dinitrogen in aqueous solution and surprisingly, in view of its weak ligand properties, the dinitrogen is able to displace an aquo-group from these complexes.[34-37] These reactions, being in aqueous solutions, have been studied extensively, especially the reaction of $[RuA_5(OH_2)]^{2+}$ with dinitrogen.[34,35,38-40]

2:2. *The Reaction of the Aquopenta-ammineruthenium(II) Ion with Dinitrogen.*—

The products from the reaction between $[RuA_5(OH_2)]^{2+}$ and dinitrogen[34,35] are the complex of Allen and Senoff, $[RuA_5N_2]^{2+}$, and a dinuclear complex, $[A_5RuN_2RuA_5]^{4+}$. The products can be isolated from the reaction solution as the tetrafluoroborate salts. $[RuA_5N_2](BF_4)_2$ is characterised by the strong nitrogen-nitrogen stretch at 2144 cm^{-1} in its infrared spectrum[3] and an absorption at 221 nm ($\varepsilon = 1.8 \times 10^4$ $M^{-1}cm^{-1}$) in its electronic spectrum.[40] $[A_5RuN_2RuA_5](BF_4)_4$ has only a broad, weak absorption around 2060 cm^{-1} in its infrared spectrum[35] but has a very strong absorption at 2100 cm^{-1} in its Raman spectrum[41] due to the nitrogen-nitrogen stretch. In its electronic absorption spectrum it is characterised by a strong absorption at 262 nm ($\varepsilon = 4.8$ $M^{-1}cm^{-1}$).[38]

The kinetics of the reaction of dinitrogen with $[RuA_5(OH_2)]^{2+}$ (produced electrolytically from $[RuA_5Cl]Cl_2$) have been studied by Page and co-workers.[38,39] The dinitrogen complexes were considered to form according to the reactions:-

$$A' + N_2 \xrightarrow{k_M} \text{Monomer} \qquad 1$$

and $$A' + \text{Monomer} \xrightarrow{k_D} \text{Dimer} \qquad 2$$

so $$d[\text{Monomer}]/dt = k_M[A'][N_2] - k_D[A'][\text{Monomer}] \qquad 3$$

and $$d[\text{Dimer}]/dt = k_D[A'][\text{Monomer}] \qquad 4$$

For a solution saturated with dinitrogen at one atmosphere

$$d[\text{Monomer}]/dt = k_M'[A'] - k_D[A'][\text{Monomer}] \qquad 5$$

where $k_M' = k_M[N_2]$.

(A' is $[RuA_5(OH_2)]^{2+}$, the monomer is $[RuA_5N_2]^{2+}$ and the dimer is $[A_5RuN_2RuA_5]^{4+}$.)

Reaction 1 was studied at low initial concentrations of $[RuA_5(OH_2)]^{2+}$ ($< 2 \times 10^{-4}$ M), with the formation of the dimer only becoming noticeable after 4-5 hours. The formation of the dimer (reaction 2) was studied separately by the addition of solid monomer to a solution of $[RuA_5(OH_2)]^{2+}$. At initial concentrations of $1\text{-}3 \times 10^{-3}$ M $[RuA_5(OH_2)]^{2+}$, the formation of both the monomer and dimer could be followed together.[38]

The reactions 1 and 2 were shown[39] to be first order with respect to each reactant and second order rate constants at 25°C and an ionic strength (μ) of 0.30 M are, $k_M = 8.0 \times 10^{-2}\ M^{-1}sec^{-1}$

and $k_D = 3.6 \times 10^{-2}\ M^{-1}sec^{-1}$.

These results suggest that the reactivity of co-ordinated dinitrogen towards substitution of the aquo-ligand in $[RuA_5(OH_2)]^{2+}$ is similar to the reactivity of free dinitrogen.[38]

Armor and Taube[40] have also determined k_M and k_D. Their value of k_M ($7.3 \times 10^{-2}\ M^{-1}sec^{-1}$ at 25°C and μ = 0.10 M) is in good agreement with the result of Page and co-workers but the marked effect of ionic strength on k_D does not allow a comparison to be made.

2:3. The Dependence of the Final Concentrations of the Monomer and Dimer on the Reaction Conditions.—

As a consequence of the reaction scheme proposed by Page and co-workers[38,39] the concentrations of the monomer and dimer which are formed in the reaction between $[RuA_5(OH_2)]^{2+}$ and dinitrogen will depend on the reaction conditions. An idea of how the initial concentration of $[RuA_5(OH_2)]^{2+}$ and the pressure of dinitrogen above the reaction solution will affect these concentrations will be useful later when the reaction between $[RuA_5(OH_2)]^{2+}$ and nitrous oxide is considered.

As the decomposition of the monomer (equation 6) has been shown to be

$$[RuA_5N_2]^{2+} + H_2O \longrightarrow [RuA_5(OH_2)]^{2+} + N_2 \qquad 6$$

much slower than its rate of formation,[40] it will not be considered in this discussion.

2:3:1. Effect of the initial concentration of $[RuA_5(OH_2)]^{2+}$.—

The ratio of the rate of formation of the monomer to the rate of formation of the dimer given by dividing equation 3 by equation 4 is;

$$d[\text{Monomer}]/dt \Big/ d[\text{Dimer}]/dt = \frac{k_M[N_2]}{k_D[\text{Monomer}]} - 1 \qquad 7$$

This expression indicates that at a constant pressure of dinitrogen above the reaction solution (*i.e.* the concentration of dinitrogen in the solution is constant), and providing there is excess $[RuA_5(OH_2)]^{2+}$ present, the rate of formation of the dimer will increase more than the rate of formation of the monomer if the concentration of the monomer is increased. That is the ratio $d[\text{Monomer}]/dt \Big/ d[\text{Dimer}]/dt$ will decrease.

An increase in the initial concentration of $[RuA_5(OH_2)]^{2+}$ will mean that the concentration of the monomer formed in the first minutes of the reaction will be higher. However the rate of formation of the dimer will also be greater under these conditions because the concentration of the monomer and $[RuA_5(OH_2)]^{2+}$, even though some of the latter has reacted to form the monomer, will both be increased. As the formation of the dimer involves the loss of monomer, the ratio, $[\text{Dimer}]_f/[\text{Monomer}]_f$, will be expected to increase with increasing initial concentration of $[RuA_5(OH_2)]^{2+}$

because the formation of the dimer will become faster the more excess of $[RuA_5(OH_2)]^{2+}$ there is present, resulting in less of the monomer being present at the end of the reaction.

Thus an increase in the initial concentration of $[RuA_5(OH_2)]^{2+}$ may be considered to increase the "initial" concentration of the monomer and so from equation 7, an increase in the ratio, $[Dimer]_f/[Monomer]_f$, would be expected.

2:3:2. Effect of the pressure of dinitrogen.—

An increase in the pressure of dinitrogen above the reaction will increase the concentration of the gas in the solution. Hence the rate of formation of the monomer will be expected to increase as the pressure of dinitrogen above the reaction is increased. However at a constant initial concentration of $[RuA_5(OH_2)]^{2+}$, a corresponding increase in the rate of formation of the dimer will not be observed because there would not be an excess of $[RuA_5(OH_2)]^{2+}$ available to react with the monomer. The concentration of unreacted $[RuA_5(OH_2)]^{2+}$ after a constant reaction time (*e.g.*, 30 minutes) will decrease as the pressure of dinitrogen is increased due to the increased rate of formation of the monomer. At high pressures of dinitrogen the reaction of $[RuA_5(OH_2)]^{2+}$ with dinitrogen could be so rapid that very little dimer would be formed. Thus the ratio, $[Dimer]_f/[Monomer]_f$, will be expected to decrease as the pressure of dinitrogen above the solution is increased.

Page and co-workers[38] observed that there was more dimer formed when they increased their initial concentration of $[RuA_5(OH_2)]^{2+}$ from 10^{-4} to 10^{-3} M, but the effect of the dinitrogen pressure on the formation of the monomer and the dimer was not reported.[39]

2:4. Properties and Reactions of Nitrous Oxide.—

The data in Table 2:1 shows that the bond length and stretching frequencies of the nitrogen-nitrogen bond in nitrous oxide are similar to the corresponding properties of dinitrogen in the complexes. If nitrous oxide is considered as a dinitrogen compound of oxygen then it may be expected that it would show a similar affinity towards substituting the aquo-ligand in $[RuA_5(OH_2)]^{2+}$ as does co-ordinated dinitrogen.

Although there have been many reports of nitrous oxide being decomposed at elevated temperatures, prior to 1967 very few reactions of it at room temperature were known (see Table 2:2) which suggested that it was an extremely inert molecule.

This is surprising in view of its positive free energy of formation[56] (ΔG° = +24.9 kcal mol^{-1}) and its potential oxidising power indicated by the half reactions,[57]

$$N_2O + 2H^+ + 2e^- \longrightarrow N_2 + H_2O \qquad E^\circ = +1.77 \text{ eV} \qquad 8$$

and

$$N_2O + H_2O + 2e^- \longrightarrow N_2 + 2OH^- \qquad E^\circ = +0.94 \text{ eV} \qquad 9$$

However nitrous oxide is a product and substrate of bacterial metabolism. It is one of the products of the denitrification process, and it is a competitive inhibitor of dinitrogen reduction by nitrogenase, being itself reduced to dinitrogen in the process.[58]

Recently, several reactions of nitrous oxide with transition metal complexes, at room temperature, have been established and it appears that its apparent inertness is due in part, to the lack of study in this field. Previously only ammoniacal chromous chloride[49] and titanium(III) chloride[48] were known to react with nitrous oxide (Table 2:2). Banks *et al.*[56] have now found that cobalt(I), generally, and some rhodium(I) complexes also react with nitrous oxide with the evolution of dinitrogen. However they were unable to reproduce the reaction with titanium(III). Their results are tabulated in Table 2:3.

A detailed investigation of the reaction of nitrous oxide with the cobalt(I) corrin, vitamin B_{12s}, has shown that the reduction of nitrous oxide to dinitrogen is a two electron step involving the cobalt atom.[56] The overall reaction can be written as

$$2Co^{I} + N_2O \longrightarrow 2Co^{II} + N_2 \uparrow \qquad 10$$

and vitamin B_{12r}, which contains cobalt(II), can be isolated from the reaction. A similar reduction of nitrous oxide to dinitrogen with cobaloximes (vitamin B_{12} model complexes derived from bis-dimethylglyoxime cobalt complexes) has also been reported.[59]

Of particular interest are reactions of nitrous oxide with systems known to form dinitrogen complexes. $[CoH_3(PPh_3)_3]$ and the dinitrogen complex, $[CoH(N_2)(PPh_3)_3]$, have been shown to react with nitrous oxide.[60] In the presence of excess triphenylphosphine, catalytic reduction of nitrous oxide to dinitrogen and oxidation of triphenylphosphine to triphenylphosphineoxide were observed. In the case of $[CoH_3(PPh_3)_3]$ there was evidence from solution infrared spectra for the formation of $[CoH(N_2)(PPh_3)_3]$ as an intermediate where the co-ordinated dinitrogen in the complex comes from the nitrous oxide.

In all the reactions of nitrous oxide with transition metal complexes an intermediate containing nitrous oxide has been postulated. However no evidence for such an intermediate has been observed.

In view of the properties of nitrous oxide discussed above, the reaction of nitrous oxide with $[RuA_5(OH_2)]^{2+}$ was studied to see whether a dinitrogen complex could be isolated and to obtain evidence for any nitrous oxide intermediates which may have formed.

Since this work was started, it has been reported[33] that nitrous oxide can be used instead of dinitrogen to prepare the dinitrogen complexes, $[OsX_2(N_2)(QR_3)_3]$ (X = Cl or Br; QR_3 = tertiary phosphine or arsine), from *mer*-$[OsX_3(QR_3)_3]$ and amalgamated zinc. In this reaction the dinitrogen has remained co-ordinated, instead of being released as was observed in the other reactions when nitrous oxide was reduced by transition metal

complexes.

Armor and Taube's work on the ruthenium system was first reported at "A Symposium on Nitrogen Fixation" in 1969.[61]

2:5. Results and Discussion.—

Although the higher solubility of nitrous oxide in aqueous solution results in a much faster reaction, the reactions of nitrous oxide and dinitrogen with $[RuA_5(OH_2)]^{2+}$ show many similarities.

It was found that nitrous oxide reacted quantitatively with $[RuA_5(OH_2)]^{2+}$, prepared *"in situ"* by the reduction of $[RuA_5Cl]Cl_2$, in the presence of a reducing agent (Zn/Hg, $Pt(H_2)$ or electrolytic reduction) to give a mixture of the two dinitrogen complexes, $[RuA_5N_2]^{2+}$ and $[A_5RuN_2RuA_5]^{4+}$. The products were isolated as their tetrafluoroborate salts and characterised by their infrared and ultraviolet spectra, and by the release of the calculated amount of dinitrogen on oxidation with cerium(IV) sulphate.

At a pressure of one atmosphere of nitrous oxide above the reaction solution, quantitative conversion to the dinitrogen complexes was achieved after two hours (Figure 2:1). The reaction with dinitrogen was much slower under the same conditions, and finally reached a position of equilibrium, with about 80% conversion, after 5-8 hours (see Table 2:6).

The parameter chosen to indicate the extent of the reaction with nitrous oxide is the "% Fixed N_2".

$$\% \text{ Fixed } N_2 = \frac{[\text{Monomer}] + [\text{Dimer}]}{[RuA_5Cl_3]_i} \times 100$$

$$= \% \text{ Monomer} + \% \text{ Dimer} \qquad 11$$

$$\text{where } \% \text{ Monomer} = \frac{[\text{Monomer}]}{[RuA_5Cl_3]_i} \times 100$$

$$\% \text{ Dimer} = \frac{[\text{Dimer}]}{[RuA_5Cl_3]_i} 100$$

and $[RuA_5Cl_3]_i$ is the initial concentration of $[RuA_5Cl]Cl_2$.
It will be shown later that the % Fixed N_2 is the percentage $[RuA_5(OH_2)]^{2+}$ which has reacted with nitrous oxide to yield the dinitrogen complexes.

TABLE 2:4

Extinction coefficients of the dinitrogen complexes used in the calculations*

	221 nm	262 nm
$[RuA_5N_2]^{2+}$	1.69×10^4 (a)	0.084×10^4
$[A_5RuN_2RuA_5]^{4+}$	0.30×10^4	4.8×10^4
$[RuA_5(OH_2)]^{2+}$	0.068×10^4	0.055×10^4

*Extinction coefficients were taken from reference 38 except (a) which was taken from reference 62.
(Armor and Taube[40] have since published an extinction coefficient of 1.8×10^4 $M^{-1}cm^{-1}$ for $[RuA_5N_2]^{2+}$ at 221 nm.)

The reactions were followed spectrophotometrically using the extinction

coefficients in Table 2:4 to calculate the concentrations of dinitrogen complexes which had formed. Because the absorption due to unreacted $[RuA_5(OH_2)]^{2+}$ has a much lower extinction coefficient than that of the products it was not considered in the calculations.

2:5:1. The dependence of the concentrations of the monomer and dimer on the reaction conditions.—

(a). The effect of the initial concentration of $[RuA_5(OH_2)]^{2+}$ on the reaction (Zn/Hg was the reducing agent) is shown in Figure 2:2. It was found that the rate of increase of the % Fixed N_2 was unaffected by a ten-fold variation in the initial concentration of $[RuA_5(OH_2)]^{2+}$. As the plot is of the percent extent of the reaction (*i.e.* the % Fixed N_2) its independence of the initial concentration of $[RuA_5(OH_2)]^{2+}$ suggests that the reaction is first order with respect to $[RuA_5(OH_2)]^{2+}$. These results are tabulated in Table 2:5 (runs 1 and 2).

For the four reactions whose results are tabulated in Table 2:5, the final % Fixed N_2 was not the same and was always less than 100%. This is because there is a second reaction occuring which does not involve a reaction with nitrous oxide. It is the formation of the dimer by the reaction of the monomer, which is the initial reaction product, with unreacted $[RuA_5(OH_2)]^{2+}$. The formation of the dimer in this subsequent reaction means that there is less $[RuA_5(OH_2)]^{2+}$ present to react with nitrous oxide and so the % Fixed N_2 cannot reach 100%.

The faster the initial reaction with nitrous oxide the lower will be the conversion to the dimer and so the highest values for the % Fixed N_2 will be achieved by the fastest reactions.

However the % Total Ru given by:-

$$\% \text{ Total Ru} = \% \text{ Monomer} + 2 \% \text{ Dimer} \qquad 12$$

does reach 100% in all these reactions as is shown in Figure 2:1 and Table 2:5 which means that complete reaction does occur.

(b). The effect of the pressure of nitrous oxide above the reaction solution is shown in Figure 2:3 and the results are tabulated in Table 2:6. Decreasing the pressure of nitrous oxide had a pronounced effect on the rate of change of the % Fixed N_2 (*i.e.* the rate of the reaction). At atmospheric pressure of nitrous oxide the reaction proceeded to completion within two hours. As the nitrous oxide pressure was decreased the reaction gradually became slower until at 0.065 atmospheres it had a rate comparable with the rate of the reaction of dinitrogen with $[RuA_5(OH_2)]^{2+}$ at atmospheric pressure of dinitrogen (Figure 2:3). For these latter two reactions, Table 2:6 shows that the concentrations of the monomer and the dimer formed in these reactions, and also the rate at which the % Fixed N_2 increases, are almost the same, which indicates that their rate constants must be very similar. (At these pressures, the concentration of nitrous oxide and dinitrogen in solution are similar.)

Further evidence of the similarity of these two reactions is indicated by the variation of the ratio, % Dimer/% Monomer.

(c). Variations in the ratio, % Dimer/% Monomer. In the nitrous oxide reaction there was a large increase in the ratio, % Dimer/% Monomer, when the initial concentration of $[RuA_5(OH_2)]^{2+}$ was increased from 10^{-3} M to 10^{-2} M (Table 2:5). It is interesting to note that the ratio is higher in the cases where the $[RuA_5Cl]Cl_2$ was completely reduced under argon before the reaction was initiated by the introduction of nitrous oxide. In these cases the initial concentration of $[RuA_5(OH_2)]^{2+}$ is the concentration of $[RuA_5Cl]Cl_2$ used and it is higher than the maximum concentration of $[RuA_5(OH_2)]^{2+}$ generated under nitrous oxide because formation of the dinitrogen complexes has commenced before the reduction is complete in the latter case.

Increasing the pressure of nitrous oxide from 0.065 to one atmosphere increases the concentration of nitrous oxide in solution and results in the ratio decreasing markedly with very little of the dimer being formed at one atmosphere of nitrous oxide (Table 2:6).

It has been shown for the reaction between dinitrogen and $[RuA_5(OH_2)]^{2+}$ that similar changes in the ratio, $[Dimer]_f/[Monomer]_f$, are expected for increases in the initial concentrations of $[RuA_5(OH_2)]^{2+}$ and the pressure of dinitrogen above the solution (section 2:3).

As the dimer to monomer ratios in both these reactions are affected in the same way by the reaction conditions, it may be concluded that in the nitrous oxide reaction, the dimer is formed by the reaction of the monomer with unreacted $[RuA_5(OH_2)]^{2+}$ just as in the dinitrogen reaction.

2:5:2. Stoichiometry of the reaction.—

The potentials for the half reaction of nitrous oxide, equations 8 and 9,[57] indicate that nitrous oxide is potentially a powerful oxidising agent and recently it has been catalytically reduced to dinitrogen in the presence of cobalt(I) complexes.[60] Also it has been reduced electrolytically to hydrazine - the most efficient reduction (10-15% current efficiency) being achieved with a mercury cathode and an ammonium sulphate supporting electrolyte.[57]

Because of these reported reductions of nitrous oxide, the reaction solutions were tested for dinitrogen and hydrazine to check that nitrous oxide and not one if its reduction products was reacting with $[RuA_5(OH_2)]^{2+}$.

Tests for hydrazine using *para*-aminobenzaldehyde[63] gave negative results and samples of the gas above the reaction solution were found, mass spectrometrically, to contain nitrous oxide with only traces of dinitrogen and dihydrogen.

Conclusive proof that nitrous oxide itself reacted with $[RuA_5(OH_2)]^{2+}$ in this reaction was obtained from the manometric measurement of the volume

of nitrous oxide absorbed during the reaction. The results obtained are tabulated in Table 2:7 and they indicate that one mole of nitrous oxide is absorbed for each mole of $[RuA_5(OH_2)]^{2+}$ which reacts.

TABLE 2:7

Uptake of nitrous oxide

Volume of N_2O introduced	(at STP)	= 8.73_6 cc
Volume of N_2O recovered	(at STP)	= 7.10_5 cc
Volume of N_2O used	(at STP)	= 1.63_1 cc

From spectral measurements the

calculated* volume of N_2O used (at STP) = 1.72_3 cc

$$N_2O:Ru = \frac{1.63_1}{1.72_3} : 1 = 0.94_6:1$$

*Calculated assuming one mole of N_2O is used for each mole of $[RuA_5(OH_2)]^{2+}$ which reacts.

2:5:3. Suggested mechanism.—

From these results the reactions occuring in the presence of Zn/Hg can be written as:-

1. Reduction of $[RuA_5Cl]Cl_2$,

$$[RuA_5Cl]^{2+} + H_2O + e^- \longrightarrow [RuA_5(OH_2)]^{2+} + Cl^- \qquad 13$$

2. Reaction with nitrous oxide,

$$[RuA_5(OH_2)]^{2+} + N_2O + 2e^- \longrightarrow [RuA_5N_2]^{2+} + 2OH^- \qquad 14$$

3. Formation of the dimer,

$$[RuA_5N_2]^{2+} + [RuA_5(OH_2)]^{2+} \longrightarrow [A_5RuN_2RuA_5]^{4+} + H_2O \qquad 15$$

The reaction of nitrous oxide results in the formation of the monomer initially, but this can react with unreacted $[RuA_5(OH_2)]^{2+}$ to form the dimer. To measure the extent of the reaction of nitrous oxide with $[RuA_5(OH_2)]^{2+}$, both the monomer and dimer which have been formed must be considered and so the extent of the reaction, % Fixed N_2, was defined as

$$\% \text{ Fixed } N_2 = \% \text{ Monomer} + \% \text{ Dimer} \qquad 11$$

The kinetic behaviour of this system and its similarity to the dinitrogen system is consistent with a mechanism in which the rate determining step is the formation of an intermediate nitrous oxide complex, with a rate similar to the rate of formation of $[RuA_5N_2]^{2+}$ from dinitrogen, which is rapidly reduced to the dinitrogen complex by the Zn/Hg. However, the kinetic evidence cannot distinguish between such a mechanism and one in which the intermediate is formed in low concentrations in a rapid pre-equilibrium with its reduction proceeding at a rate comparable with the rate of formation of the monomer in the reaction of dinitrogen with $[RuA_5(OH_2)]^{2+}$. Of these two mechanisms the former seems the more likely.

In both cases the dimer is formed from the monomer at the same rate as it is in the dinitrogen reaction.

2:5:4. Reaction in the absence of an external reducing agent.—

The reaction was studied in the absence of the external reducing agent, Zn/Hg, in an attempt to prevent the nitrous oxide intermediate being reduced. However, the monomer and the dimer were still observed to form, and there was also a shoulder at 298 nm on the absorption of the dimer. This new absorption is probably the ruthenium(III) complex, $[RuA_5(SO_4)]^+$ (λ_{max} = 310-308 nm).[64] The results for this reaction are given in Table 2:8.

In this reaction, where there is no Zn/Hg, the only potential reducing agent present is $[RuA_5(OH_2)]^{2+}$. If two moles of it are considered to be oxidised for each mole of nitrous oxide which is reduced (*i.e.*, for each mole of Fixed N_2 which is formed) then,

$$\% \text{ Ru}^{III} \text{ formed} = 2(\% \text{ Fixed } N_2)$$
$$= 2(\% \text{ Monomer} + \% \text{ Dimer}) \qquad 16$$

$$\text{and } \% \text{ Total Ru} = \% \text{ Ru}^{III} \text{ formed} + \% \text{ Monomer} + 2 \% \text{ Dimer}$$
$$= 3 \% \text{ Monomer} + 4 \% \text{ Dimer} \qquad 17$$

The results in Table 2:8 show that at high initial concentrations of $[RuA_5(OH_2)]^{2+}$ (10^{-2} M), the % Total Ru calculated this way does tend to

100% indicating that two moles of $[RuA_5(OH_2)]^{2+}$ are required for each mole of nitrous oxide which is reduced.

Because this reaction is more dependent on the concentration of $[RuA_5(OH_2)]^{2+}$ compared with the reaction in the presence of Zn/Hg, reactions at lower initial concentrations (10^{-3} M) are much slower. The final results are not significant at this concentration of $[RuA_5(OH_2)]^{2+}$ because of other effects (*e.g.*, exhaustion of the reducing agent, loss of co-ordinated ammonia or dinitrogen) which are important over the longer reaction times.

These reactions also indicate that, even in the absence of an external reducing agent, an intermediate nitrous oxide complex will be reduced at high concentrations of $[RuA_5(OH_2)]^{2+}$ and will probably be stable only in very dilute solutions.

In an attempt to observe the nitrous oxide intermediate, reactions with even lower initial concentrations of $[RuA_5(OH_2)]^{2+}$ ($1\text{-}5 \times 10^{-4}$ M) were used. The reaction was followed directly on solutions under nitrous oxide in a spectrophotometer cell. The spectral changes were usually very small and were similar to those observed at higher concentrations (*i.e.* absorptions at 221 nm and 262 nm were observed). However, occasionally in the initial spectrum (after 3-5 minutes) the absorption which was usually at 221 nm, was very broad and extended from 230 nm to 218 nm. It may be that another species with an absorption maximum around 230 nm was responsible for this spectral change, but this could not be confirmed.

2:5:5. Effect of pH on the reaction.—

The reactions in which Zn/Hg was used as the reducing agent were at pH 6-7 because of the buffering action of the reducing agent. The buffering action is achieved by zinc ions, generated during the reductions, which remove any hydroxide ions as zinc hydroxide, and by the ruthenium(II) complex which catalyses the evolution of dihydrogen from acids by the Zn/Hg. The evolution of dihydrogen is such that an acid reaction medium (*e.g.* 0.1 M sulphuric acid) was neutral after 15 minutes.

Alternative reducing agents were sought which would permit the study of the reaction at various pH values. Electrolytic reduction and $Pt(H_2)$ were chosen as the external reducing agents and the results obtained with them are given in Tables 2:9a and 2:9b.

(a). Electrolytic reduction. Potassium sulphate solutions of $[RuA_5(OH_2)]^{2+}$ were electrolysed using a mercury pool cathode at -0.6 V relative to a standard calomel electrode. The results in Table 2:9a show that for the neutral solution, the concentrations of the monomer and dimer formed during this reaction are very similar to those obtained when Zn/Hg was used as the reducing agent (see Table 2:5). The slightly higher dimer concentration indicates that this reaction is slightly slower, but this is probably because the design of the electrolysis vessel gave a smaller surface area to the reacting solution and although the solution was rapidly stirred, it may not have been completely saturated with nitrous oxide.

The final pH of the solution was 10.4 when 0.1 M potassium sulphate was used as the electrolyte. As this increase in pH during the reaction did not appear to affect the reaction, further studies in alkaline solutions were not made.

In the most acidic solution the rate of increase of the % Fixed N_2 (*i.e.* the rate of the reaction) appeared to be slower and higher concentrations of the dimer were formed. This increase in the concentration of the dimer is consistent with a slower rate of formation of the monomer, but it may also be due to an increase in the rate of formation of the dimer. Over the pH range 2.3-10.7 only a slight decrease in the rate of formation of the dinitrogen complexes was found as the pH of the reaction solution was increased.[39] This decrease may be due to an increase in the concentration of the less reactive $[RuA_5OH]^{2+}$ at high pH values (pKa of $[RuA_5(OH_2)]^{2+}$ is 10.7[65]). Hence, little change in the rate of formation of the dinitrogen complexes would be expected by decreasing the pH of the solution from 7.0 to 1.0. There was no attempt to keep the ionic strength of the solutions constant in any of these reactions and, as the rate of formation of the dimer has been found to be very dependent on the ionic strength of the solution,[40] this may explain the results. The rate of formation of the dimer has been found to increase as the ionic strength of the solution is increased,[40] so it would be expected to be fastest in 0.5 N sulphuric acid. Also the higher ionic strength of this solution may lower the solubility of nitrous oxide in the solution, which would also favour the formation of the dimer. Even so,

the changes observed in the acid solution are not very great (especially in the 0.1 N sulphuric acid) which indicate that the reaction of nitrous oxide with $[RuA_5(OH_2)]^{2+}$, under these conditions, is not markedly affected by the acid.

(b). Dihydrogen on platinum black, $Pt(H_2)$. Using $Pt(H_2)$ the conversion to the dinitrogen complexes was always much slower than that achieved using either of the other two external reducing agents, and much higher values of the ratio, % Dimer/% Monomer, were observed (Table 2:9b). This is because the partial pressure of dihydrogen and nitrous oxide in the gas mixture must each be less than one atmosphere. Thus not only the reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide is slower but also the reduction of the nitrous oxide intermediate will be slower and may even be rate determining.

The rate of reduction of the intermediate also depended on the platinum black surface used. Three surfaces were prepared. Surface A was deposited on platinum which had been etched with acid so that it had a very large surface area. Surface B was deposited on a cylindrical surface of platinum gauze and surface C was deposited on a cylindrical surface of platinum foil. The surface area of these surfaces decreased in the order A >> B > C. The rates of the reactions with these surfaces were found to decrease in this same order, consistent with the largest surface area giving the fastest reaction.

Reproducible conditions were very difficult to maintain because of variations in the mixture of dihydrogen and nitrous oxide which was used. Also the activity of the platinum black surface would be expected to change during a reaction due to poisoning of active sites. Hence not much significance can be placed on the changes observed with $Pt(H_2)$ as the external reducing agent.

(c). Conclusion. Although the reactions in acidic solutions have not been investigated thoroughly they do not show any marked acid dependence, and the changes observed may only be due to variations in the ionic strength of the solutions.

2:6. The Results of Armor and Taube.—

The results of this investigation, using Zn/Hg as the external reducing agent, were reported at "A Symposium on Nitrogen Fixation" in 1969. At the same conference Taube[61] reported spectral evidence for the existence of $[RuA_5(N_2O)]^{2+}$ which was formed when dilute solutions of $[RuA_5(OH_2)]^{2+}$ ($< 6 \times 10^{-4}$ M) were saturated with nitrous oxide. The kinetics[61] of its formation and decomposition were measured by following the appearance and decay of its characteristic absorption at 238 nm. The second order rate constant for the formation of $[RuA_5(N_2O)]^{2+}$ is 4.51×10^{-2} $M^{-1}sec^{-1}$ at 20.1°C (μ = 0.02 M, N_2O (aq) rather than N_2O (g) was used as the standard state for nitrous oxide).[66] This is very similar to the rate constant for the formation of the monomer in the dinitrogen

system.[39] At 6.8°C the rate constant for the formation of $[RuA_5(N_2O)]^{2+}$ is 9.5×10^{-3} $M^{-1}sec^{-1}$ (μ = 0.023 M). The complex is very unstable and has an equilibrium constant of only 7.0 at 6.8°C. Bubbling argon through the solution is sufficient to displace the co-ordinated nitrous oxide and regenerate $[RuA_5(OH_2)]^{2+}$.

In the presence of a reducing agent (chromium(II)) rapid and quantitative conversion to the dinitrogen complex, $[RuA_5N_2]^{2+}$, was observed.[61] The reaction had kinetics which were first order in nitrous oxide and $[RuA_5(OH_2)]^{2+}$ but independent of chromium(II). The rate constant (10×10^{-3} $M^{-1}sec^{-1}$ at 6.8°C) is the same as the rate constant for the formation of $[RuA_5(N_2O)]^{2+}$ within experimental error.[61]

These kinetic results indicate that in both these reactions the rate of formation of the $[RuA_5(N_2O)]^{2+}$ is the rate determining step. From this it was concluded by Taube[61] that, in the presence of a reducing agent, the nitrous oxide complex is reduced virtually as fast as it is formed. This conclusion is in agreement with the mechanism proposed in this work where Zn/Hg is used as the reducing agent.

The failure to observe the intermediate in this work was due to the sampling technique. Reaction samples were diluted into argon saturated solutions to observe the spectrum and in so doing any $[RuA_5(N_2O)]^{2+}$ present would have been decomposed to $[RuA_5(OH_2)]^{2+}$ which was not observed because of its low extinction coefficient relative to those of the products.

However when the initial samples from the reactions were diluted under nitrous oxide an absorption at 238 nm was observed. When samples were kept under nitrous oxide for three to four hours, the maximum at 238 nm gradually shifted to 221 nm (characteristic of the monomer). Armor and Taube[66] also observed that net reduction of the nitrous oxide complex does occur over long periods.

The previous attempts to observe this nitrous oxide intermediate in the dilute solutions of $[RuA_5(OH_2)]^{2+}$ (10^{-4} M) under nitrous oxide were unsuccessful because the solutions were too dilute and so a distinct absorption was not observed.

2:7. Conclusion.—

A study of the reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide, in the presence of an external reducing agent, has been difficult because of the heterogeneous nature of the system. In any case a detailed study of the reaction has been made redundant by the results of Armor and Taube.[61,66]

However, the reaction has provided a convenient synthesis for the dinitrogen complex, $[RuA_5N_2]^{2+}$, and the reaction conditions can be controlled so that very little of the dinuclear complex, $[A_5RuN_2RuA_5]^{4+}$, is formed as a contaminant.

Also evidence of a nitrous oxide intermediate has been observed in this reaction and an understanding of the reactions taking place in the

system has made it possible to design conditions for the preparation and isolation of this nitrous oxide complex. This is discussed in the next chapter.

TABLE 2:1

Nitrogen-Nitrogen bond properties

	N-N Bond Length (Å)	Vibrational Frequency (cm^{-1})	Reference
N_2 (g)	1.097	2331	42, 43a
N_2O (g)	1.127	2224	44, 43b
$[RuA_5N_2]Cl_2$	1.12	2105	45, 3
$[RuA_5N_2](BF_4)_2$	*ca.* 1.03	2144	45, 3
$[A_5RuN_2RuA_5](BF_4)_4$	1.124	2100	46, 41
$[Ru(en)_2N_3(N_2)](PF_6)$	1.106	2103	47

TABLE 2:2

Reactions of nitrous oxide at room temperature

reagent	product	reference
reducing agents		
$TiCl_3$	NH_3	48
$SnCl_2$	NH_2OH	48
Na_2SO_3	N_2	48
$CrCl_2/NH_3$	N_2	49
organometallic compounds		
PhCaI	PhN=NPh	50
Ph_3CNa	$Ph_3CNNONa$	51
MeLi	CH_2N_2	52
PhLi	PhN=NPh	53
phosphoranes		
$Ph_3P{=}CH_2$	CH_2N_2	54
metal amides		
$LiNH_2$	LiN_3	55
$NaNH_2$	NaN_3	55

TABLE 2:3

Reaction of nitrous oxide with transition metal complexes

solution	colour change on admitting nitrous oxide	gases formed (in addition to H_2)
$[Co(DMG)_2pyCl]$ in 50% aq. ethanol with excess of KBH_4	green → brown	N_2
$[Co(bipy)_3](ClO_4)_3$ in 50% aq. ethanol with excess of KBH_4	blue → yellow	N_2
$[Co(diphos)_2]$ in benzene	none (3 hr.)	no reaction
$[Co(diphos)_2Br]$ in benzene or ethanol	brown → green	N_2 with stoichiometry: $N_2O + 2.0\ Co^I \rightarrow N_2$
0.1 M $CoCl_2$ and 0.505-0.515N KCN in water with excess of KBH_4	yellow brown → transient purple after *ca.* 30 sec.	
$CoCl_2$ and *o*-phenanthroline in water with excess of KBH_4	dark brown → light brown	
$CoCl_2$ and sodium oximesulphonate in water with excess of KBH_4	dark brown → light brown	
Na_3RhCl_6 boiled with bipy in 50% aq. ethanol then reduced with sodium amalgam	red → yellow	

TABLE 2:3 (cont'd)

solution	colour change on admitting nitrous oxide	gases formed (in addition to H_2)
Na_3RhCl_6 boiled with dimethylglyoxime in 50% aq. ethanol then reduced with KBH_4	dark green → yellow	
$[Co(PhNC)_5](ClO_4)$ in ethanol	none (24 hr.)	

No reaction was observed with $[IrCO(PPh_3)_2Cl]$, $Fe(CO)_5$, $NaMn(CO)_5$, $Na_2Cr(CO)_5$ or $Na_2Mo(CO)_5$ in THF.

TABLE 2:5

Reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide in the presence of Zn/Hg

$[RuA_5Cl]Cl_2$ reduced under nitrous oxide in run number 1 and 2

$[RuA_5Cl]Cl_2$ reduced under nitrous oxide in run number 3 and 4

Run Number	$[RuA_5Cl_3]_i$	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Total Ru	% Dimer / % Monomer ($\times 10^2$)
1	$0.986_1 \times 10^{-2}$ M	0.50	37.8_2	2.2_6	40.0_8	42.3_4	5.9_8
		1.08	76.5_2	3.5_7	80.0_9	83.6_6	4.6_7
		2.00	91.5_3	3.3_1	94.8_4	98.1_5	3.6_2
		3.00	91.1_5	3.7_4	94.8_9	98.6_3	4.1_0
		8.00	94.2_7	3.7_3	98.0_0	101.7_3	3.9_6
2	$1.10_1 \times 10^{-3}$ M	0.50	58.7_5	0.6_6	59.4_1	60.0_7	1.1_2
		1.00	77.2_3	0.9_1	78.1_4	79.0_5	1.1_8
		1.50	93.0_6	1.3_5	94.4_1	95.7_6	1.4_5
		2.50	97.8_4	1.3_1	99.1_5	100.4_6	1.3_4
3	$1.04_0 \times 10^{-2}$ M	0.50	37.8_0	3.8_1	41.6_1	45.4_2	10.0_8
		1.00	58.7_6	8.1_1	66.8_7	74.9_8	13.8_1
		1.50	75.6_3	9.9_9	85.6_2	95.6_1	13.2_1
		2.00	79.9_8	10.2_7	90.2_5	100.5_2	12.8_4
		3.00	79.9_0	9.4_7	89.3_7	98.8_4	11.8_5

TABLE 2:5 (cont'd)

Run Number	$[RuA_5Cl_3]_i$	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Total Ru	% Dimer / % Monomer ($\times 10^2$)
4	$0.871_6 \times 10^{-3}$ M	0.60	69.5_2	0.6_5	70.1_7	70.8_2	0.9_3
		1.00	90.0_4	1.1_1	91.1_5	92.2_6	1.2_3
		1.50	94.8_9	0.9_6	95.8_5	96.8_1	1.0_1
		2.00	94.2_1	1.0_1	95.2_2	96.2_3	1.0_7
		3.00	97.4_8	1.4_6	98.9_4	100.4_0	1.5_0

TABLE 2:6

Effect of the partial pressure of nitrous oxide on the reaction

Reducing Agent: Zn/Hg

pN_2O (atmos.)	$[RuA_5Cl_3]_i$	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Total Ru	% Dimer / % Monomer ($\times 10^2$)
0.065	$1.11_0 \times 10^{-2}$ M	1.00	10.4_7	3.0_5	13.5_2	16.5_7	29.1_3
		2.00	18.0_8	9.8_0	27.8_8	37.6_8	54.2_0
		3.16	18.6_0	19.3_5	37.9_5	57.3_0	104.0_1
		18.00	32.0_7	36.0_0	68.0_7	104.0_7	112.2_1
0.110	$1.05_6 \times 10^{-2}$ M	4.50	46.5_3	17.7_5	64.2_8	82.0_3	38.1_5
0.107	$1.17_3 \times 10^{-2}$ M	6.00	49.7_7	15.8_3	65.6_0	81.4_3	31.8_0
0.128	$1.10_7 \times 10^{-2}$ M	18.00	60.8_8	14.2_5	75.1_3	89.3_8	23.4_1
0.139	$0.942_7 \times 10^{-2}$ M	96.00	57.5_9	19.7_9	77.3_8	97.1_7	34.3_6
1.00	$1.04_0 \times 10^{-2}$ M	0.50	37.8_0	3.8_1	41.6_1	45.4_2	10.0_8
		1.00	58.7_6	8.1_1	66.8_7	74.9_8	13.8_1
		1.50	75.6_3	9.9_9	85.6_2	95.6_1	13.2_1
		2.00	79.9_8	10.2_7	90.2_5	100.5_2	12.8_4
		3.00	79.9_0	9.4_7	89.3_7	98.8_4	11.8_5

TABLE 2:6 (cont'd)

pN_2O (atmos.)	$[RuA_5Cl_3]_i$	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Total Ru	% Dimer / % Monomer ($\times 10^2$)
$pN_2 = 1.00$	$1.07_7 \times 10^{-2}$ M	0.50	7.8_2	1.9_5	9.7_7	11.7_2	24.9_4
		1.00	10.9_3	5.1_3	16.0_6	21.1_9	46.9_4
		2.00	14.3_8	12.3_5	26.7_3	39.0_8	85.8_8
		3.16	15.1_7	20.9_0	36.0_7	56.9_7	137.8_1
		4.66	19.3_2	29.6_3	48.9_5	78.5_8	153.4_1
		5.75	19.5_0	31.4_1	50.9_1	82.3_2	161.1_1

TABLE 2:8

Reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide in the absence of an external reducing agent

$[RuA_5Cl_3]_i$	pH of the solution initially	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Ru^{III} Formed †	% Total Ru ††
$1.25_3 \times 10^{-2}$ M	7.0	1.00	11.7_0	2.2_3	13.9_3	27.8_6	44.0_2
		3.00	15.3_9	7.0_9	22.4_8	44.9_6	74.5_3
		5.00	15.1_6	9.8_3	24.9_9	49.9_8	84.8_0
		21.00	12.8_5	14.5_2	27.3_7	54.7_4	96.6_3
$1.33_6 \times 10^{-2}$ M	7.0	18.00	13.3_0	15.6_9	28.9_9	57.9_8	102.6_6
$3.18_9 \times 10^{-3}$ M	7.0	2.00	8.2_9	1.4_3	9.7_2	19.4_4	30.5_9
		4.00	10.4_2	2.2_3	12.6_5	25.3_0	40.1_8
		8.00	11.9_5	4.4_8	16.4_3	32.8_6	53.7_7
	final pH = 8.9_8	22.50	14.2_7	9.2_2	23.4_9	46.9_8	79.6_9
$3.23_4 \times 10^{-3}$ M	2.0	1.00	6.6_9	0.9_9	7.6_8	15.3_6	24.0_3
		2.00	9.2_4	1.4_6	10.7_0	21.4_0	33.5_6
		4.00	11.1_7	2.2_4	13.4_1	26.8_2	42.4_7
		7.25	12.3_2	4.4_7	16.7_9	33.5_8	54.8_4

TABLE 2:8 (cont'd)

$[RuA_5Cl_3]_i$	pH of the solution initially	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Ru^{III} Formed†	% Total Ru††
$3.26_8 \times 10^{-3}$ M	2.0	21.50	12.4_3	10.6_9	23.1_2	46.2_4	80.0_5
		45.00	11.2_9	9.3_8	20.6_7	41.3_4	71.3_9

† % Ru^{III} Formed = 2(% Monomer + % Dimer) = 2% Fixed N_2

†† % Total Ru = % Ru^{III} Formed + % Monomer + 2% Dimer = 3% Monomer + 4% Dimer

TABLE 2:9a

Effect of pH on the reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide

Reducing Agent: Electrolytic Reduction

Electrolyte	$[RuA_5Cl_3]_i$	pH	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Total Ru
0.1 N K_2SO_4	$3.07_6 \times 10^{-3}$ M	6.14	0.50	65.6_5	1.8_9	67.5_4	69.4_3
			1.00	85.0_0	3.2_9	88.2_9	91.5_8
			2.00	88.7_7	3.5_0	92.2_7	95.7_7
			3.00	90.4_8	3.2_2	93.7_0	96.9_2
			4.00	88.1_8	4.8_7	93.0_5	97.9_2
0.1 N H_2SO_4	$3.12_7 \times 10^{-3}$ M	1.41	0.50	50.6_6	1.8_9	52.5_5	54.4_4
			1.00	72.8_6	3.1_4	76.0_0	79.1_4
			1.50	83.5_0	4.0_6	87.5_6	91.6_2
			2.00	89.7_5	5.1_9	94.9_4	100.1_3
			3.00	91.2_3	4.9_2	96.1_5	101.0_7
			5.50	93.2_7	5.5_3	98.8_0	104.3_3
0.5 N H_2SO_4	$3.65_7 \times 10^{-3}$ M	0.65	0.50	44.8_4	3.4_2	48.2_6	51.6_8
			1.00	63.1_3	6.9_8	70.1_1	77.0_9
			2.00	70.7_8	12.5_1	83.2_9	95.8_0
			3.00	71.0_9	13.5_6	84.6_5	98.2_1
			5.00	71.0_9	14.3_7	85.4_6	99.8_3

TABLE 2:9b

Effect of pH on the reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide

Reducing Agent: $Pt(H_2)$

Surface*	$[RuA_5Cl_3]_i$	pH	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Total Ru
A	$0.970_0 \times 10^{-2}$ M	7.0	1.00	57.1_1	6.1_6	63.2_7	69.4_3
			2.00	73.1_5	9.3_4	82.4_9	91.8_3
			3.00	75.3_3	10.7_7	86.1_0	96.8_7
C	$1.08_6 \times 10^{-2}$ M	7.0	1.00	28.1_0	2.2_8	30.3_8	32.6_6
			2.00	40.0_4	5.2_7	45.3_1	50.5_8
			4.00	50.7_3	10.2_1	60.9_4	71.1_5
			6.00	56.9_1	13.8_5	70.7_6	84.6_1
B	$1.18_9 \times 10^{-2}$ M	1.5	1.00	37.0_0	7.2_7	44.2_7	51.5_4
			2.00	37.0_6	13.0_8	50.1_4	63.2_2
			3.00	40.2_8	16.3_0	56.5_8	72.8_8
			5.00	45.9_7	19.9_0	65.8_7	85.7_7
			7.00	49.7_9	22.3_3	72.1_2	94.4_5

TABLE 2:9b (cont'd)

Surface*	$[RuA_5Cl_3]_i$	pH	Time (hrs.)	% Monomer	% Dimer	% Fixed N_2	% Total Ru
C	$1.10_5 \times 10^{-2}$ M	1.5	0.75	14.8_8	10.7_3	25.6_1	36.3_4
			1.75	15.3_4	17.0_8	32.4_2	49.5_0
			3.00	16.6_1	22.1_7	38.7_8	60.9_5
			4.00	17.7_7	24.3_1	42.0_8	66.3_9
			8.50	23.7_4	36.3_5	60.0_9	96.4_4

*Surface A: platinum foil etched with acid - very large surface area.

Surface B: cylindrical surface of platinum gauze.

Surface C: cylindrical surface of platinum foil.

FIGURE 2:1

Reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide

in the presence of Zn/Hg

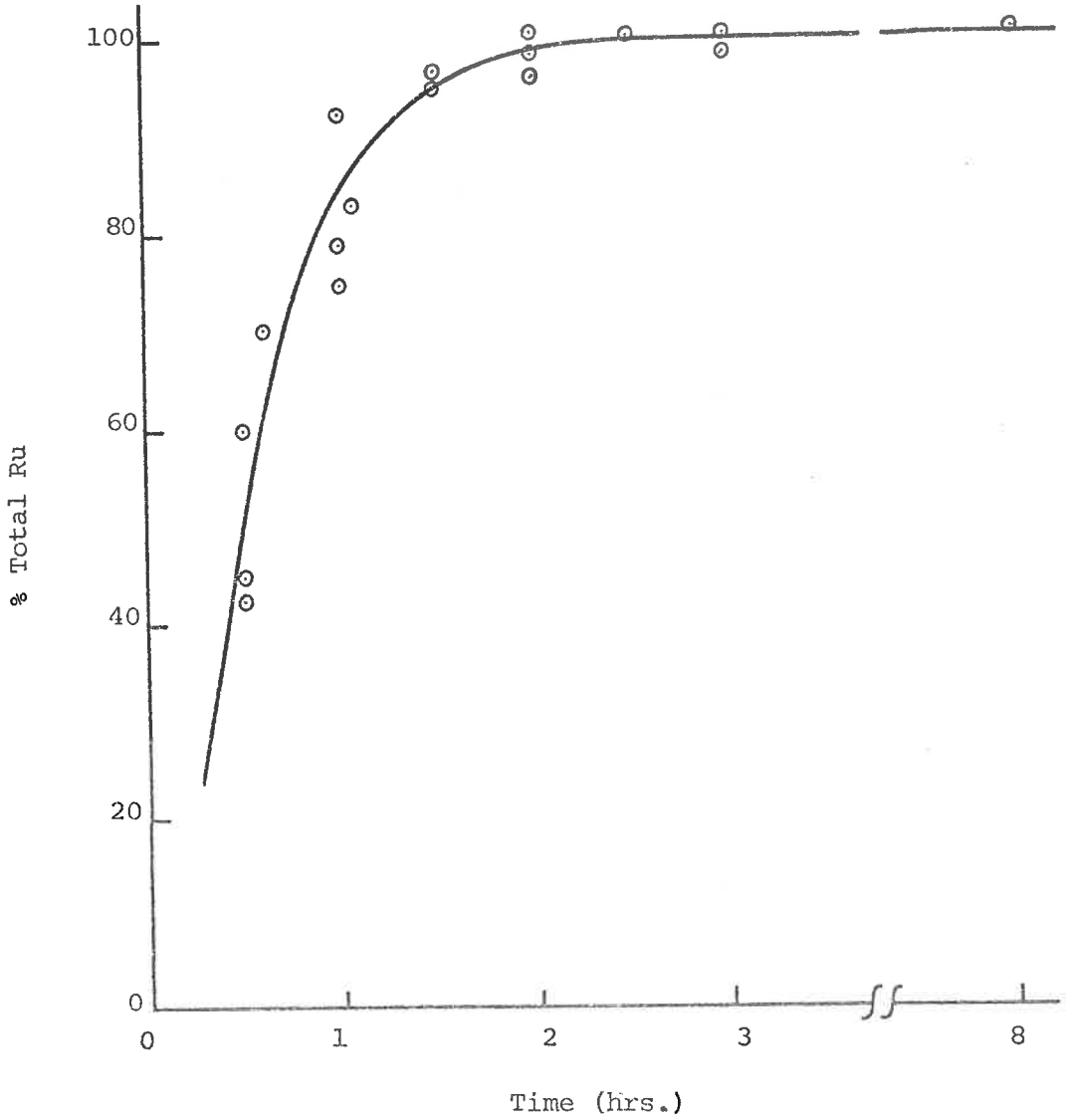


FIGURE 2:2

Effect of the initial concentration of $[RuA_5(OH_2)]^{2+}$ on the reaction of nitrous oxide with $[RuA_5(OH_2)]^{2+}$

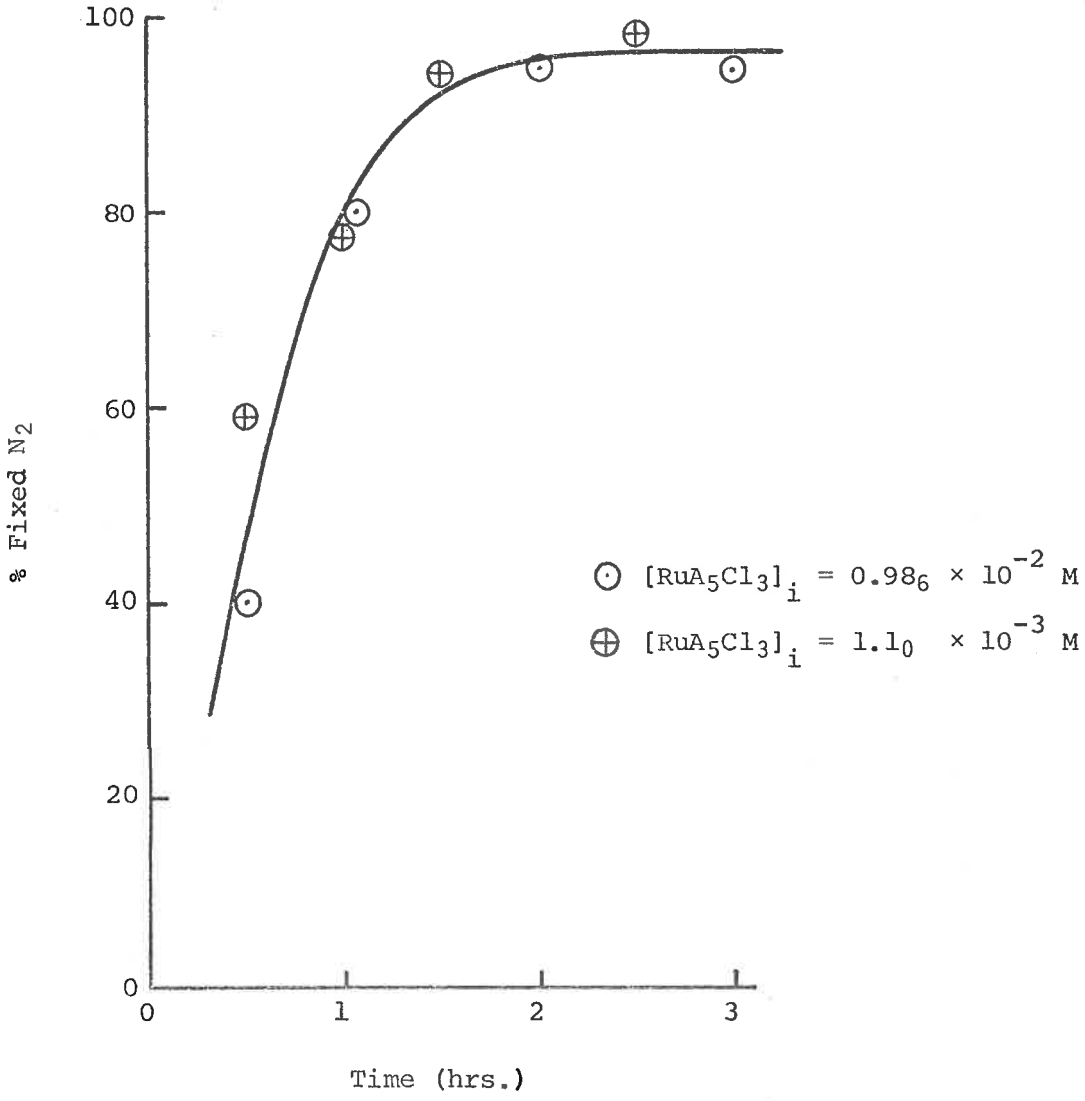
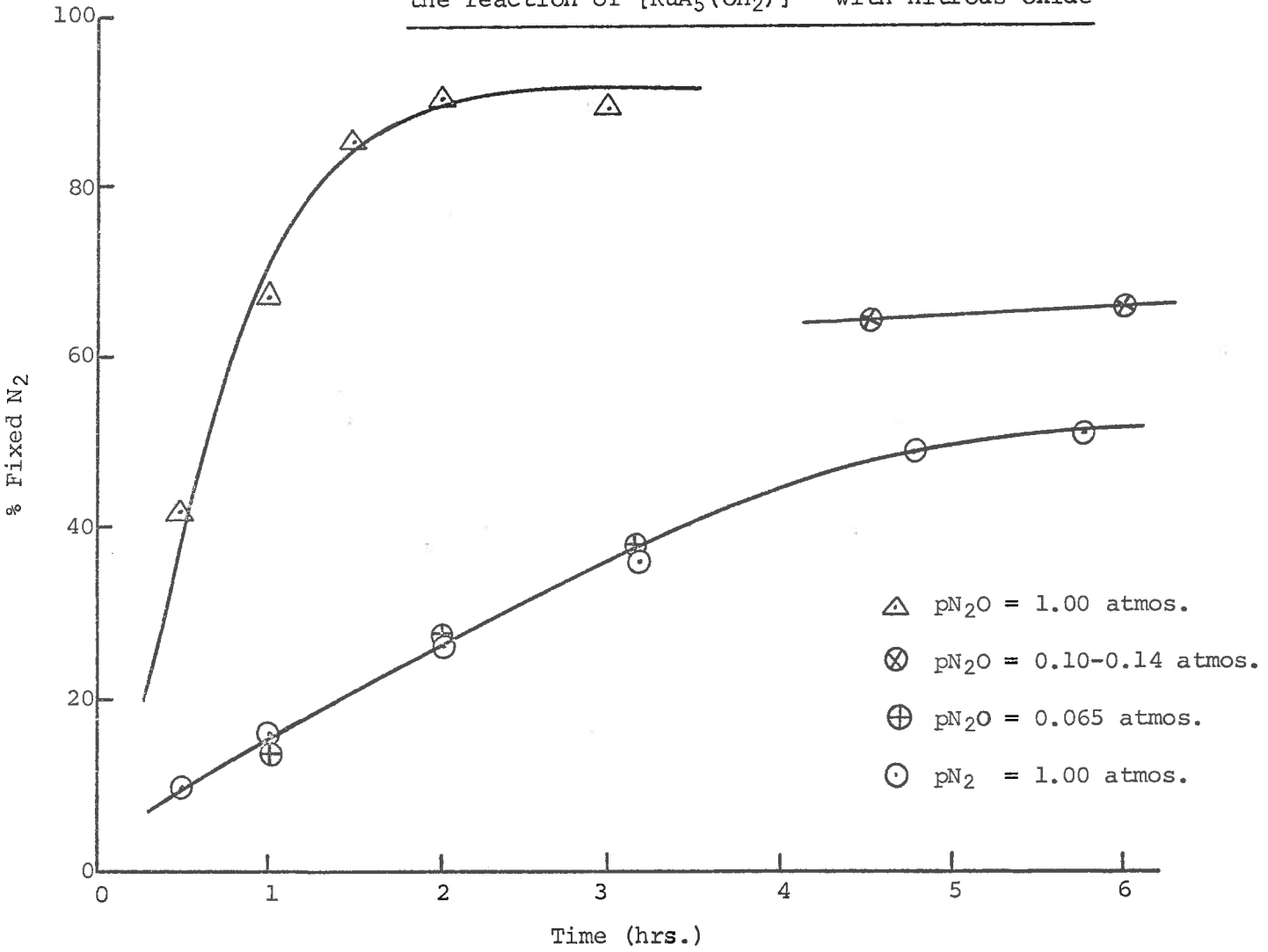


FIGURE 2:3. Effect of the partial pressure of nitrous oxide on the reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide



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CHAPTER 3

ISOLATION AND CHARACTERISATION OF PENTA-AMMINE(DINITROGEN OXIDE)RUTHENIUM(II) COMPLEXES

3:1. Introduction.—

In this chapter the isolation and characterisation of the nitrous oxide complexes are reported.

The conditions for their isolation were designed from the understanding of the reaction between $[RuA_5(OH_2)]^{2+}$ and nitrous oxide described in the previous chapter, and from the related work of Armor and Taube.[1]

3:2. Formation and Stability of the $[RuA_5(N_2O)]^{2+}$ *Ion in Solution.*—

Armor and Taube[1] observed the appearance of a new absorption at 238 nm when dilute solutions of $[RuA_5(OH_2)]^{2+}$ (*ca.* 3×10^{-4} M) were saturated with nitrous oxide. The absorption increased in intensity when the concentration of nitrous oxide was increased, disappeared when the nitrous oxide was removed by passing argon through the solution, and was restored when nitrous oxide was again added.

A kinetic investigation of the system led to the representation of the reaction by,

$$[RuA_5(OH_2)]^{2+} + N_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [RuA_5(N_2O)]^{2+} + H_2O \qquad 1$$

The rate constants k_f and k_r are given in Table 3:1.

TABLE 3:1

Kinetic data for the reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide[1]

k_f ($M^{-1}sec^{-1}$)	k_r ($M^{-1}sec^{-1}$)	formation constant (k_f/k_r)	temp. (°C)	ionic strength (Cl^- as anion)
4.51×10^{-2}	9.1×10^{-3}	5.5	20.1	0.02 M
9.5×10^{-3}	1.35×10^{-3}	7.0	6.8	0.02 M

N_2O (aq) rather than N_2O (g) was used as the standard state for nitrous oxide.

In the presence of chromium(II), Armor and Taube[1] found that the reaction

$$2Cr^{2+} + [RuA_5(OH_2)]^{2+} + N_2O + 2H^+ \xrightarrow{k} 2Cr^{3+} + [RuA_5N_2]^{2+} + 2H_2O \qquad 2$$

took place quantitatively with a rate law (equation 3) which was independent of the concentration of chromium(II).

$$d[\text{Monomer}]/dt = k[A'][N_2O] \qquad 3$$

where A' is $[RuA_5(OH_2)]^{2+}$ and the monomer is $[RuA_5N_2]^{2+}$.

At 6.8°C the rate constant, k, was found to be 10×10^{-3} $M^{-1}sec^{-1}$. The agreement of k with k_f of reaction 1 indicates that the formation of $[RuA_5(N_2O)]^{2+}$ is the rate determining step in the reaction. This suggests

that the nitrous oxide complex is reduced by the chromium(II) as rapidly as it is formed.

Armor and Taube[1] have calculated an extinction coefficient of $(1.7 \pm 0.2)\ M^{-1}cm^{-1}$ for the characteristic absorption of $[RuA_5(N_2O)]^{2+}$ at 238 nm. Using this value it can be estimated that at equilibrium, there is only a 12% conversion to $[RuA_5(N_2O)]^{2+}$ at one atmosphere of nitrous oxide.

The low conversion to the nitrous oxide complex at atmospheric pressure, the fast dissociation of the complex, and the rapid reduction of the co-ordinated nitrous oxide in the presence of reducing agents, mean that the isolation of the complex requires carefully controlled reaction conditions.

3:3. Choice of Experimental Conditions.—

The reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide at atmospheric pressure reaches a position of equilibrium,[1] and so an increase in the pressure of nitrous oxide above the solution would be expected to give higher conversions to the nitrous oxide complex. To see how much higher this conversion could be, dilute solutions of $[RuA_5(OH_2)]^{2+}$ (10^{-4} M) were pressurised with oxygen free nitrous oxide to forty atmospheres (its vapour pressure at room temperature) and after ten minutes the pressure was released and the spectrum of the solution was recorded rapidly. The optical

density at 238 nm indicated that a conversion of greater than 50% (based on the extinction coefficient calculated by Armor and Taube[1]) had been achieved. However, during the recording of the spectrum the optical density was rapidly decreasing, indicating that considerable decomposition of the complex was occuring. Thus the actual conversion to $[RuA_5(N_2O)]^{2+}$, before the pressure was released, must have been even greater than 50%.

To take advantage of this in the preparation, an excess of precipitating agent was added to the reaction solution before it was pressurised, so that the nitrous oxide complex was precipitated while still under pressure. The immediate precipitation of the product also minimises side reactions. In Chapter 2 it was shown that $[RuA_5(OH_2)]^{2+}$ is able to reduce $[RuA_5(N_2O)]^{2+}$ to the dinitrogen complex;

$$2[RuA_5(OH_2)]^{2+} + [RuA_5(N_2O)]^{2+} \longrightarrow [RuA_5N_2]^{2+} + 2[RuA_5OH]^{2+} + H_2O \qquad 4$$

Hence, using solutions initially 10^{-2} M in $[RuA_5(OH_2)]^{2+}$, appreciable reduction to the dinitrogen complex would be expected if the nitrous oxide complex were not precipitated quickly. To assist the precipitation of the complex the reaction vessel was cooled in ice during the reaction. Armor and Taube have shown[1] that the formation constant of $[RuA_5(N_2O)]^{2+}$ is increased on lowering the temperature, so cooling the reaction vessel also has the advantage of increasing the conversion to the product.

Hence, the complexes were prepared by

(i). adding a solution containing excess precipitating agent to a freshly prepared solution of $[RuA_5(OH_2)]^{2+}$ (*ca.* 10^{-2} M).

(ii). pressurising the solution to forty atmospheres with the deoxygenated nitrous oxide.

(iii). cooling the pressure vessel in ice for thirty minutes.

and (iv). releasing the pressure and quickly filtering the product under nitrous oxide.

It was found that it was not necessary to use a saturated solution of the precipitating agent to obtain the best yields. In fact, too high a concentration of the anion led to contamination of the product.

3:4. Preparation and Purity of the Complexes.—

Using this preparative scheme the bromide, iodide, tetrafluoroborate and hexafluorophosphate salts of penta-ammine(dinitrogen oxide)ruthenium(II) were isolated as yellow microcrystalline solids in 40-50% yields.

The purity of the product was found to depend on the counter-anion used. Anions which caused a rapid precipitation of the nitrous oxide complex gave pure compounds by removing the product from the solution before reduction of the co-ordinated nitrous oxide could take place. The tetrafluoroborate and hexafluorophosphate salts were the most insoluble and so were obtained free of the dinitrogen complex. The bromide, and to a

lesser extent the iodide salt, were more soluble and were always contaminated with the dinitrogen complex which was detected by its nitrogen-nitrogen stretching vibration in the infrared spectrum of the product. This absorption is very strong in the pure dinitrogen complex[2] but its intensity in the bromide and iodide salts was only weak, indicating that not much was present in the complexes. The chloride salt was very soluble and only small quantities of impure solid were obtained.

When initially precipitated, the iodide salt usually contained a pale-green impurity, most of which could be removed by washing with water. The iodide salt of the aquo-complex, $[RuA_5(OH_2)]I_2$, was also a pale-green colour and in Chapter 5 (section 5:2) it is suggested that this may be due to $[RuA_5I]I$ which is formed because of the excess of iodide ion in the solution.

When the complexes were redissolved they decomposed very rapidly, with the loss of nitrous oxide, and this precluded their purification by recrystallisation.

3:5. Stability of the Complexes.—

The complexes were stable for about a day when stored at 20°C, *in vacuo*, and in the absence of light, but they decomposed on exposure to air, especially moist air. The tetrafluoroborate salt was the most unstable, and when it was exposed to air it became a dull brown colour

within hours, and overnight it decomposed almost entirely to a red-purple solid.

All the complexes could be kept for longer periods (over a week) with very little decomposition occuring by storing them at -5°C, in the absence of light, in a dry atmosphere.

3:6. Characterisation of the Complexes.—

The bromide, iodide and tetrafluoroborate salts have been characterised as $[RuA_5(N_2O)]Br_2$, $[RuA_5(N_2O)]I_2$ and $[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$ respectively. Although the hexafluorophosphate salt has not been analysed it is formulated as $[RuA_5(N_2O)](PF_6)_2 \cdot H_2O$ on the basis of its solution properties (see section 3:6:2).

The tetrafluoroborate and hexafluorophosphate salts were diamagnetic, consistent with their formulation as octahedral ruthenium(II) complexes.

3:6:1. Microanalyses.—

The microanalyses were carried out in Melbourne, usually three days after the complex had been prepared. Although the samples were sealed under nitrous oxide and over silica gel, the microanalyses results indicated that some decomposition had occured before they were analysed. The results were consistent with the loss of nitrous oxide from the complex.

The most unstable complex was the tetrafluoroborate salt. This complex had usually become a light brown colour by the time it was analysed and the results indicated extensive decomposition. However when a sample was analysed within two days of its preparation and was still yellow, better agreement with the calculated values was obtained. The results are given in Table 3:2.

Because the complexes decomposed before they could be analysed in Melbourne, it was decided to analyse them in Adelaide as soon as possible after their preparation. Consequently, the halogen content of the bromide and iodide salts was determined potentiometrically and the results are given in Table 3:2. Although they could have been analysed for ruthenium also, this was not done. The only determination that could be made on the tetrafluoroborate and hexafluorophosphate salts, was for the metal. However, it was found that the determination of the metal in $[RuA_5(OH_2)](PF_6)_2 \cdot H_2O$ did not give consistent results due to a reaction with the combustion boats during the ignition of the sample (section 5:3:1), and so metal analyses were not attempted with the nitrous oxide complexes.

3:6:2. Solution properties.—

The solution properties of the complexes were used to obtain further confirmation for the proposed formulae.

(a). Conversion to $[RuA_5(OH_2)]^{2+}$. When the complexes were dissolved

in 0.1 M methanesulphonic acid, under argon, nitrous oxide was lost and the complexes were quantitatively converted to the aquo-complex (Table 3:3: the extinction coefficients for aquo-complexes are taken from Table 5:1).

The extinction coefficient obtained for the bromide salt is high and indicates a 15-20% impurity of the dinitrogen complex in the samples analysed (based[3] on $\varepsilon_{262} = 840 \quad M^{-1}cm^{-1}$ for $[RuA_5N_2]^{2+}$).

(b). Conversion to $[RuA_5Cl]^{2+}$. When the fluoro-salts were oxidised by the air in 1 M hydrochloric acid, almost quantitative conversion to $[RuA_5Cl]^{2+}$ was achieved (Table 3:3). The conversions were similar to those achieved with the aquopenta-ammine complex, $[RuA_5(OH_2)](PF_6)_2 \cdot H_2O$ (section 5:3:2) so it appears that the formation of the chloro-complex does not quite proceed to completion under these conditions. However, the fact that both the aquo- and nitrous oxide complexes gave similar extinction coefficients for $[RuA_5Cl]^{2+}$, provides support for the formulations.

The bromide and iodide salts were not investigated in this way because the corresponding aquo-complexes had been observed to form the bromo- (or iodo-) penta-ammineruthenium(III) complex as well as $[RuA_5Cl]^{2+}$ when oxidised in this way (section 5:3:2).

(c). Conversion to $[RuA_5OH]^{2+}$. Eliades *et al.*[6] have obtained $[RuA_5OH]^{2+}$ ($\lambda_{max} = 295$ nm, $\varepsilon = 2100 \quad M^{-1}cm^{-1}$) by the addition of dilute ammonia to a solution of $[RuA_5(OH_2)]^{3+}$ and Broomhead *et al.*[5] have reported

it as the product from the base hydrolysis of $[RuA_5I]^{2+}$ with sodium hydroxide (λ_{max} = 297 nm, ε = 2145 $M^{-1}cm^{-1}$).

It was expected that the oxidation of the nitrous oxide complexes with ferric sulphate, under argon, would form the aquo-ruthenium(III) complex, $[RuA_5(OH_2)]^{3+}$, which would be rapidly converted to the hydroxy-penta-ammine complex on the addition of excess dilute ammonia. (The pKa of the aquo-complex is around 4.0.)[6,7] However, when the iron hydroxides had been removed, it was found that quantitative conversion to $[RuA_5OH]^{2+}$ had not been achieved. The initial extinction coefficients of the solutions were only 1620-1660 $M^{-1}cm^{-1}$ at 297 nm (Table 3:3). After standing for 1-2 hours there was an increase in the intensity of the absorption, and extinction coefficients between 2100-2190 $M^{-1}cm^{-1}$ were recorded. After two hours there was very little increase in the optical density. These spectral changes suggest that there is another species present in the reaction solution.

The acid hydrolysis of $[RuA_5Cl]^{2+}$ with sulphuric acid has been observed[7] to form the sulphato-complex, $[RuA_5(SO_4)]^{+}$. The mechanism for the reaction is a slow aquation followed by a fast anation.

$$[RuA_5Cl]^{2+} + H_2O \xrightarrow{SLOW} [RuA_5(OH_2)]^{3+} + Cl^{-} \qquad 5$$

$$[RuA_5(OH_2)]^{3+} + SO_4^{=} \xrightarrow{FAST} [RuA_5(SO_4)]^{+} + H_2O \qquad 6$$

As the oxidation with ferric sulphate was carried out in sulphuric acid,

the sulphato-complex as well as the aquo-complex must have formed. The reproducibility of the initial extinction coefficient at 297 nm after the addition of the ammonia indicates that similar conversions to the sulphato-complex had occured in all the reactions. The increase in optical density as the $[RuA_5(SO_4)]^+$ was substituted indicates that 20-25% of the $[RuA_5(OH_2)]^{3+}$ was converted to the sulphato-complex during the oxidation.

The sulphato-complex has an absorption maximum at 310 nm[7] ($\varepsilon > 10^3$ $M^{-1}cm^{-1}$) but attempts to observe it were unsuccessful. In the acid solutions the absorption of the iron complexes obscured this region while in the alkaline solution the tail of the strong absorption at 297 nm, due to $[RuA_5OH]^{2+}$, covered the region.

(d). Conclusion. The solution properties of the complexes are in good agreement with the formulae proposed from the microanalytical results. The conversion to $[RuA_5(OH_2)]^{2+}$ is a very good criterion for the purity of the complexes because any $[RuA_5N_2]^{2+}$, the main impurity expected in the complexes, which is present will be observed in the spectrum of the final solution. This is because the absorption of $[RuA_5N_2]^{2+}$, although its extinction coefficient at 262 nm is similar to that of $[RuA_5(OH_2)]^{2+}$ at 262 nm,[3] increases rapidly towards higher energy while the absorption of the aquo-complex decreases. Although the absorption of $[RuA_5N_2]^{2+}$ may not be observed in the conversion to $[RuA_5Cl]^{2+}$ because of the strong charge transfer absorption of the chloro-complex in the region of the absorption

maximum of the dinitrogen complex, its presence in the nitrous oxide complex will be evident by a low extinction coefficient for the chloro-complex at 297 nm. The conversion to $[RuA_5OH]^{2+}$ is not as good a criterion of purity as the other two reactions because the reaction conditions result in $[RuA_5N_2]^{2+}$ being converted to the hydroxy-complex also.

The solution data are the only quantitative results for the hexa-fluorophosphate salt and a microanalysis is necessary to confirm its formulation as $[RuA_5(N_2O)](PF_6)_2 \cdot H_2O$.

3:6:3. Release of nitrous oxide from $[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$.—

(a). Oxidation in aqueous solution. The nitrous oxide content of the complex was determined by oxidising the tetrafluoroborate salt with cerium(IV) sulphate, ferric sulphate or dioxygen and determining the volume (manometrically) and composition (mass spectrometrically) of the gases evolved.

Although cerium(IV) sulphate[8,9] and ferric sulphate[1] have been found to release dinitrogen quantitatively from the dinitrogen complexes, the yields of nitrous oxide were found to depend on the oxidising agent used. The yields obtained were 71-77% when cerium(IV) sulphate was used, 56.6% with ferric sulphate and only 47.7% with dioxygen (Table 3:4). This dependence on the oxidising agent indicated that the release of nitrous oxide was not a simple reaction following the oxidation of the ruthenium

complex, but that other reactions, in which some of the nitrous oxide was converted to dinitrogen, also took place. This is consistent with the observation that the highest yields of nitrous oxide were obtained with the most efficient oxidising agent, which was able to oxidise the complex the fastest and so minimise the side reactions.

All the determinations were made by first degassing the solution of the oxidant by the freeze-thaw method and then adding the solid complex to the frozen solution, which was then thawed as quickly as possible. However, it could have been possible for the complex to dissolve in a small volume of solution before the bulk of the solution had melted, and so form a local high concentration of the complex with only a limited amount of the oxidising agent present. Under these conditions any $[RuA_5(OH_2)]^{2+}$, which may have formed by hydrolysis of the nitrous oxide complex, could have reacted with the nitrous oxide complex as it dissolved and reduced it to the dinitrogen complex, $[RuA_5N_2]^{2+}$. The effect of cerium(IV) sulphate on any dinitrogen complex formed would be to release the dinitrogen. These conditions should be contrasted with those under which the conversions to $[RuA_5(OH_2)]^{2+}$ were determined. In those dilute, argon saturated solutions, no evidence of the dinitrogen complex was observed.

When the total gas above the reaction mixture was collected, it was found mass spectrometrically to contain nitrous oxide, water vapour and dinitrogen. When allowance was made for the water vapour, the volume of

gas evolved was 85-90% of the calculated value based on one mole of gas being evolved per mole of complex. These results and the composition of the gas evolved are given in Table 3:4.

Although the yield is still low this may only be due to a systematic error in the manometric method which was used. However, the results do indicate that there is one mole of co-ordinated nitrous oxide in the complex.

(b). Thermal decomposition of the complex. Thermal decomposition has been used to determine the dinitrogen content of $[CoH(N_2)(PPh_3)_3]$[10] and $[RuA_5N_2](BF_4)_2$.[2] The same method applied to the tetrafluoroborate salt was unsatisfactory in determining its nitrous oxide content. Below 90°C only water was released, but as the temperature was increased to 135°C the solid became very dark red and nitrous oxide and dinitrogen were released. After five hours at 135°C the solid was a purple-red colour. The gas released was mainly nitrous oxide at first, but after 1-2 hours there was more dinitrogen than nitrous oxide and the dinitrogen content increased further with time.

The infrared spectrum of the solid, after five hours, had a very strong absorption at 2140 cm^{-1} characteristic of $[RuA_5N_2](BF_4)_2$.[2] In aqueous solution the absorption of the dinitrogen complex at 221 nm[8] was observed as well as an absorption at 532 nm which gave the solution an intense red colour. When the solution was acidified, it became yellow and the absorption in the visible region shifted to 455 nm. These colour

changes are characteristic of ruthenium red,[11] $[A_5RuORuA_4ORuA_5]^{6+}$ (in acidic solutions, λ_{max} = 465 nm; in neutral solutions, λ_{max} = 532 nm).

The presence of the dinitrogen complex in the decomposed solid is evidence that the reduction of the nitrous oxide, which occurs very rapidly in solution, can also occur in the solid state with the ruthenium(II) complex being oxidised in the process.

Due to the significant conversions to the dinitrogen complex, thermal decomposition was not used to estimate the nitrous oxide content of the complex.

3:7. Infrared Spectra of the Complexes.—

Further evidence for co-ordinated nitrous oxide in these complexes was obtained from their infrared spectra. The infrared absorptions are tabulated in Table 3:5. All the complexes have absorptions which can be assigned to co-ordinated nitrous oxide, but these will be discussed in the next chapter. The discussion here will be restricted to the other absorptions.

In Table 3:6 the ammonia absorptions of several ruthenium(II) and ruthenium(III) complexes are tabulated. The positions of the absorptions of the nitrous oxide complexes are similar to those of the corresponding dinitrogen complexes.[2] They are higher than those in the hexa-ammine-ruthenium(II) complexes,[12] and in the dinitrogen complexes this has been

interpreted as resulting from back-bonding from the metal to the ligand which decreases the electron density on the metal and so gives it some ruthenium(III) character. Thus, the positions of the absorptions are shifted towards those of ruthenium(III) complexes which occur at higher energy.[2] The position of the absorptions in the nitrous oxide complexes indicates that the back-bonding in them is similar to that in the dinitrogen complexes, but less than that in the carbonyl complexes.

In the tetrafluoroborate and hexafluorophosphate salts, there were, in addition to the absorptions of the anion, two sharp absorptions between 3640 and 3540 cm^{-1} and a shoulder at 1700 cm^{-1} due to lattice water. This is consistent with their formulation. Broomhead *et al.*[14] have observed lattice water in similar positions in a series of ruthenium(III)-ethylene-diamine complexes.

The position of the metal-ammonia stretching vibrations will be discussed in the next chapter because it was difficult to distinguish them from those absorptions of nitrous oxide which occured in the same region.

3:8. Electronic Absorption Spectrum of $[RuA_5(N_2O)]^{2+}$.—

The absorption spectrum of $[RuA_5(N_2O)]^{2+}$ was recorded in 0.1 M hydrochloric acid and in 0.1 M methanesulphonic acid by rapidly scanning the region 200-320 nm immediately after the solid was dissolved. The spectrum (Figure 3:1) has an absorption maximum at 238-240 nm, in

agreement with the spectrum obtained by Armor and Taube (λ_{max} = 238 nm).[1]

When the solution was sealed under nitrous oxide, the intensity of the absorption maximum decreased slowly after the initial rapid decay, and gradually shifted to 221 nm, characteristic[8] of $[RuA_5N_2]^{2+}$, as the nitrous oxide was reduced to dinitrogen by $[RuA_5(OH_2)]^{2+}$ formed during the initial decomposition of the complex.

When the solution was prepared in the air the absorption at 238 nm decayed rapidly and new absorptions due to ruthenium(III) complexes were observed. The products were $[RuA_5Cl]^{2+}$ in hydrochloric acid, and $[RuA_5(OH_2)]^{3+}$ in methanesulphonic acid.

It was not possible to obtain directly an extinction coefficient for the complex from these spectra, so the rate of decomposition of the complex at 25°C was determined in order to estimate an extinction coefficient for the complex.

3:9. The Rate of Decomposition of $[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$.—

Armor and Taube[1] have obtained rate constants at 6.8 and 20.1°C for the decomposition of $[RuA_5(N_2O)]^{2+}$ from their equilibrium studies of the reaction of $[RuA_5(OH_2)]^{2+}$ with nitrous oxide. So a determination of this rate at 25°C would not only make it possible to estimate the extinction coefficient of the complex, but would also make it possible to calculate the activation parameters for the reaction.

Now that the complex had been isolated, its rate of decomposition could be measured by dissolving the solid and following the decay of its absorption at 238 nm. This was done in 1 M hydrochloric acid, in the air, because the product, $[RuA_5Cl]^{2+}$, did not have any appreciable absorption at 238 nm[4] (ε_{238} *ca.* 170 $M^{-1}cm^{-1}$).

It was found that, when the nitrous oxide complex was dissolved in water, in the air, it decomposed so rapidly that its absorption at 238 nm had decayed before there was any appreciable absorption due to $[RuA_5OH]^{2+}$, which is the oxidation product of $[RuA_5(OH_2)]^{2+}$. This suggested that the decomposition of the nitrous oxide complex was much faster than the oxidation of ruthenium(II) complexes, and so it was concluded that dioxygen did not affect the rate of decomposition of the complex by oxidising the ruthenium. In hydrochloric acid, the chloro-complex is formed by substitution of the chloride ion into the oxidation product, $[RuA_5(OH_2)]^{3+}$.

A first order decay of the absorption at 238 nm was observed, and a Guggenheim plot of the results (Figure 3:2) gave rate constants of 1.79×10^{-2} and 1.83×10^{-2} sec^{-1} for two runs. These values are in good agreement with each other and indicate that a detailed kinetic study of this decomposition could be made easily now that the solid has been isolated.

These rate constants and those reported by Armor and Taube[1] gave a good Arrhenius plot (Figure 3:3) and activation parameters calculated for

25°C were $\Delta H^{\ddagger}$ = 23.0 kcal $mole^{-1}$ and $\Delta S^{\ddagger}$ = 10.7 e.u. The activation energies for the decomposition of the dinitrogen complexes $[RuA_5N_2]^{2+}$ and $[Ru(N_2)Cl_2(OH_2)_2THF]$ have been found to be 27.7 ± 0.8[15] and 23[16] kcal $mole^{-1}$, respectively. These values correspond to the strength of the ruthenium-dinitrogen bond in the complexes. Thus, it can be seen that the strength of the ruthenium-nitrous oxide bond is very similar to the strength of the ruthenium-dinitrogen bond. This is further evidence that the bonding in the nitrous oxide complexes is similar to the bonding in the dinitrogen complexes.

3:10. Extinction Coefficient of $[RuA_5(N_2O)]^{2+}$.—

From the kinetic results, a half life of 38 seconds was calculated for the decomposition of the nitrous oxide complex. This value was used to estimate the extinction coefficient of the complex.

The tetrafluoroborate and hexafluorophosphate salts were dissolved in 1 M hydrochloric acid and the optical density at 238 nm was measured after 35 and 75 seconds respectively. The solutions were allowed to oxidise to $[RuA_5Cl]^{2+}$ and the final optical density of this complex was used to calculate the initial concentration of the nitrous oxide complex.

An extinction coefficient of $1.1_5 \times 10^4$ $M^{-1}cm^{-1}$ was calculated from the tetrafluoroborate salt and $1.2_2 \times 10^4$ $M^{-1}cm^{-1}$ from the hexafluorophosphate salt. These values are slightly lower than the value of

$(1.7 \pm 0.2) \times 10^4$ $M^{-1}sec^{-1}$ reported by Armor and Taube.[1] However, under their equilibrium conditions, the dinitrogen complexes, $[RuA_5N_2]^{2+}$ and $[A_5RuN_2RuA_5]^{4+}$, may also be present. As the extinction coefficient of the nitrous oxide complex was calculated from the optical density of a solution in which there was only 10-15% conversion to the nitrous oxide complex, small concentrations of the dinitrogen complexes (especially $[RuA_5N_2]^{2+}$) will markedly increase the calculated extinction coefficient.

3:11. Interpretation of the Electronic Absorption Spectrum of $[RuA_5(N_2O)]^{2+}$.—

To interpret the ultraviolet spectrum of $[RuA_5(N_2O)]^{2+}$ it is necessary to consider the spectra of related complexes in the series $[Ru^{II}A_5X]^{2+}$ where X = NH_3, OH_2, CO and N_2.

The absorption maxima of the dinitrogen[8] and nitrous oxide complexes are very similar in their positions and extinction coefficients. This similarity suggests that the absorption arises from a similar transition in both the complexes.

Stanko and Starinshak[17] have assigned the absorption in the dinitrogen complex as a $2p\pi_g \rightarrow 2p\pi_g^*$ transition in the co-ordinated dinitrogen. In the free gas this absorption occurs at 166 nm[18] but it is suggested that the lengthening of the nitrogen-nitrogen bond on co-ordination decreases the energy separation of these levels so that the absorption is observed at 221 nm.

However, Ferguson and Love[19] have concluded that the energy separation of the $2p\pi_g$ and $2p\pi_g^*$ levels of dinitrogen would not be decreased sufficiently to place this transition above 200 nm, and they have assigned the absorption as a metal to ligand charge transfer. Treitel *et al.*[20] have proposed a similar assignment for this absorption.

Penta-ammineruthenium(II) complexes have C_{4v} symmetry and as well as any metal to ligand charge transfer or internal ligand transitions there should also be metal d-d transitions. Complexes which have O_h symmetry have two metal d-d transitions but in complexes of lower symmetry these d-d transitions may be split due to the removal of some degeneracy in the triplet $^1T_{1g}$ and $^1T_{2g}$ states of the octahedral complex. In complexes with C_{4v} symmetry this splitting is very small and is not usually observed.

Many d^6 low spin octahedral complexes have been investigated and the electronic transitions observed in these complexes, especially cobalt(III) complexes, have been well characterised. In Table 3:7 the assignments which have been made for several complexes are tabulated. In the cobalt(III) complexes, the extinction coefficients for the d-d transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, are low because these transitions are symmetry forbidden. The lowest energy transition of the corresponding ruthenium(II) complexes (Table 3:7) also have a low extinction coefficient and so are assigned as a d-d transition ($^1A_{1g} \rightarrow {}^1T_{1g}$ for octahedral symmetry). Because of its high extinction coefficient, the other absorption in $[RuA_6]^{2+}$ has been assigned

as a metal to ligand charge transfer transition.[23] However the extinction coefficient of this band is small compared with that normally expected for this type of transition.

In complexes of the heavier transition metals, there is a greater opportunity for mixing the ligand field d-d transitions with charge transfer or internal ligand transitions. It is possible that the higher energy absorption in the ruthenium(II) complexes, $[RuA_6]^{2+}$, $[RuA_5(OH_2)]^{2+}$ and $[RuA_5CO]^{2+}$, is mainly a d-d transition which has been mixed with other transitions in the complex resulting in a higher transition probability and so a higher extinction coefficient. If this is correct then it would mean that the assignment of the band at 277 nm in $[RuA_5CO]^{2+}$ is incorrect and that this band is actually the second d-d transition in the complex. The metal to ligand(π^*) transition must therefore occur at higher energy and probably with a higher extinction coefficient. Stanko and Starinshak[17] have observed that the carbonyl complex does have a strong absorption up to the limit of their spectrophotometer at 200 nm, and it is likely that the metal to ligand(π^*) transition in the complex is at a higher energy than 200 nm.

Hence, the very strong absorptions at 221 nm in $[RuA_5N_2]^{2+}$ and at 238 nm in $[RuA_5(N_2O)]^{2+}$ are assigned as metal to ligand(π^*) transitions. The d-d transitions of these complexes have not been observed, probably because the spectral solutions were too dilute.

Further evidence for this assignment can be obtained by considering the energies of the molecular orbitals of carbon monoxide, dinitrogen and nitrous oxide which are tabulated in Table 3:8. The lowest energy, empty, antibonding π^*-orbitals in these gases are the 2π, $1\pi_g$ and 3π molecular orbitals respectively.[25,26] On co-ordination of these gases the energy of their molecular orbitals will be modified, but because they all form similar complexes it may be assumed that their energies will still be in the same relative position with respect to each other. The energy of the orbitals on the metal ion may be expected to be of similar energy, with perhaps those of the carbonyl complex being slightly lower in energy because of the better bonding properties of the carbonyl ligand.

If these assumptions are valid, then it should be possible to predict from the energy of the antibonding π^*-orbital in the free gases, the order in which the metal to ligand(π^*) transition will occur in the complexes.

In carbon monoxide this π^* orbital has been observed at 1 eV higher energy than in dinitrogen.[26] With an energy difference of this magnitude in the complexes the metal to ligand(π^*) transition in the carbonyl complex would be expected at around 190 nm if the corresponding transition in the dinitrogen complex is observed at 221 nm. This value for the carbonyl complex is in agreement with the observations of Stanko and Starinshak.[17]

Although molecular orbital calculations vary depending on the basis functions chosen, they do indicate that the 3π orbital of nitrous oxide

is lower in energy than the $1\pi_g$ orbital of dinitrogen ($3\pi(N_2O)$, calculated = -7.7 eV;[25] $1\pi_g(N_2)$, observed = -7 eV[26]). So the metal to ligand(π^*) transition in the nitrous oxide complex would be expected to be lower in energy than the corresponding transition in the dinitrogen complex, as is observed.

It is not possible that the strong absorption in the dinitrogen and nitrous oxide complexes is a $\pi \rightarrow \pi^*$ transition in the ligand because the energy of this transition (Table 3:8) is so high that it would be below 200 nm even if the energy difference of the orbitals did become less on co-ordination.

A metal to ligand transition in the ammine- and aquo- complexes is not observed because in these complexes the ligands do not have any suitable orbitals available to accept electrons from the metal and so only the two metal d-d transitions are observed.

Recently $[RuA_5(HCN)]^{2+}$ and $[RuA_5(CH_3CN)]^{2+}$ have been isolated[28,29] and they also have an absorption in the same region as the dinitrogen and nitrous oxide complexes. Ford and co-worker have assigned this absorption in these complexes as a metal to ligand(π^*) transition. The energy of the lowest energy, empty, antibonding π^*-orbital of hydrogen cyanide (2π) has been calculated.[27] However its energy is too high and it does not fit into the sequence in Table 3:8.

Even so, these molecular orbital considerations do indicate that the strong absorption in the dinitrogen and the nitrous oxide complexes is a metal to ligand(π^*) transition and so the assignment made by Stanko and Starinshak[17] for the dinitrogen complex is incorrect.

3:12. Crystal Structure of $[RuA_5(N_2O)]Br_2$.—

The crystal structure of $[RuA_5N_2]Cl_2$ and its related salts has been reported by Bottomley and Nyburg.[30] The complexes crystallise in a cubic system with one of the space group $Fm3m$, F432 or $F\bar{4}3m$. These space groups are indistinguishable because all the non-hydrogen atoms are on special positions. The ruthenium atom is at the origin and the anions are at the positions 1/4,1/4,1/4 and 3/4,3/4,3/4. The ammonia groups and the dinitrogen are disordered. The five nitrogen atoms of the ammonia groups and the co-ordinated nitrogen atom of the dinitrogen randomly occupy the six octahedral sites $\pm x_1,o,o$; $o,\pm x_1,o$; $o,o,\pm x_1$ about the ruthenium atom. The remaining nitrogen atom of the dinitrogen randomly occupies the six positions, $\pm x_2,o,o$; $o,\pm x_2,o$; $o,o,\pm x_2$. This means that dinitrogen has a site occupancy of 1/6 on each of the octahedral positions about the ruthenium. As face-centring of an atom on a special or general position in either of the three space groups generates three other atoms, these positions define the structure.

Boomsma and Snow[31] have found that $[CoA_5(NCS)]Cl_2$ also crystallises with a structure similar to that of the dinitrogen complex where the linear

NCS group replaces the NN group. The cell constants for these complexes are almost the same (Table 3:9) which suggests that the structure is determined mainly by the interactions between the central metal atom and the anions.[31] This may mean that the sixth ligand about the metal can be varied and as long as it is linear and not too bulky then the complex may crystallise with a similar structure to that of the dinitrogen complex.

TABLE 3:9

Cell constants of penta-ammine complexes

$[RuA_5N_2]Cl_2$	10.14 Å
$[CoA_5(NCS)]Cl_2$	10.16 Å
$[RuA_5N_2]Br_2$	10.41 Å
$[RuA_5(N_2O)]Br_2$	10.3 Å

As the terminal atom of nitrous oxide is smaller than the terminal atom of the isothiocyanate group, nitrous oxide in its complexes might also be able to occupy the same random positions as the isothiocyanate ion does in its complex.

Crystals of $[RuA_5(N_2O)]Br_2$ showed complete extinction through 360° under a polarising microscope with crossed polars, characteristic of a crystal in a cubic space group. A powder photograph of the bromide salt could be indexed for a face-centred cubic system and a cell constant of

10.3 Å was calculated. This is similar to the cell constant for the bromide salt of the dinitrogen complex (Table 3:9). All the reflections observed could be indexed and there was no evidence of any others arising from the dinitrogen complex, which may be present as an impurity.

That the powder photograph could be indexed in a face-centred cubic system is good evidence that $[RuA_5(N_2O)]Br_2$ also has the same basic structure as the dinitrogen complex. To check this further the structure factors for the nitrous oxide complex (nitrogen bonded) were calculated assuming that the complex did have the same disordered structure as the dinitrogen complex. The metal nitrogen distances used for the ammonia groups were those reported by Bottomley and Nyburg for the corresponding dinitrogen complex,[30] and the bond lengths of gaseous nitrous oxide[32] were used for the co-ordinated nitrous oxide.

Although the scale factor between the observed and calculated structure factors has not been fully refined, and considering that the bond lengths can only be approximately correct, there is good agreement in the trends shown by the calculated and the observed structure factors in Table 3:10. Thus, these structure factor calculations suggest that the nitrous oxide is co-ordinated linearly in the bromide salt, with a structure similar to that of the dinitrogen complex.

If the nitrous oxide is co-ordinated such that the Ru-N-N angle is not 180°, then it is very likely that interactions of the nitrous oxide with the

anions and ammonia ligands will result in changes in the cell parameters (especially if the nitrous oxide is not disordered) so that the complex will not crystallise in a cubic space group (*i.e.* the cell parameters will not all be the same). However, if such a complex does crystallise in the same cubic space group as $[RuA_5N_2]Cl_2$ then, on the basis of the structure factor calculations, it is unlikely that it will be possible to distinguish this structure from that in which the nitrous oxide is linearly co-ordinated. This is because the contribution of the ruthenium atoms and the anions to the structure factors will be much greater than that of the nitrous oxide and changing the position of the nitrous oxide will not affect the structure factors greatly. Unfortunately, it will not be possible to obtain an X-ray crystal structure of the nitrous oxide complex to determine how the nitrous oxide is co-ordinated because the complex must be precipitated as soon as it forms to prevent decomposition, so that only a microcrystalline solid can be obtained.

The suggestion that the complexes have a structure similar to that of the corresponding dinitrogen complex was made after all the preparative work had been completed and measurements were taken on the only powder photograph which was available. The remaining salts are being investigated now,[33] and it is expected that they will also have a similar structure.

In the next chapter the infrared absorptions of the co-ordinated nitrous oxide are used to obtain further insight into the bonding of nitrous oxide in these complexes.

TABLE 3:2

Analytical data for the nitrous oxide complexes

$[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$

		%H	%N	%F
Found;	for a brown sample;	3.8_6	21.2_0	39.2
	for a yellow sample;	4.0_2	22.2_2	36.8
Calculated;		4.06	23.25	36.02

$[RuA_5(N_2O)]Br_2$

	%H	%N	%Br microanalysis*	%Br potentiometrically†
Found;	4.0_1	23.8_0	42.0	41.5_0, 41.7_7 41.7_4, 41.8_6
Calculated;	3.88	25.15	40.98	

$[RuA_5(N_2O)]I_2$

	%I potentiometrically†
Found;	51.7_7, 52.3_5
Calculated;	52.43

*C.S.I.R.O. Microanalysis Division, Melbourne.

†Determined by potentiometric titration in Adelaide.

TABLE 3:3

Solution properties of the nitrous oxide complexes

(a) Conversion to $[Ru^{II}A_5(OH_2)]^{2+}$

The extinction coefficient was measured at 268 nm in 0.1 M methanesulphonic acid which was flushed with argon.

anion	$[RuA_5(N_2O)]X_2$ ε_{max} ($M^{-1}cm^{-1}$)	$[RuA_5(OH_2)]X_2$ ε_{max} ($M^{-1}cm^{-1}$)
Br^-	627 ± 3	569 ± 2
I^-	617 ± 3*	644 ± 4*
BF_4^- †	569 ± 2	
PF_6^- †	559 ± 2	569 ± 3

*Iodide ion contributes to the absorption also.

†This salt also contains one molecule of lattice water.

(b) Conversion to $[Ru^{III}A_5Cl]^{2+}$

After aerial oxidation in 0.1 M hydrochloric acid, the extinction coefficient was measured at 327 nm.

$[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$ $\varepsilon = 1.81 \times 10^3$, 1.80×10^3 $M^{-1}cm^{-1}$

$[RuA_5(N_2O)](PF_6)_2 \cdot H_2O$ $\varepsilon = 1.77 \times 10^3$, 1.82×10^3 $M^{-1}cm^{-1}$

$[RuA_5(OH_2)](PF_6)_2 \cdot H_2O$ $\varepsilon = 1.78 \times 10^3$, 1.80×10^3 $M^{-1}cm^{-1}$

lit.[4] for $[RuA_5Cl]^{2+}$; $\lambda_{max} = 327$ nm; $\varepsilon = 1.93 \times 10^3$ $M^{-1}cm^{-1}$

TABLE 3:3 (cont'd)

(c) Conversion to $[Ru^{III}A_5OH]^{2+}$

The extinction coefficient was measured at 295 nm.

	$\varepsilon_{initially}$ ($\times 10^{-3}$) ($M^{-1}cm^{-1}$)	$\varepsilon_{finally}$ ($\times 10^{-3}$) ($M^{-1}cm^{-1}$)
$[RuA_5(N_2O)]Br_2$		1.91
$[RuA_5(N_2O)]I_2$	1.63, 1.66	
$[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$	1.62, 1.65, 1.66	2.15, 2.19
$[RuA_5(OH_2)]^{2+}$	1.63, 1.66	2.10

lit.[5] for $[RuA_5OH]^{2+}$; λ_{max} = 295 nm; $\varepsilon = 2.14_5 \times 10^3$ $M^{-1}cm^{-1}$.

TABLE 3:4

Release of nitrous oxide

oxidising agent	wt. of complex	total volume (N_2 + N_2O)		volume of N_2O		calculated volume*
	mg	cc	%	cc	%	cc
cerium(IV) sulphate	14.10			0.53_4	71.3	0.749
	9.07	0.45_0	93.3	0.34_7	72.1	0.482
	13.13	0.63_5	91.0	0.54_0	77.5	0.697
	14.38	0.65_4	85.7	0.55_8	73.1	0.764
ferric sulphate	16.92			0.50_8	56.6	0.898
oxygen	10.30			0.26_0	45.5	0.571

*Based on one mole of gas evolved per mole of complex.

TABLE 3:5

Infrared spectra of the nitrous oxide complexes

assignment/anion	Br^-	I^-	BF_4^-	PF_6^-
ν_{OH}			3610 3540	3640 3575
ν_{NH}	3290 (br) 3230 (sh) 3175 (sh)	3290 (br) 3230 (sh) 3175 (sh)	3370 3290 3222	3375 3305 3220
δ_{OH_2}			1700 (sh)	1700 (sh)
δ_{NH_3} asym	1610	1604	1630	1627
δ_{NH_3} sym	1268	1272	1295	1296
ρ_{NH_3}	792	772	760[a]	770[a]
ν_{Ru-NH_3}	445 428 (sh)	424 (w)	423 (w)	416 (w)
ν_3 BF_4^-, PF_6^-			1155 (br)	840 (br)
ν_4 BF_4^-, PF_6^-			520	555
ν_3 (N_2O)	2239	2252	2270	2280 2222
ν_1 (N_2O)	1161	1180	1209	1222
$2\nu_1$ (N_2O)	2315 (w)		2415 (w)	
ν_{N_2} (impurity)	2110	2128		2165
other bands	605 476 (w) 336 301	600 321 301	600 460 313 305	 470 (w) 308 (sh) 301

TABLE 3:6

Ammonia absorptions of ruthenium-ammine complexes

	$[RuA_6]X_3$ [12]	$[RuA_5X]X_2$ [12]	$[RuA_5CO]X_2$ [13]	$[RuA_5N_2]X_2$ [2]	$[RuA_5(N_2O)]X_2$	$[RuA_5(OH_2)]X_2$	$[RuA_6]X_2$ [12]
X = Br^-							
δ_{NH_3} asym	1607	1601	1608	1618	1610	1608	1605
δ_{NH_3} sym	1338, 1316	1299	1278, 1250	1266	1268	1234	1226
ρ_{NH_3}	777	791	790	788	792	762	760
X = I^-							
δ_{NH_3} asym		1584	1606	1605	1604	1600	1603
δ_{NH_3} sym	1333, 1314	1296, 1270 (sh)	1285, 1250	1276	1272	1246	1243
ρ_{NH_3}	770	774	778	775	772	753	749
X = BF_4^-							
δ_{NH_3} asym	1629		1637	1630	1630	1628	1628
δ_{NH_3} sym	1353, 1293		1313, 1288 (sh)	1297	1295	1273	1273
ρ_{NH_3}	774		787, 775	768	760	747	741

TABLE 3:7

Electronic transitions in d^6 low spin complexes

complex	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	assignment*	reference
$[CoA_6]^{3+}$	476	55.3	$^1A_{1g} \rightarrow {}^1T_{1g}$	21, 22
	339	46.2	$^1A_{1g} \rightarrow {}^1T_{2g}$	
$[CoA_5(OH_2)]^{3+}$	485	48.3	$^1A_{1g} \rightarrow {}^1T_{1g}$	21, 22
	340	46.2	$^1A_{1g} \rightarrow {}^1T_{2g}$	
$[RuA_6]^{2+}$	*ca.* 400	*ca.* 30		23
	275	624	metal-ligand charge transfer	
$[RuA_5(OH_2)]^{2+}$	410	44		24
	267	*ca.* 530		
$[RuA_5CO]^{2+}$	360	17.0	$^1A_{1g} \rightarrow {}^1T_{1g}$	17
	277	258	$d\pi \rightarrow \pi^*(CO)$	
$[RuA_5N_2]^{2+}$	221	18000		15
$[RuA_5(N_2O)]^{2+}$	238	17000		1

*Assignments assuming octahedral symmetry.

TABLE 3:8

Energy of the molecular orbitals*

molecule (XY)	highest energy π bonding orbital		lowest energy π* antibonding orbital		energy difference** for the transitions		absorption maximum in $[RuA_5(XY)]^{2+}$ (nm)
	orbital	energy	orbital	energy	ligand π → π*	metal → ligand(π*)	
N_2O	2π	-12.9	3π	-7.7†	5.2	5.3	238
N_2	$1\pi_u$	-17.1	$1\pi_g$	-7	10.1	6	221
CO	1π	-16.6	2π	-6	10.6	7	< 200
HCN	1π	-13.7†	2π	+4.5†	18.2	11.5	241

*All energies are in electron volts.

**Assuming the energy of the metal d orbital is -13 eV.

†Calculated value.

TABLE 3:10

Observed and calculated structure factors for $[RuA_5(N_2O)]Br_2$

h k l	F obs.	F calc.
111	a	0.097
200	0.0[b]	0.002
220	0.195	0.217
311	0.098	0.073
222	0.086	0.098
400	0.171	0.259
331	0.071	0.059
420	0.0[b]	0.014
422	0.195	0.157
333, 511	0.117	0.131
440	0.163	0.187
531	0.131	0.068
442	0.0[b]	0.018
600	0.0[b]	0.007
620	0.181	0.145
533	0.105	0.059
622	0.0[b]	0.034
444	0.135	0.143
551, 711	0.128	0.119
640	0.0[b]	0.000
642	0.211	0.115
731	0.142	0.045
800	0.102	0.122
660, 822	0.160	0.195
555, 751	0.140	0.105

TABLE 3:10 (cont'd)

h k l	F obs.	F calc.
840	0.151	0.099
753, 911	0.131	0.091

a Not observed because it was obscured by the beam stop.

b Although these reflections were not observed their expected value was calculated. Their calculated values are very low which is why they were not observed.

FIGURE 3:1. Electronic absorption spectrum of $[RuA_5(N_2O)]^{2+}$

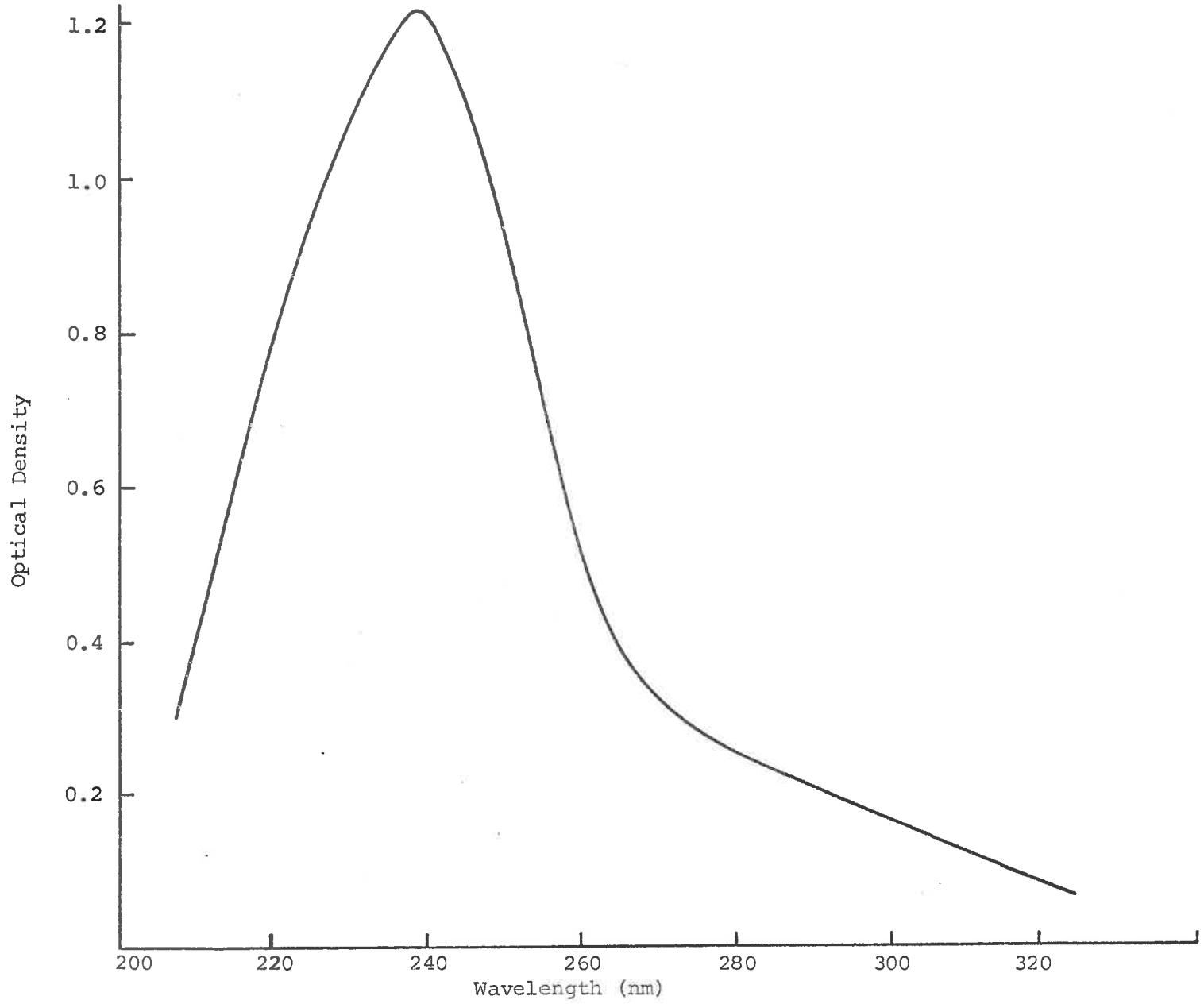


FIGURE 3:2

Guggenheim plot for the decomposition of

$[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$ at 25°C

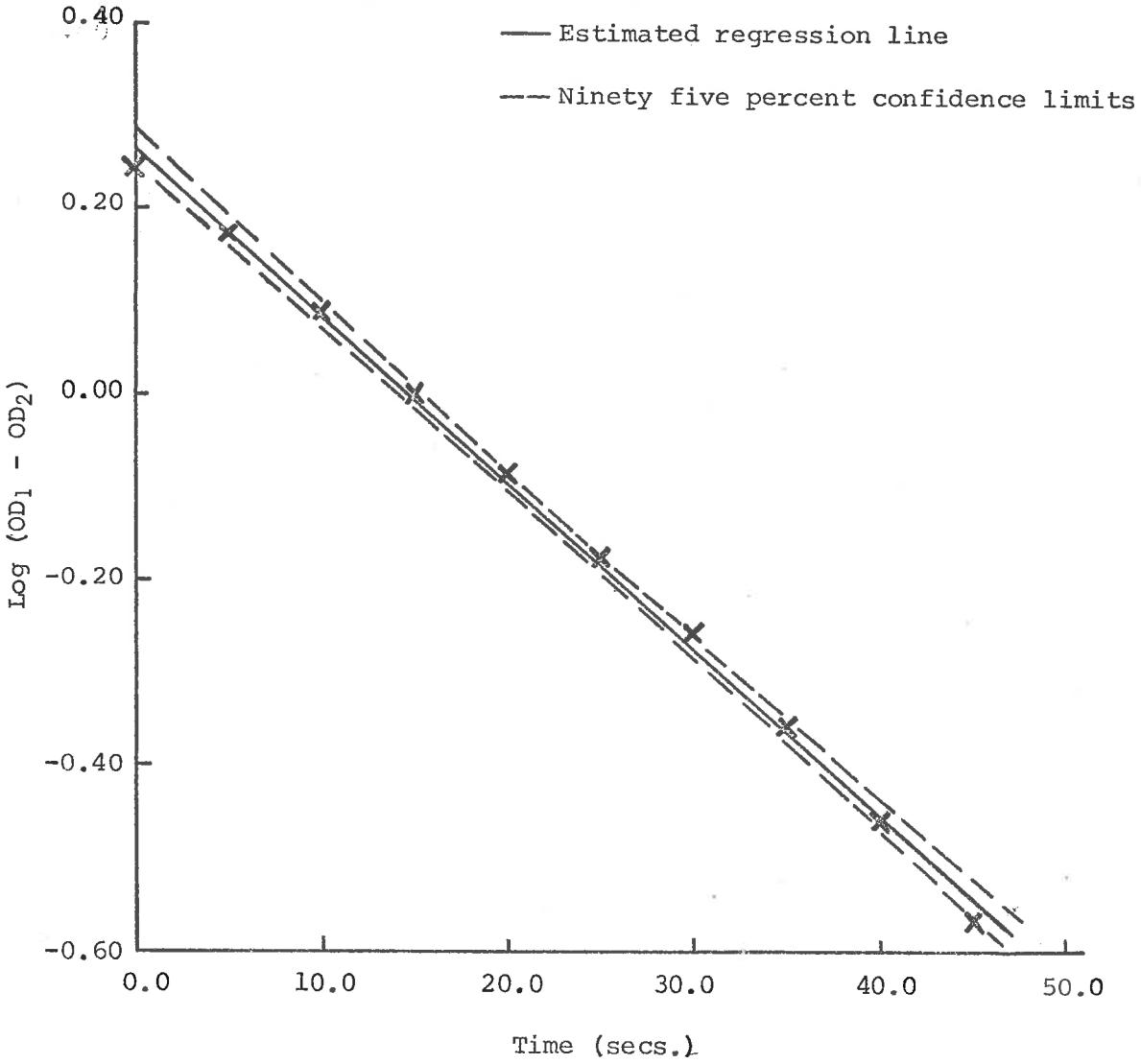
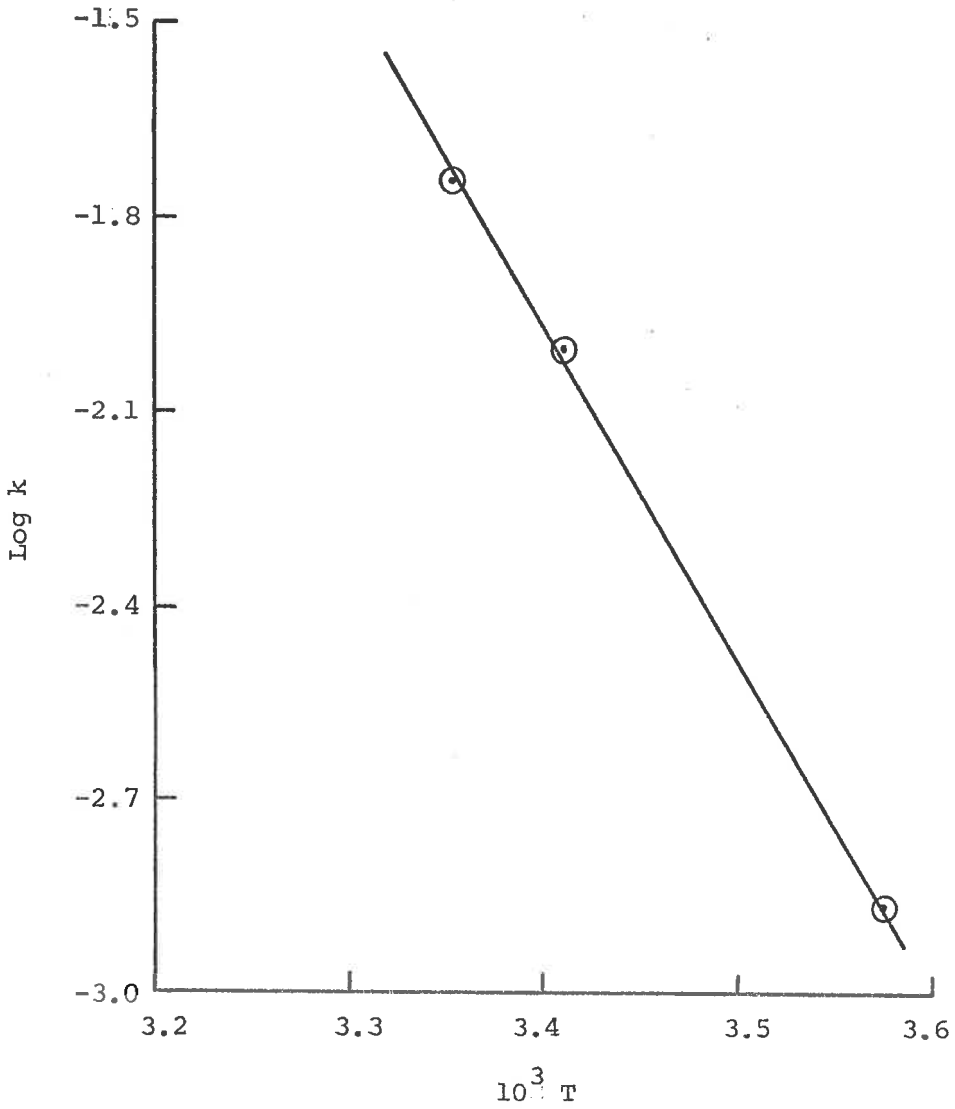


FIGURE 3:3

Arrhenius plot for the decomposition of $[RuA_5(N_2O)]^{2+}$



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CHAPTER 4

INFRARED SPECTRA OF THE NITROUS OXIDE COMPLEXES

4:1. Introduction.—

In the previous chapter the ammonia absorptions in the infrared spectra of the complexes were discussed. They indicated that the complexes contained ruthenium(II) and that there was some back-bonding from the metal to the co-ordinated nitrous oxide. In this chapter the absorptions due to the co-ordinated nitrous oxide are discussed. These absorptions have been assigned in the complexes containing $^{14}N^{14}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$, and they have been used to calculate approximate force constants for the co-ordinated nitrous oxide. From the calculations the nitrous oxide has been shown to be co-ordinated to the metal through the oxygen atom.

4:2. Fundamental Vibrations of Nitrous Oxide.—

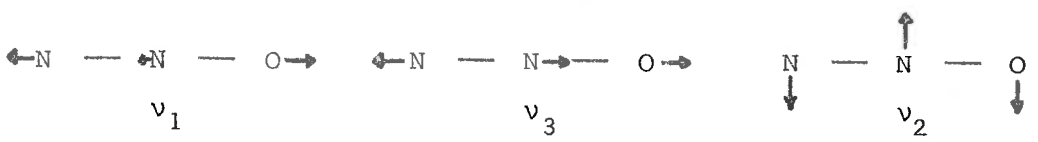
Nitrous oxide is a linear molecule which has $C_{\infty v}$ symmetry. Its four fundamental vibrations[1] are:-

(1). ν_1, the pseudo-symmetric stretch

(2). ν_3, the pseudo-asymmetric stretch

and (3). ν_2, the doubly degenerate bend.

These absorptions are observed at 2224, 1286 and 589 cm^{-1} respectively in gaseous nitrous oxide.[1]



Both the stretching vibrations have Σ^+ symmetry and the bending vibration has Π symmetry.

Although each stretching vibration involves the stretching of both bonds, it is usual to consider that ν_1 is mainly a stretching of the nitrogen-oxygen bond and that ν_3 is mainly a nitrogen-nitrogen stretching vibration. This approximation is useful because it provides a qualitative correlation between the frequencies of the fundamentals and the force constants in the molecules.

4:3. Infrared Spectrum of Adsorbed Nitrous Oxide.—

Kozirovski and Folman[2,3] have recorded the infrared spectrum of nitrous oxide adsorbed on evaporated alkali halide films. All three fundamentals of the nitrous oxide were observed and they are tabulated in Table 4:1. Adsorption of the nitrous oxide caused an increase in the frequency of ν_3 and a decrease in the frequencies of ν_1 and ν_2. This suggests that the nitrogen-nitrogen bond has been strengthened and the nitrogen-oxygen bond has been weakened as a result of the interaction with the alkali halide film.

The multiple absorptions observed for the fundamentals in some cases may be because the nitrous oxide was adsorbed on more than one type of site, or with different orientations on the surface. Kozirovski and Folman[2] noted that all the absorptions were sharp and narrow excluding the possibility of a three dimensional rotation of the nitrous oxide on the surface. Hence the multiple absorptions are probably due to the nitrous oxide being adsorbed on

different sites, or in different fixed orientations, on the surface. Kozirovski and Folman[2] assumed that, on sodium chloride, the nitrous oxide was adsorbed on a cation through its oxygen atom such that it was perpendicular to the surface. The suggestion that the nitrous oxide was adsorbed through the oxygen atom was based on the charge distribution in the molecule (nitrous oxide has a small permanent dipole moment which is directed towards the oxygen atom[4]). However, Kozirovski and Folman did not discount the possibility that the nitrous oxide could be adsorbed through the nitrogen atom.

When nitrous oxide was adsorbed on synthetic zeolites,[5] similar shifts in the positions of the stretching fundamentals ν_3 and ν_1 were observed (Table 4:1). Although there was no discussion of how the nitrous oxide was adsorbed on these zeolites, the shifts in the positions of the fundamentals indicate that it was adsorbed in the same way as on the alkali halide films.

4:4. Infrared Spectrum of Co-ordinated Nitrous Oxide.—

For the purpose of predicting the number of vibrations expected for nitrous oxide co-ordinated to a metal, the complex may be considered as linear XYZW, where W represents the RuA_5 unit and XYZ the nitrous oxide. Seven degrees of freedom would be expected for this system. The three vibrations corresponding to the fundamentals of nitrous oxide account for four of these degrees of freedom since ν_2 is doubly degenerate. Also there

will be a metal-ligand stretch and a doubly degenerate metal-ligand bend. This model has $C_{\infty v}$ symmetry and so all the stretching vibrations will have Σ^+ symmetry and the bending vibrations Π symmetry.[6]

The model neglects any interactions of these vibrations with the rest of the molecule. These interactions are not expected to be very great and so this should be a good model for co-ordinated nitrous oxide.

4:4:1. Stretching vibrations.—

In the nitrous oxide complexes, absorptions corresponding to the stretching fundamentals of nitrous oxide (ν_3 and ν_1) could be assigned, and these will be referred to as the ν_3 and ν_1 vibrations of the complex. These frequencies, and the overtone $2\nu_1$ which was also observed in some salts, are tabulated in Table 4:2. The assignment of the metal-ligand stretching vibration is made in section 4:5:4.

The spectra of the bromide and iodide salts were recorded as potassium bromide discs or as Nujol mulls. The spectra of the tetrafluoroborate and hexafluorophosphate salts could only be recorded as Nujol mulls because these complexes decomposed during the preparation of the potassium bromide discs. Red coloured discs (probably due to the presence of ruthenium red) were obtained, and the spectra showed the absorptions characteristic of the bromide salt (due to anion exchange) with only weak absorptions of the fluoro-salt. For example, a disc of the tetrafluoroborate salt had weak absorptions at 2269 and 1206 cm^{-1} and an absorption at 2103 cm^{-1} and a

shoulder at 1155 cm^{-1} on the ν_3 absorption of the tetrafluoroborate anion.

On co-ordination of the nitrous oxide, the shifts in the positions of the ν_3 and ν_1 absorptions are in the same direction, but of greater magnitude, as the shifts observed in the corresponding absorptions when nitrous oxide was adsorbed on the alkali halide films or the synthetic zeolites. The magnitude of these shifts and the intensity of the absorptions are dependent on the anion associated with the complex.

4:4:2. Effect of the anion on the ν_3 and ν_1 absorptions of co-ordinated nitrous oxide.—

(a). Position of ν_3 and ν_1. In the carbonyl[7] and dinitrogen[8] complexes $[RuA_5(XY)]Z_2$ (XY = CO or N_2, Z is a monovalent anion), the position of the ligand stretch, ν_{XY}, is found to depend on the anion. In both complexes the frequency ν_{XY} decreases in the anion sequence, PF_6^- > BF_4^- > I^- > Br^- > Cl^-, which is also the order of decreasing size of the anion. The decrease in this frequency indicates that the force constant of the X-Y bond is decreased, and the effect is greatest for the smallest anions.

Borodko *et al.*[9] and Chatt *et al.*[10] have discussed how the anion may produce these effects in the carbonyl and dinitrogen complexes. They have both concluded that the weakening of the bond is caused by an increase of the electron density in the antibonding π^* orbital of the ligand. However their suggestions as to how this occurs are different.

Chatt *et al.*[10] propose that the anion is able to polarise the ammonia ligands with a consequent increase of electron density on the ruthenium atom, followed by delocalisation into the antibonding π^* orbital of the ligand. The smaller the anion the more effective this is, so the frequency of ν_{XY} is lowest with the smallest anions. Evidence of this interaction is seen in the shape of the nitrogen-hydrogen stretching vibrations in the infrared spectra of the complexes. In the chloride, bromide and iodide salts these absorptions are very broad, indicating a strong interaction with the anion. However, in the tetrafluoroborate and hexafluorophosphate salts the corresponding absorptions are sharp, well defined peaks indicating that there is little interaction of these anions with the ammonia ligands.

A similar polarisation of the co-ordinated dinitrogen, and carbon monoxide, by the anion would be expected to increase ν_{XY} because electron density in the antibonding π^* orbital of the ligand would be decreased as electrons are released on to the metal. However as ν_{XY} is observed to be lowest with the smallest counteranion, Chatt *et al.*[10] consider that this interaction is only weak and is obscured by the interaction of the anion with the ammonia ligands.

Borodko *et al.*[9] have suggested that the electron density in the antibonding π^* orbital of the ligand XY is increased by an electron transfer from the anion into an antibonding orbital which is mainly localised on the ligand. This electron transfer will be most efficient with the smallest anion and so the lowest frequency would be expected in the chloride salt.

Borodko *et al.*[9] have also considered that the anion may interact directly with the ligand XY. They suggest that this interaction (at the atom X) will produce a more polar bond (structure II) which will have a lower stretching frequency.

$[A_5Ru\text{-}X\equiv Y]^{2+}$ $\qquad\qquad$ $[A_5Ru{=}\overset{+}{X}{=}\overset{-}{Y}]^{2+}$

I $\qquad\qquad$ II

The crystal structure of $[RuA_5N_2]Cl_2$ and its related salts[11] has shown that in these complexes the anion is close enough to interact with the ammonia groups and the *endo* nitrogen atom of the dinitrogen. The smaller the anion the closer it is to these atoms. Although $[RuA_5CO]Cl_2$ has a different structure[12], it is probable that similar interactions, at least with the ammonia groups, are also present in the carbonyl complexes.

In summary, it appears that in these complexes the polarisation of the ammonia groups by the anion is probably the main mechanism by which the anion affects the position of ν_{XY}, as the effect of this interaction is also observed in the ammonia absorptions. However the other interactions suggested above may also contribute to the observed changes in ν_{XY}.

As the nitrous oxide complexes have structures similar to the corresponding dinitrogen complexes (section 3:12), the anion would be expected to affect the stretching frequencies of the co-ordinated nitrous oxide in the same way. Hence the hexafluorophosphate salt will be expected to have the highest frequency for the stretching vibrations because the

effect of the anion is the least in this complex. In the hexafluorophosphate salt, absorptions at 2280 and 2222 cm^{-1} were observed. The higher absorption fits into the sequence of the ν_3 absorptions in the other salts, and so it is assigned as the ν_3 absorption for this salt. The origin of the second absorption is discussed in section 4:5:2.

As the interaction by the anion is the smallest in the hexafluorophosphate salt, it gives the best indication of how the nitrous oxide fundamentals are affected on co-ordination. It may be considered that, if there were no interaction by the anion, then the fundamentals of nitrous oxide, ν_3 and ν_1, would occur at about 2280 and 1222 cm^{-1} respectively. The observed frequencies are due to the shifts from these positions produced by the anion.

(b). Intensity of ν_3 *and* ν_1. In gaseous nitrous oxide the intensity of the fundamental vibrations decrease in the order:-

$$\nu_3 > \nu_1 > \nu_2$$

The same order is observed when nitrous oxide is adsorbed on the alkali halide films.[2,3] However, in its complexes this order is changed and the intensities of the three corresponding absorptions decrease in the order:-

$$\nu_1 > \nu_3 > \nu_2$$

The intensities of ν_1 and ν_3 in the complexes are also dependent on the counteranion. The affect of the anion on the intensity of the bending

vibration (ν_2) is not known because it has not been possible to assign it unambiguously (see section 4:6:2).

The intensity of ν_1 was found to increase in the anion sequence,

$$PF_6^- < BF_4^- < I^- < Br^- \simeq Cl^-$$

while the intensity of ν_3 decreases in the anion sequence,

$$PF_6^- \simeq BF_4^- > I^- > Br^- > Cl^-.$$

The ν_3 absorption of the chloride salt was so weak that it could not be observed and that of the bromide salt was also very weak making it difficult to determine its position accurately.

As the ruthenium atom is heavy compared with the nitrous oxide ligand, it will not move very much during the vibrations of the ligand and so the nitrous oxide may be considered to be co-ordinated to an infinite mass. Hence, the vibrations ν_3 and ν_1 (for oxygen co-ordination of the nitrous oxide) may be represented as;

ν_3 $\qquad\qquad$ ν_1

In the ν_1 vibration (the pseudo-symmetric stretch in gaseous nitrous oxide) the movement of the oxygen atom is restricted and so the molecule will not be stretched as symmetrically as it is in gaseous nitrous oxide and this is probably why the intensity of this vibration is increased on

co-ordination of the nitrous oxide. It is not as easy to predict qualitatively whether the restriction in the motion of the oxygen atom will make the ν_3 vibration more or less symmetric.

In the nitrous oxide complexes the bonding appears to be similar to that in the dinitrogen and carbonyl complexes, $[RuA_5(XY)]^{2+}$ (XY = N_2 or CO). Thus the strength of the bonding in the complexes will depend on which anion is present. As discussed in section 4:4:2(a), the interaction of the anion with the complex cation results in a weakening of the bonds in the nitrous oxide due to back-bonding from the metal to the lowest energy antibonding π^* orbital of the nitrous oxide. An increase in the back-bonding will also mean that the metal-ligand bond is strengthened. The strengthening of this bond and the weakening of the two nitrous oxide bonds in the complexes will be greatest for the smallest anion. Thus in the ν_1 vibration, the movement of the oxygen atom will be restricted more but the motion of the nitrogen atoms will be easier as the anion becomes smaller and so this vibration will be expected to become more asymmetric the smaller the anion. Hence, the highest intensities for this absorption would be expected with the smallest anions. The changes in the strength of the bonds will also affect the other stretching vibration, ν_3, and apparently it becomes more symmetric with smaller anions because its intensity decreases as the size of the anion becomes smaller.

4:4:3. Bending vibrations.—

Although the ν_3 and ν_1 absorptions could be assigned easily, it was not possible to assign the other vibrations expected for this system. These absorptions, the bending modes and the metal-ligand stretching vibration, should be below 600 cm^{-1}. However in the region 600-250 cm^{-1} (the limit of the instrument used) absorptions due to the metal-ammine stretches and deformations are also expected. Although several absorptions were observed in this region they were usually weak and very broad and they could not be assigned confidently.

4:5. Infrared Spectra of Isotopically Labelled Nitrous Oxide Complexes.—

The preparation of isotopically labelled complexes has been widely used to assist in assigning infrared absorptions. The complexes containing nitrogen 15 labelled nitrous oxide were prepared to confirm the assignment of the ν_3 and ν_1 stretches and to see whether the other vibrations expected for the system could be assigned. Also, it was hoped that it might be possible to determine whether the nitrous oxide was bonded through its nitrogen or oxygen atom.

The complexes were prepared from nitrous oxide which was labelled in the *exo* ($^{15}N^{14}N^{16}O$) or *endo* ($^{14}N^{15}N^{16}O$) position. Although the reaction conditions used to obtain the pressure of nitrous oxide required resulted in the products being contaminated with $[RuA_5(OH_2)]X_2$ and $[RuA_5N_2]X_2$, their absorptions were easily discerned. The positions of the absorptions

were measured to better than ±0.5 cm^{-1}.

4:5:1. Stretching vibrations ν_3 *and* ν_1.—

The absorptions corresponding to the ν_3 and ν_1 vibrations of the nitrous oxide were observed to shift when the labelled nitrous oxide was used (Table 4:3). The shifts in ν_3 and ν_1 are represented diagramatically in Figures 4:1 and 4:2 respectively and they are tabulated in Table 4:4.

The magnitudes of the shifts are dependent on the anion and when the complexes are considered in the order bromide, iodide, tetrafluoroborate, hexafluorophosphate the magnitudes of these shifts tend toward those observed in gaseous nitrous oxide (Table 4:4). This is further evidence that the effect of the anion is the smallest in the hexafluorophosphate salt. (The shifts observed for the ν_3 absorption in the complexes prepared with $^{15}N^{14}N^{16}O$ do not follow any discernible trend.)

4:5:2. Multiple absorptions in the ν_3 *region.*—

The isotopically labelled nitrous oxide complexes were usually contaminated with the dinitrogen complex. Thus between 2000-2200 cm^{-1} the nitrogen-nitrogen stretch, ν_{N_2}, was observed. Its position was in good agreement with the reported values[8] for all the salts except the chloride. In this salt, ν_{N_2} was much lower than that reported by Allen *et al.*[8] for $[RuA_5N_2]Cl_2$. However, Norman[14] has found that chloride ions catalyse the loss of co-ordinated ammonia from $[RuA_5(OH_2)]^{2+}$ and so the

dinitrogen complex isolated in the presence of chloride ion is probably $[RuA_4(OH_2)N_2]Cl_2$.

In the *hexafluorophosphate salt* there was an absorption at 2221.9 cm^{-1} which was observed to shift when labelled nitrous oxide was used. The position of this absorption was almost the same as that observed in the corresponding gaseous nitrous oxide. The absorption is not due to nitrous oxide dissolved in the mull because its intensity did not decrease noticeably when the mull was kept for one hour in a dessicator. (The absorptions due to nitrous oxide dissolved in Nujol was found to disappear over this time.) Neither is it likely that a clathrate complex of nitrous oxide (*i.e.* a complex in which the nitrous oxide is held in the lattice by Van der Waals forces) is responsible for this absorption, because its decomposition in the infrared radiation (see later) would only be expected to release the nitrous oxide and not lead to the formation of further complexes. Hence, it appears that this absorption is also due to co-ordinated nitrous oxide.

The relative intensities of the two ν_3 absorptions in this salt were never the same for two preparations. This indicates that there is more than one complex present. (Two absorptions due to co-ordinated nitrous oxide would be observed if the complex was a tetra-ammine complex and both *cis-* and *trans-* isomers were present. However, the solution properties of this complex (Table 3:3) indicate that it is a penta-ammine complex.) The two absorptions were both very sharp and had similar shifts when the

labelled nitrous oxide was used, which suggests that the bonding of the nitrous oxide is similar in the two complexes. It is possible that both the oxygen and nitrogen linked isomers of penta-ammine(dinitrogen oxide)-ruthenium(II) are present in the solid.

A ν_1 absorption associated with the lower ν_3 absorption was not observed. If this ν_1 absorption has a frequency similar to the ν_1 absorption in gaseous nitrous oxide, then it should occur around 1285 cm^{-1}. However, the ammonia deformation, $\delta_{NH_3\ asym}$, occurs at 1296 cm^{-1} in the complex, and this broad absorption covers the region where the ν_1 absorption is expected. If there is a ν_1 absorption associated with the lower absorption in the ν_3 region, then deuteration of the ammonia groups in the complex would allow it to be observed. This would confirm that two forms of co-ordinated nitrous oxide are present in the hexafluorophosphate salt.

When the hexafluorophosphate salt was irradiated with infrared radiation for two hours the lower ν_3 absorption was observed to decrease while the higher absorption and the ν_1 absorption were unaffected. A similar change was observed when the complexes were stored for over a week at 20°C. Associated with the decrease in intensity of the lower absorption in the ν_3 region was the appearance of two new absorptions. Between 2000-2200 cm^{-1} a weak absorption was observed, and between 1164-1154 cm^{-1} there was a medium to strong absorption. The positions of both these absorptions were dependent on the position of the label in the nitrous oxide (Table 4:5). During the two hours the mull was in the infrared radiation it gradually

became a dark red colour.

The decomposition appears to form the dinitrogen complex (although 2080 cm^{-1} is low for $[RuA_5(^{15}N^{14}N)](PF_6)_2$) and ruthenium red. This suggests that the lower absorption in the ν_3 region may be due to the nitrogen linked isomer which decomposed to the dinitrogen complex and ruthenium red. It is not known what the absorption between 1164-1154 cm^{-1} is due to, but the fact that the lowest frequency was obtained when $^{15}N^{14}N^{16}O$ was used to prepare the complex, suggests that it may be associated with a ruthenium-nitride bond. This bond could be formed by the cleavage of the nitrogen-nitrogen bond in the nitrogen linked isomer of the nitrous oxide complex. However, if this is correct, then the positions of this vibration from the decomposition of the complexes prepared from $^{14}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ should be closer than is observed.

The *tetrafluoroborate salt* of the labelled nitrous oxide complexes was also observed to have two absorptions in the ν_3 region (Table 4:6). The higher absorption was sharp and shifted as expected on using the labelled nitrous oxide. The lower absorption was broad and did not shift appreciably when the nitrous oxide was labelled. The lower absorption was absent in the unlabelled complex when it was prepared in the larger pressure vessel. However, when the unlabelled complex was prepared in the small pressure vessel both absorptions in the ν_3 region were present indicating that the lower absorption is due to an impurity which only forms in the small

pressure vessel.

TABLE 4:6

Multiple absorptions in the ν_3 region of the tetrafluoroborate salt

isotope	ν_3	ν_3'	ν_{N_2}
$^{14}N^{14}N^{16}O$	2269.8	2145.6	
$^{15}N^{14}N^{16}O$	2246.1	2146.6	2110 (sh)
$^{14}N^{15}N^{16}O$	2228.6	2145.4	2110 (w)

4:5:3. Absorptions between 600-400 cm^{-1}.—

This region could not be calibrated as accurately as the other regions (2500-2000 cm^{-1} and 1250-1100 cm^{-1}) because the absorptions of the water vapour calibrant were not sharp, and as they occured below 400 cm^{-1}, it was necessary to extrapolate up to the absorptions in the complexes. Also the absorptions in the complexes were weak and not very well defined. The observed absorptions are tabulated in Table 4:7.

Co-ordinated nitrous oxide is expected to have a metal-ligand stretch and two bending vibrations below 600 cm^{-1}, and all of these absorptions should show a noticeable shift in the labelled nitrous oxide complexes.

The absorptions between 460-400 cm^{-1} were usually weak and very broad.

They have been assigned as metal-ammonia stretching vibrations as they are very similar to the metal-ammonia vibrations in other penta-ammine-ruthenium(II) complexes.

The absorption between 490-465 cm^{-1} was very sharp when it was present. Its position was shifted in some of the complexes when the nitrous oxide was labelled although there was no definite trend in these shifts. However, as a similar absorption has not been observed in other penta-ammine-ruthenium(II) complexes this absorption may be associated with the co-ordinated nitrous oxide.

The absorption around 600 cm^{-1} is due to the wagging mode of the aquo-ligand in $[RuA_5(OH_2)]X_2$ which is present as an impurity in the complexes (see section 5:4). The other absorptions are probably associated with impurities in the complexes.

4:5:4. Absorptions between 350-250 cm^{-1}.—

It was not possible to measure accurately the absorptions in this region of the spectrum because they were in the same positions as the absorptions of the water vapour used to calibrate the region. Thus they could not be recorded on the expanded wavenumber scale and so have a larger error than the other absorptions (*e.g.*, ±2 cm^{-1}).

In this region there are two strong absorptions in all the salts except the hexafluorophosphate salt, in which there is only one strong absorption

and a weak shoulder (Table 4:7). The position of the higher frequency absorption was dependent on the anion and the separation of these absorptions decreased in the order:-

$$Cl^- \text{ (unlabelled)} > Br^- > I^- > BF_4^- > PF_6^-$$

In the labelled complexes the absorptions appeared to shift to lower frequencies in some of the salts. However the shifts were very small and so accurate measurements are needed to verify that they are real.

Borodko *et al.*[15] have assigned the absorptions in the osmium dinitrogen complex, $[OsA_5N_2]X_2$ (X = Br, I), down to 90 cm^{-1}. They have assigned an absorption at 300 cm^{-1} as a metal-ammonia stretch (ν_{Os-NH_3}) and one at 270 cm^{-1} as an osmium-ligand deformation, $\delta_{N_2-Os-NH_3}$. In $[RuA_5N_2]Br_2$ the corresponding vibrations were assigned to absorptions at 355 cm^{-1} and 242 cm^{-1} respectively. Below 380 cm^{-1}, $[RuA_4(OH_2)N_2]Cl_2$ has been observed[16] to have absorptions at 306, 284(sh) and 258 cm^{-1}. Thus, these are assigned as ν_{Ru-NH_3} (306 cm^{-1}) and $\delta_{N_2-Ru-NH_3}$ (284(sh) and 258 cm^{-1}).

The solid obtained from the attempted preparation of the chloride salt of the nitrous oxide complex, $[RuA_5(N_2O)]Cl_2$, had absorptions at 340, 306, 284(sh) and 258 cm^{-1} in this region. However as the complex was always heavily contaminated with $[RuA_4(OH_2)N_2]Cl_2$, the absorptions at 306, 284 and 258 cm^{-1} can be associated with the dinitrogen complex and that at 340 cm^{-1} with the nitrous oxide complex. In the other nitrous oxide complexes there were two absorptions in this region at 336-308 cm^{-1} and 305-301 cm^{-1}. The

higher absorption was strongly dependent on the anion but the lower absorption was almost the same in all the complexes. Based on the assignments of Borodko *et al.*[15] for dinitrogen complexes, the lower absorption in this region is assigned as a metal-ammonia stretch. The higher absorption corresponds to the absorption at 340 cm^{-1} in the chloride salt and so may be associated with the co-ordinated nitrous oxide. The highest frequency for this absorption is observed in the chloride salt and the lowest in the hexafluorophosphate salt which is the opposite anion sequence to that observed for the ν_3 and ν_1 absorptions of the co-ordinated nitrous oxide. The interaction of the anion in the complexes results in a weakening of the nitrogen-oxygen and nitrogen-nitrogen bonds in the co-ordinated nitrous oxide and so ν_3 and ν_1 decrease as this interaction increases. However it is expected to increase the metal-ligand bond strength and so a stretching vibration associated with this bond would be expected to increase as the size of the anion decreases. Hence, the absorption between 340-308 cm^{-1} in the complexes is assigned as the metal-ligand stretch, ν_{Ru-N_2O}. Further evidence for this assignment was obtained from the normal co-ordinate analysis of the infrared spectra (section 4:6:2).

4:5:5. Conclusion.—

The infrared spectra of the isotopically labelled nitrous oxide complexes have given further evidence that nitrous oxide is present in the complexes. They have confirmed that the absorptions corresponding to the ν_3 and ν_1 fundamentals of nitrous oxide have been correctly assigned, and

indicate that there are two absorptions below 600 cm^{-1} which can also be associated with the co-ordinated nitrous oxide. All the other absorptions below 600 cm^{-1} (which could not be assigned in the unlabelled nitrous oxide complexes) have now been assigned.

In the spectra of the hexafluorophosphate salt, two absorptions were always observed in the ν_3 region. On using labelled nitrous oxide, their shifts suggested that both were associated with co-ordinated nitrous oxide. The decomposition of the complex associated with the lower absorption indicated that it may be the nitrogen linked isomer, and as the higher absorption fitted into a sequence with the ν_3 absorptions of the other salts, it is suggested that the nitrous oxide is co-ordinated through the oxygen atom in the other complexes.

To gain further insight on how the nitrous oxide was co-ordinated, it was decided to prepare the labelled dinitrogen complexes by reducing the labelled nitrous oxide complex as it was formed. The nitrogen-nitrogen stretch of the dinitrogen complex had been observed in some of the nitrous oxide complexes as an impurity but the metal-dinitrogen stretch had not been observed.

However, before this could be attempted, Armor and Taube[17] reported the isolation of the labelled dinitrogen complexes, $[RuA_5(^{15}N^{14}N)]Br_2$ and $[RuA_5(^{14}N^{15}N)]Br_2$, by the reduction of the nitrous oxide complex from the reaction of $[RuA_5(OH_2)]^{2+}$ and the appropriately labelled nitrous oxide.

From the shifts in the absorption around 500 cm^{-1} in the products (assigned as the metal-dinitrogen stretch[8]) they concluded that the nitrous oxide was co-ordinated to the ruthenium through the *exo* nitrogen atom.

As this was contrary to the tentative conclusion which had been made from the labelled nitrous oxide complexes, a normal co-ordinate analysis of the infrared spectra was made.

4:6. Normal Co-ordinate Analysis of the Infrared Spectra.—

Normal co-ordinate analyses of infrared spectra have been reported for several transition metal complexes.[18] The accuracy of the calculated force constants depends on how many interactions are considered. The greater the number of interaction constants that can be considered (*e.g.*, ligand-ligand, metal-ligand and intraligand if they occur), the more accurate will be the valence bond force constants. One of the difficulties in these calculations is that a rigorous treatment usually involves too many unknown force constants and not enough known frequencies. Isotopically labelled complexes are usually prepared to give more known frequencies but even so, there is usually insufficient information to solve the equations and check the results. Hence approximations have to be made in the calculations.

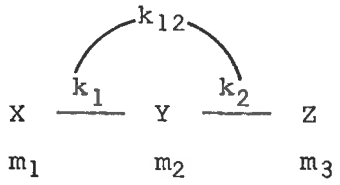
Generally, the method of Wilson, Decius and Cross[19] is used for these calculations. However, as only the force constants associated with the co-ordinated nitrous oxide were required to indicate how the nitrous oxide is co-ordinated in the complexes, simple models were chosen for the

complexes and the calculations were made using the method of Herzberg.[6] This method is given in Appendix I and the calculations for the two models which were used, linear XYZ and linear XYZW, are given in Appendix II.

4:6:1. Linear XYZ Model.—

The first calculations were made assuming that the nitrous oxide was only slightly perturbed on co-ordination so that it could still be considered as "free" nitrous oxide.

These calculations were made using the model,



where the masses of the atoms, the force constants of the bonds, k_1 and k_2, and the interaction constant, k_{12}, are as shown. The secular equation for this model and its solution are given in Appendix II. The relationships between the two stretching frequencies were found to be:-

$$\lambda_1 + \lambda_3 = 4\pi^2(\nu_1^2 + \nu_3^2) = k_1\left(\frac{m_1 + m_2}{m_1 \cdot m_2}\right) + k_2\left(\frac{m_2 + m_3}{m_2 \cdot m_3}\right) - \frac{2k_{12}}{m_2} \qquad 1$$

$$\text{and } \lambda_1\lambda_3 = 16\pi^4\nu_1^2\nu_3^2 = \frac{m_1 + m_2 + m_3}{m_1 \cdot m_2 \cdot m_3}(k_1k_2 - k_{12}^2) \qquad 2$$

For nitrous oxide, X and Y are the nitrogen atoms and Z is the oxygen atom so that k_1 is the nitrogen-nitrogen force constant (k_{NN}) and k_2 is the

nitrogen-oxygen force constant (k_{NO}).

The interaction constant of gaseous nitrous oxide[20] (1.36×10^5 dyne cm^{-1}) was used for k_{12}, and values for the two frequencies, ν_3 and ν_1, were calculated for numerous combinations of the other two force constants using the program F CONST (Appendix III). The force constants which gave the best agreement with the observed frequencies are given in Table 4:8.

Even with this simple model, the force constants are almost independent of the position of the labelled nitrogen atom in the model. The calculations for all the salts, gave k_{NN} in the range $(19.4_5 - 19.8_1) \times 10^5$ dyne cm^{-1} and k_{NO} in the range $(8.6_9 - 9.8_0) \times 10^5$ dyne cm^{-1}. These may be compared with the values,[20] $k_{NN} = 17.8_8 \times 10^5$ dyne cm^{-1} and $k_{NO} = 11.3_9 \times 10^5$ dyne cm^{-1}, calculated for gaseous nitrous oxide from its observed frequencies, without correcting for anharmonicity.

Calculations were made to find how variation of the three force constants affected the postion of the two stretching vibrations in the nitrous oxide. The frequencies calculated when two of the force constants were kept constant and the third was changed are tabulated in Table 4:9. A change in k_{NN} has a much greater effect on ν_3 than it does on ν_1 ($\Delta\nu_3 = 6.8\ \Delta\nu_1$) while a change in k_{NO} has a similar effect on the position of both ν_3 and ν_1 ($\Delta\nu_1 = 1.5\ \Delta\nu_3$). The interaction constant does not affect the frequencies as much as k_{NN} and k_{NO}. A 100% increase in the interaction constant gives less than a 3% change in the stretching frequencies ν_1 and

ν_3 (increasing the interaction constant increases the frequency of ν_1 but decreases the frequency of ν_3).

In the hexafluorophosphate salt, in which the effect of the anion is the smallest, the shifts of ν_3 and ν_1 from their frequencies in gaseous nitrous oxide[13] were +66 and -64 cm^{-1} respectively. The results in Table 4:9 indicate that these shifts are consistent with an increase in k_{NN} and a decrease in k_{NO}, as an increase in k_{NN} will increase the frequency of ν_3 much more than ν_1, while a decrease in k_{NO} will produce a similar lowering in the frequencies of both ν_1 and ν_3 thus giving the observed shifts.

In the other salts the anion interaction with the complex cation will affect the strength of the bonds in the nitrous oxide. This interaction is expected to weaken both bonds, the greatest effect being produced by the smallest anion. Thus, when the complexes are considered in the order; hexafluorophosphate, tetrafluoroborate, iodide, bromide, the force constants, k_{NO} and k_{NN}, should become smaller. The force constants calculated from the observed frequencies (Table 4:8) show that k_{NN} and k_{NO} do depend on the anion in this way, and indicate that k_{NO} is affected by the anion more than k_{NN} is.

Using this model for co-ordinated nitrous oxide it has been found that, on co-ordination, the strength of the nitrogen-nitrogen bond is increased while that of the nitrogen-oxygen bond is decreased. Both bonds were affected by the anion as it became smaller, the nitrogen-oxygen bond being weakened much more than the nitrogen-nitrogen bond. As the nitrogen-

nitrogen bond would be expected to be weakened if the nitrous oxide were co-ordinated through the *exo* nitrogen atom, these results suggest that the nitrous oxide may be co-ordinated through the oxygen atom.

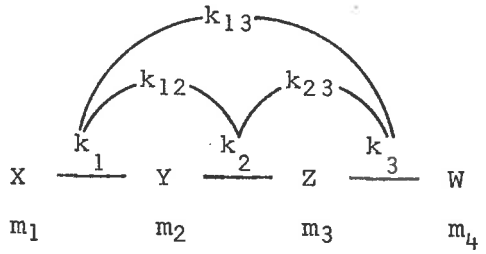
As this model did not consider the effect of the metal, and in particular the metal-ligand bond, another model was chosen to confirm whether or not the nitrous oxide was co-ordinated through the oxygen atom.

4:6:2. Linear XYZW model.—

The second model chosen for co-ordinated nitrous oxide in the complexes was linear XYZW. In this model XYZ represents the co-ordinated nitrous oxide and W the metal atom and the five ammonia groups. A linear system was chosen because the powder photograph of $[RuA_5(N_2O)]Br_2$ (section 3:12) indicated that the nitrous oxide was co-ordinated linearly. General expressions for the model were derived (Appendix II) so that calculations for the nitrous oxide co-ordinated through the oxygen atom or the *exo* nitrogen atom could be made.

Linear four atom systems have three stretching vibrations and two doubly degenerate bending vibrations.[6] Here the stretching vibrations will be designated ν_1, ν_3 and ν_4 and the bending vibrations ν_2 and ν_5 such that ν_1, ν_2 and ν_3 correspond to the fundamentals ν_1, ν_2 and ν_3 of nitrous oxide. The other vibrations (ν_4 and ν_5) correspond to the metal-nitrous oxide stretch and bend respectively.

The expressions involving the three stretching vibrations were determined using the model



where the force constants for the bonds (k_1, k_2 and k_3) and the interaction constants between the bonds are as shown.

The relations between the stretching frequencies were found to be:-

$$\lambda_1 + \lambda_3 + \lambda_4 = k_1\left(\frac{m_1 + m_2}{m_1 \cdot m_2}\right) + k_2\left(\frac{m_2 + m_3}{m_2 \cdot m_3}\right) + k_3\left(\frac{m_3 + m_4}{m_3 \cdot m_4}\right)$$

$$- 2k_{12}\left(\frac{1}{m_2}\right) - 2k_{23}\left(\frac{1}{m_3}\right) - 2k_{13}(0) \qquad 3$$

$$\lambda_1\lambda_4 + \lambda_3\lambda_4 + \lambda_1\lambda_3 = \frac{m_1 + m_2 + m_3}{m_1 \cdot m_2 \cdot m_3}(k_1k_2 - k_{12}^2) + \frac{m_2 + m_3 + m_4}{m_2 \cdot m_3 \cdot m_4}(k_2k_3 - k_{23}^2)$$

$$+ \frac{(m_1 + m_2)(m_3 + m_4)}{m_1 \cdot m_2 \cdot m_3 \cdot m_4}(k_1k_3 - k_{13}^2) + \frac{2}{m_3}\left(\frac{m_1 + m_2}{m_1 \cdot m_2}\right)(k_{13}k_{12} - k_1k_{23})$$

$$+ \frac{2}{m_2}\left(\frac{m_3 + m_4}{m_3 \cdot m_4}\right)(k_{13}k_{23} - k_3k_{12}) + \frac{2}{m_2 \cdot m_3}(k_{12}k_{23} - k_2k_{13}) \qquad 4$$

and

$$\lambda_1\lambda_3\lambda_4 = \frac{m_1 + m_2 + m_3 + m_4}{m_1 \cdot m_2 \cdot m_3 \cdot m_4}(k_1k_2k_3 + 2k_{12}k_{23}k_{13} - k_1k_{23}^2 - k_2k_{13}^2 - k_3k_{12}^2) \qquad 5$$

where $\lambda_i = 4\pi^2\nu_i^2$ and ν_1 and ν_3 are essentially the stretching frequencies of the nitrous oxide, and ν_4 is the metal-nitrous oxide stretching frequency.

In the initial calculations of the force constants k_1, k_2 and k_3, the interaction constants used were $k_{12} = 1.36 \times 10^5$ dyne cm^{-1} and $k_{23} = k_{13} = 0$. This value of k_{12} was chosen because it had given similar force constants in the isotopically labelled molecules when XYZ was used as the model. The calculations were made by substituting the observed frequencies, ν_3 and ν_1, for the labelled and unlabelled complexes into equation 3 and solving the simultaneous equations for k_1, k_2 and k_3. As ν_4 was not known, this was set to zero initially. The calculated force constants were substituted into equation 5 to calculate ν_4 for each isotope, and this calculated frequency was then used to recalculate the force constants. The cycle was repeated until there was no change in the force constants. These calculations were made using the program K AND V (Appendix III).

The force constants were calculated for both oxygen and nitrogen co-ordination of the nitrous oxide and the results are given in Table 4:10. These calculations have been made using a mass of 101 for W (*i.e.* ignoring the ammonia groups on the metal atom). However, in the complex the motion of the ruthenium atom will be influenced by the ammonia groups as well as by the nitrous oxide. This effect can be incorporated into the model by using a larger mass for W. (*i.e.* increasing the effective mass of the ruthenium atom.) If the ammonia groups are considered to be localised at

the position of the ruthenium atom then W will have a mass of 186. Calculations have been made using this mass for W and the results are tabulated in Table 4:11. The results in Tables 4:10 and 4:11 show that this mass change has little effect on the calculated force constants for each mode of co-ordination by the nitrous oxide. Actually the effective mass of the ruthenium atom will be between 101 and 186 but these values will be used in the calculations to give the extreme values for the calculated force constants.

When the complexes are considered in the order; bromide, iodide, tetrafluoroborate, hexafluorophosphate, the ligand force constants (k_{NO} and k_{NN}) are expected to increase due to the interaction of the anion with the complex cation. The force constants calculated for nitrous oxide co-ordinated through the *exo* nitrogen atom were found to vary a great deal with the anion and although the force constant for the nitrogen-nitrogen bond (k_2) did increase when the complexes were considered in the anion sequence above, the force constant for the nitrogen-oxygen bond decreased. Calculations for the nitrous oxide co-ordinated through the oxygen atom gave force constants for the nitrogen-nitrogen bond which were almost unaffected by the anion whereas those for the nitrogen-oxygen bond (k_2) increased, as expected, when the complexes were considered in the anion sequence above.

For nitrous oxide co-ordinated through the *exo* nitrogen atom, the calculated force constant for the nitrogen-oxygen bond was similar to

(hexafluorophosphate salt) or higher than the force constant of the nitrogen-nitrogen bond. In gaseous nitrous oxide, k_{NN} is greater than k_{NO},[20] and although co-ordination would be expected to affect the force constants of the bonds in the nitrous oxide, it is unlikely that the nitrogen-oxygen bond would be strengthened as much as is indicated by the calculations for the nitrogen linked nitrous oxide. The force constants calculated for nitrous oxide co-ordinated through the oxygen atom suggest that the nitrogen-nitrogen bond is slightly strengthened and the nitrogen-oxygen bond is weakened on co-ordination of the nitrous oxide. The changes in the force constants for the oxygen bonded nitrous oxide are more acceptable than those for the nitrogen bonded isomer and thus it is concluded that, in the complexes, the nitrous oxide is co-ordinated through the oxygen atom.

The ν_3 absorptions in the bromide salts were very weak and broad and it was difficult to find their peak maxima. An incorrect frequency for one of these absorptions may be why the force constants, k_{NN} and k_{NO}, for this salt appear to be in error. For example, the force constant for the nitrogen-nitrogen bond, calculated for co-ordination through the oxygen atom, differs from that in the other salts in which it is almost constant, and the force constant for the nitrogen-oxygen bond appears to be too high. For nitrous oxide co-ordinated through the *exo* nitrogen atom, the value calculated for k_{NN} appears to be higher than expected from its values in the other salts, while k_{NO} is lower than expected.

The final values of ν_4, calculated from the force constants, are tabulated in Table 4:12. The position of this frequency was very dependent on the anion and varied over the range 690-420 cm^{-1} which was much more than was expected. Hence, the calculations were checked by using the calculated force constants to obtain the stretching frequencies for the co-ordinated nitrous oxide.

This was achieved by solving the cubic equation;

$$\lambda^3 - \lambda^2(\text{R.H.S. equation 3}) + \lambda(\text{R.H.S. equation 4}) - (\text{R.H.S. equation 5}) = 0$$

Equation 4 was not required to calculate the force constants so the frequencies obtained by solving the cubic equation will be near the observed frequencies for the salts only if the calculated force constants satisfy equation 4. The coefficients were evaluated and the cubic equation was solved by the root squaring method of Dandelin, Lobachevsky and Graeffe[21] using the program CUBIC (Appendix III).

The frequencies which were calculated for the tetrafluoroborate salt are given in Table 4:13. Unfortunately there is not very close agreement between the calculated frequencies and the observed frequencies used in the calculations. The calculated frequencies are too low for ν_3 but too high for ν_1. The agreement is closer for nitrous oxide co-ordinated through the oxygen atom than for nitrous oxide co-ordinated through the nitrogen atom. However, some disagreement between the calculated and observed frequencies

would be expected because there are several factors which have not been considered in the calculations.

As previously mentioned, the effective mass of the ruthenium atom is not known. Also this model neglects any interactions between the co-ordinated nitrous oxide and the ammonia ligands. These two effects are expected to be small and should not influence the results very much.

Probably the main reason for the disagreement between the calculated and the observed frequencies are the small differences which are generated in the calculations. Small errors in the values used for the observed frequencies will result in larger errors in these differences and hence in the calculated force constants and frequencies. Thus the calculated frequencies will differ from the observed frequencies. The errors in the observed frequencies not only arise in measuring the position of the absorption but also arise because anharmonicity effects cannot be corrected for. The mathematical analysis[6] assumes that the system undergoes simple harmonic motion and so corrections for anharmonicity are necessary if complete agreement between observed and calculated frequencies is to be obtained. Corrections for anharmonicity are made from the overtone and combination bands in the spectrum. However in the complexes this correction was not possible because only one overtone ($2\nu_1$) was present, and even this was not observed in all the complexes.

The interaction constants used in the calculations are another reason

why the calculated and observed frequencies are not in closer agreement. The value chosen for k_{12} (1.36×10^5 dyne cm^{-1}) is probably too high, while setting the other two interaction constants (k_{23} and k_{13}) to zero is ignoring interactions which exist (although k_{13} will be very small). In an attempt to obtain better agreement between the observed and calculated frequencies the force constants and interaction constants were varied to see how they affected the calculated frequencies.

Jones *et al.*[22] have calculated the force constants of tetracarbonylnickel(0) from its infrared spectrum. The calculated force constants were:-

$$k_{CO} = 17.85 \times 10^5 \text{ dyne cm}^{-1}$$

$$k_{NiC} = 2.08 \times 10^5 \text{ dyne cm}^{-1}$$

and $$k_{interaction} = 0.52 \times 10^5 \text{ dyne cm}^{-1}$$

As the bonding of nitrous oxide and carbon monoxide in their complexes is similar, it may be expected that the metal-ligand force constant and the metal-ligand interaction constant in the nitrous oxide complex would be of similar magnitude to the corresponding force constants in tetracarbonylnickel(0). The calculated metal-ligand force constants (k_3) in Tables 4:10 and 4:11 are much higher than the corresponding force constant, k_{NiC}, obtained by Jones *et al.*[22] for the carbonyl complex and so calculations were carried out, using the program CUBIC, for various values of k_{NN} and k_{NO} with k_{RuO} between 1-3 $\times 10^5$ dyne cm^{-1}. The calculated frequencies for oxygen co-ordination are tabulated in Table 4:14. Calculations were also made for

various combinations of the interaction constants k_{12} and k_{23} (k_{13} was considered to be small enough to be neglected, *i.e.* $k_{13} = 0$). Using the frequencies for the tetrafluoroborate salt, the force constants (program K AND V) and then the frequencies (program CUBIC) were calculated and the results are tabulated in Table 4:15.

The frequencies in Table 4:14 show that when a smaller metal-ligand force constant is used the values for ν_1 are better but those for ν_3 are still too low. For k_{RuO} in the range 1-3 × 10^5 dyne cm^{-1}, the calculations indicate that k_{NN} is probably greater than 18.5 × 10^5 dyne cm^{-1} while k_{NO} is around 8.5 × 10^5 dyne cm^{-1}. These calculations were made with k_{12} = 1.36 × 10^5 dyne cm^{-1} and $k_{23} = k_{13} = 0$.

The position of ν_4, the third stretching vibration in the system, is around 300 cm^{-1} in these calculations. In the complexes there was an absorption at 340-308 cm^{-1} which was assigned to the co-ordinated nitrous oxide. Thus, the positions of ν_4 for the isotopically labelled complexes were calculated to see how great a shift would be expected in a stretching vibration around 300 cm^{-1}. The results in Table 4:16 show that there is a shift of about 3 cm^{-1}, to a lower frequency, and that the frequency is independent of the position of the label. Although accurate shifts could not be obtained for the two absorptions around 300 cm^{-1} in the complexes, the higher frequency absorption probably is the metal-ligand stretching vibration. The frequency of this vibration was observed to depend on the anion in the complexes and the shifts produced by the anion are consistent

with the vibration being the metal-ligand stretch of the co-ordinated nitrous oxide (see section 4:5:4). Therefore, the other absorption between 490-465 cm^{-1}, associated with the co-ordinated nitrous oxide, must be a bending vibration because all the stretching vibrations have now been assigned. This bending vibration is either the one corresponding to the ν_2 fundamental of nitrous oxide or the metal-ligand bending vibration. The ν_2 fundamental of nitrous oxide is observed at 589 cm^{-1}, and so it may be expected to be near this position in the complexes. However, the metal-ligand bending vibration may also be in this region. In carbonyl complexes the metal-ligand bending vibration, δ_{M-C-O}, is observed at a higher frequency than the metal-ligand stretching vibration, ν_{M-C},[18,23] and in the dinitrogen complexes the metal-ligand bending vibration occurs around 500 cm^{-1} (see section 4:7). Although shifts in the position of this absorption were observed when labelled nitrous oxide was used, they are too small to be meaningful and so it is not possible to assign the vibration between 490-465 cm^{-1} in the complexes to one or other of the two possibilities.

When the interaction constants were varied (Table 4:15) it was found that better agreement between the calculated and the observed frequencies was obtained when the interaction constants were small. Increasing the ligand interaction constant (k_{12}) increased k_{NO}, decreased k_{RuO} but k_{NN} did not change greatly. Both ν_3 and ν_1 calculated for these force constants deviated further from the observed frequencies as the interaction constant was increased (ν_3 became lower while ν_1 became higher). Changes in the

metal-ligand interaction constant (k_{23}) influenced k_{RuO} but did not affect k_{NO} or k_{NN} greatly. Consequently, the frequency ν_4, but not ν_3 or ν_1, was affected by a change in this interaction constant.

4:6:3. Conclusion.—

Although it has not been possible to obtain accurate force constants for the co-ordinated nitrous oxide, the normal co-ordinate analysis has proved that the nitrous oxide is co-ordinated through its oxygen atom in these complexes. The force constants calculated for nitrous oxide co-ordinated through the *exo* nitrogen atom were very erratic and the force constant of the nitrogen-oxygen bond was greater than the force constant of the nitrogen-nitrogen bond. Also the effect of the anion on the force constant of the nitrogen-oxygen bond was the opposite to that expected, whereas the force constants calculated for nitrous oxide co-ordinated through the oxygen atom indicate that on co-ordination, the nitrogen-nitrogen bond is strengthened slightly while the nitrogen-oxygen bond is weakened. From these calculated force constants it was concluded that the nitrous oxide was co-ordinated through its oxygen atom in the complexes. Approximate force constants for the co-ordinated nitrous oxide are:-

$$k_{NN} > 18.5 \times 10^5 \text{ dyne cm}^{-1}$$
$$k_{NO} = 8.5 \times 10^5 \text{ dyne cm}^{-1}$$
$$k_{RuO} = 2.5 \times 10^5 \text{ dyne cm}^{-1}$$

and the ligand and metal-ligand interaction constants are probably less than

0.5×10^5 dyne cm^{-1}.

These values could be improved by further trial and error calculations using the XYZW model. However, as the model is very simple, there is probably a limit to how close the agreement between the calculated and observed frequencies can be.

There are now many modifications of the original F and G matrix method of Wilson, Decius and Cross,[19] and Diamantis[24] proposes to use the one developed by Beattie *et al.*[25] to confirm these calculations and obtain more accurate force constants for the complex.

The calculations have also indicated that the metal-ligand stretching frequency (ν_4) is the higher frequency absorption around 300 cm^{-1} and that the other nitrous oxide absorption between 490-465 cm^{-1} is one of the bending vibrations but it is not possible to indicate which one. Confirmation of these assignments may be obtained by preparing the complexes containing oxygen 18 labelled nitrous oxide.

4:7. Infrared Spectra of Isotopically Labelled Dinitrogen Complexes.—

In most of the infrared spectra of the labelled nitrous oxide complexes, the nitrogen-nitrogen stretch of the dinitrogen complex was observed as an impurity. It was planned to prepare the isotopically labelled dinitrogen complexes to measure the position of the remaining nitrogen-nitrogen stretches and to see if there were any shifts in the absorption around

500 cm^{-1}, which has been assigned as the metal-dinitrogen stretch,[8] because these absorptions were expected to give more information on how the nitrous oxide was co-ordinated to the ruthenium.

However, before this could be attempted, Armor and Taube[17] reported the isolation of the labelled complexes, $[RuA_5(^{15}N^{14}N)]Br_2$ and $[RuA_5(^{14}N^{15}N)]Br_2$. The complexes were prepared by the chromium(II) reduction of the labelled nitrous oxide complex, which was generated *in situ* by the reaction of $[RuA_5(OH_2)]^{2+}$ with labelled nitrous oxide. The position of the absorption assigned as the ruthenium-dinitrogen stretch was measured and found to shift when labelled nitrous oxide was used. The frequencies observed were $507._7$, $493._4$ and $500._6$ cm^{-1} when $^{14}N^{14}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ respectively, were used. Assuming that isotopic substitution in the *endo* position of the co-ordinated dinitrogen would produce a greater shift in this stretching vibration than substitution in the *exo* position, Armor and Taube concluded that the nitrous oxide became co-ordinated to the ruthenium atom through its *exo* nitrogen atom.

4:7:1. Reassignment of ν_{Ru-N_2}.—

The position of the metal-nitrous oxide stretch (ν_4) in the nitrous oxide complexes, calculated using XYZW as the model for the complex, (Table 4:12) was almost unaffected by the position of the labelled nitrogen atom in the complex. However, as Armor and Taube observed that the position of the metal-dinitrogen stretch in the labelled dinitrogen complexes did depend

on the position of the labelled nitrogen atom, the shifts from 507.7 cm^{-1} were calculated for a stretching and a bending vibration to see how they compared with the observed shifts. The calculations were made using linear XYZ as the model for the dinitrogen complex. (YZ represents the co-ordinated dinitrogen and X the rest of the complex.)

For a *stretching vibration* the calculations were made using equation 6

$$16\pi^4\nu_1^2\nu_3^2 = \frac{m_X + m_Y + m_Z}{m_X \cdot m_Y \cdot m_Z}(k_1k_2) \qquad 6$$

which is equation 2 with $k_{12} = 0$. The interaction constant, k_{12}, will be small in the RuNN system, so this approximation will be satisfactory. In this case, ν_3 for the linear three atom system corresponds to ν_{N_2}, and ν_1 is the stretching frequency to be calculated (ν_{Ru-N_2}). The force constants in equation 6 were eliminated by taking the ratio of the expressions for the labelled and unlabelled complexes. Using the observed frequencies for ν_{N_2}, ν_1 for the labelled complex was calculated using 507.7 cm^{-1} for ν_1 of the unlabelled complex. The ν_{N_2} frequencies used were those measured for the dinitrogen complex which was observed as an impurity in the bromide salt of the nitrous oxide complex.

The shifts for a *bending vibration* were calculated using the expression derived by Herzberg for a linear XYZ molecule.[6]

$$4\pi^2\nu_2^2 = \frac{1}{l_1^2 l_2^2}\left(\frac{l_1^2}{m_Z} + \frac{l_2^2}{m_X} + \frac{(l_1 + l_2)^2}{m_Y}\right)k_\delta \qquad 7$$

where l_1 and l_2 are the distances of X and Z, respectively, from Y, and k_δ

is the deformation force constant. Calculations were made using the ruthenium-nitrogen (l_1) and nitrogen-nitrogen (l_2) bond lengths reported by Bottomley and Nyburg for $[RuA_5N_2]Cl_2$.[11] The force constant was eliminated by taking the ratio of the expressions for the labelled and unlabelled complexes, and the bending frequency for the labelled complexes was calculated using ν_2 in the unlabelled complex as 507.7 cm^{-1}. The results of the calculations are tabulated in Table 4:17.

The calculations have been made using an effective mass of 101 and 186 for the ruthenium atom, but this did not affect the calculated frequencies greatly. The shifts calculated for a bending vibration are much closer to those observed by Armor and Taube than the shifts calculated for a stretching vibration, suggesting that the vibration is not a stretching vibration but a bending vibration.

Jones *et al.*[22] have recorded the ν_6 and ν_7 absorptions of tetracarbonylnickel(0). These are essentially the metal-carbon-oxygen bend and the metal-carbon stretch, respectively. In the complexes labelled with either carbon 13 or oxygen 18, ν_6 showed similar shifts to those observed by Armor and Taube in the dinitrogen complexes, while ν_7, although being shifted to a lower frequency, was unaffected by the position of the labelled atom (Table 4:18). The bending vibration of nitrous oxide (ν_2) also shows similar shifts to those observed in the dinitrogen complexes (Table 4:18). This is further evidence that the absorption at 500 cm^{-1} in the dinitrogen

complex is a bending vibration and not a stretching vibration as it has been assigned.[8]

Borodko *et al.*[15] have made a detailed study of the infrared spectrum of the osmium dinitrogen complex, $[OsA_5N_2]Br_2$. They observed that the absorption at 515.5 cm^{-1} was shifted to 501.5 cm^{-1} in the complex containing heavy dinitrogen, $^{15}N^{15}N$. A similar shift was observed for the chloride salt. This absorption was assigned as the osmium-dinitrogen stretching vibration. This assignment was claimed to be supported by the fact that the product rule was satisfied by the frequencies of the complexes.

As the absorption around 500 cm^{-1} in the dinitrogen complex, $[RuA_5N_2]Br_2$, was shown above to be due to a bending vibration and not a stretching vibration, calculations were made to see if the absorption at 515.5 cm^{-1} in the osmium-dinitrogen complex was also a bending vibration. When the calculations were made assuming that this was a bending vibration, the calculated frequency was found to be similar to the frequency observed in the complex (Table 4:19). Because the bond lengths in $[OsA_5N_2]Br_2$ have not been determined, the bond lengths in $[RuA_5N_2]Cl_2$[11] were used in the calculations. Also 2.21 Å was used for the metal-ligand bond (l_1) to see how this bond length affected the calculated frequencies (0.1 Å appears to be an upper limit for the difference in bond lengths between ruthenium and osmium complexes). Thus, with both the nitrogen atoms labelled, it is not possible to distinguish between a stretching and a bending mode for the absorption at 515.5 cm^{-1}. Hence, it appears that complexes with only one

labelled nitrogen atom are required to determine what type of vibration it is in the osmium-dinitrogen complex. However, by comparison with the corresponding ruthenium dinitrogen complex, it is probably the metal-ligand bending mode.

Norman[14] has observed that the shifts in the absorption around 500 cm^{-1} in $[RuA_4(OH_2)N_2]Cl_2$ are similar to those observed by Armor and Taube in the penta-ammine-dinitrogen complex when the dinitrogen is labelled. The calculated shifts for bending and stretching absorptions in the tetra-ammine complex (using the bond lengths of the penta-ammine complex[11]) also indicate that this absorption is a bending vibration (Table 4:20).

4:7:2. Conclusion.—

It appears that in the ruthenium-ammine-dinitrogen complexes, and perhaps the corresponding osmium complexes, the absorption around 500 cm^{-1} has been incorrectly assigned as the metal-dinitrogen stretch and that it is the bending vibration associated with the co-ordinated dinitrogen, δ_{Ru-N-N}. By comparison with the carbonyl complexes, the ruthenium-dinitrogen stretch is probably below 500 cm^{-1}. However, no other absorptions below 600 cm^{-1} have been reported to be affected by labelling the complexes.

Thus, it would have been worthwhile to prepare other salts containing labelled dinitrogen to confirm that they all showed similar shifts in their absorption around 500 cm^{-1} and to see whether the metal-dinitrogen stretch could be observed. However, there was insufficient time to attempt these

preparations.

Even though the absorption around 500 cm^{-1} in the dinitrogen complexes has been reassigned as a bending vibration, its shifts in the bromide salt prepared from the isotopically labelled nitrous oxide are still consistent with the *exo* nitrogen atom of the nitrous oxide being co-ordinated to the ruthenium atom before it is reduced to co-ordinated dinitrogen.

4:8. Interpretation of the Labelling Experiments.—

The calculations for the nitrous oxide complexes have indicated that the nitrous oxide is co-ordinated to the ruthenium atom through its oxygen atom. However the results of Armor and Taube[17] suggest that in the preparation of the dinitrogen complexes the nitrous oxide is co-ordinated through the *exo* nitrogen atom before it is reduced.

The dinitrogen complexes could not have formed by a reaction with gaseous dinitrogen in the solution because then the label would be expected to be randomly distributed between both positions. Also it has been found (section 2:5:2) that no free dinitrogen is formed in the solution during the reduction of the nitrous oxide complex.

Both terminal atoms of nitrous oxide are potentially good donor atoms. In the hexafluorophosphate salt of the nitrous oxide complex there was evidence from its infrared spectrum between 2000-2200 cm^{-1} that both the oxygen and nitrogen linked isomers were present. Thus both these isomers

must be present in solution during the preparations, and as the complex is in equilibrium with $[RuA_5(OH_2)]^{2+}$ and nitrous oxide,[26] an equilibrium will also be established between the two linkage isomers. The concentration of each isomer in solution will depend on the strength of its metal-nitrous oxide bond. The isomer with the stronger bond will have the higher concentration in solution.

In the presence of a reducing agent the nitrogen linked isomer should be reduced more rapidly than the oxygen linked isomer because the nitrogen-oxygen bond, which is broken, is easily accessible to the reducing agent, whereas in the oxygen linked isomer this bond is protected by the ammonia ligands of the complex. Reduction of the nitrogen linked isomer would result in the dinitrogen complex with the *exo* nitrogen atom of the nitrous oxide becoming the *endo* nitrogen atom of the co-ordinated dinitrogen, as was observed by Armor and Taube.[17] Reduction of the oxygen linked isomer would probably give a ruthenium-oxygen complex and free dinitrogen (although formation of the dinitrogen complex was observed during the thermal decomposition of the solid nitrous oxide complex).

As the reduction of the co-ordinated nitrous oxide is very rapid and no free dinitrogen was observed in the reaction solution (section 2:5:2), this suggests that only the nitrogen linked isomer of nitrous oxide is reduced.

In the absence of an external reducing agent, addition of a

precipitating agent to the reaction solution precipitated only the oxygen linked isomer, except when ammonium hexafluorophosphate was used, and then evidence for the nitrogen linked isomer was also observed. The precipitation of only one isomer suggests that it is more insoluble than the other. However, infrared evidence from the hexafluorophosphate salt indicated that the nitrogen linked isomer did not appear to be as stable as the oxygen linked isomer, and so in solution the latter isomer may have a higher concentration, and this could be why it is normally the only isomer isolated. Even so, the oxygen linked isomer was very soluble and good yields were obtained only with large counteranions. Apparently the hexafluorophosphate anion was so efficient that both isomers were precipitated by it.

Hence the results obtained using labelled nitrous oxide are consistent with the presence of both linkage isomers of nitrous oxide, in equilibrium with each other, in solution. In the preparation of the dinitrogen complexes the nitrogen linked isomer is more rapidly reduced than the oxygen linked isomer, whereas addition of a precipitating agent to the solution of the nitrous oxide complex precipitates the oxygen linked isomer. Because these isomers are in equilibrium with each other, both the reactions may proceed to completion even though only one isomer takes part in each reaction.

4:9. Consequences of Linkage Isomers in the Nitrous Oxide Complexes.—

4:9:1. Structure factor calculations.—

The structure factors for the bromide salt of the nitrous oxide complex were calculated assuming that the nitrous oxide was co-ordinated through the *exo* nitrogen atom. That the nitrous oxide is co-ordinated through the oxygen atom will not affect the conclusion made from these calculations because the X-ray scattering properties of the nitrogen and oxygen atoms are so similar that interchanging these atoms in the co-ordinated nitrous oxide would have little effect on the calculated structure factors. Hence the conclusion that the nitrous oxide is linearly co-ordinated still applies.

4:9:2. Electronic absorption spectra.—

The spectrum of $[RuA_5(N_2O)]^{2+}$ reported by Armor and Taube[26] is very similar to that recorded for the solid complex dissolved in 0.1 M methanesulphonic acid except for the extinction coefficient. The extinction coefficient calculated by Armor and Taube is higher.

Earlier (section 3:10) the presence of the dinitrogen complexes in the solution of Armor and Taube[26] was suggested to be the reason for their higher value. Under the equilibrium conditions of Armor and Taube,[26] both linkage isomers of the nitrous oxide complex would be expected to be present, whereas in the solution prepared from the solid, under argon, only the oxygen linked isomer will be present. This is because the nitrous oxide will not recombine with $[RuA_5(OH_2)]^{2+}$ after it has been released from the complex

and so an equilibrium mixture of the linkage isomers will not be formed. Thus, if the extinction coefficient of the nitrogen linked isomer is greater than that of the oxygen linked isomer, then this would account for the difference in the extinction coefficients. Even so, the difference between the extinction coefficients is not very great and they may even be within the experimental errors, which will be larger than normal for an extinction coefficient, because of the way that these extinction coefficients are obtained.

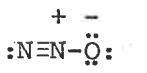
4:9:3. Kinetic results.—

As it is likely that both linkage isomers of co-ordinated nitrous oxide were present when Armor and Taube[26] obtained the rate constant for the decomposition of the nitrous oxide complex, it is surprising that their results and the rate constant for the decomposition of the oxygen linked isomer (section 3:9) gave a good Arrhenius plot. If the rate of decomposition of the nitrogen linked isomer is much faster than that of the oxygen linked isomer then the rate constant measured by Armor and Taube could have been the rate constant for the decomposition of the oxygen linked isomer. If this is the case and the rate of formation of both isomers is similar, then the formation constants reported by Armor and Taube (Table 3:1)[26] would be for the oxygen linked isomer while those for the nitrogen linked isomer would be even smaller. This is consistent with the nitrogen linked isomer being more difficult to isolate than the oxygen linked isomer.

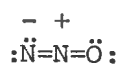
4:10. Bonding in Nitrous Oxide.—

4:10:1. Gaseous nitrous oxide.—

The nitrogen-nitrogen and nitrogen-oxygen bond lengths in nitrous oxide indicate that they have bond orders of approximately 2.5 and 1.5 respectively.[27] In the Valence Bond formulation, nitrous oxide is considered to be a resonance hybrid of structures III and IV.[28]



III



IV

With this formulation, nitrous oxide can be considered to have a lone pair of electrons on both the oxygen atom and the *exo* nitrogen atom, and so should be able to co-ordinate through either atom. However, whether or not these electrons are available for bonding will depend on their energies.

The energy sequence of the molecular orbitals in nitrous oxide has been well established.[29] The highest energy, filled molecular orbitals (2π and 7σ) have only weak bonding properties.[30,31] (The 7σ molecular orbital may even be weakly antibonding.[32]) The 1π molecular orbital is a very strongly bonding orbital.[30] The lowest energy, unfilled molecular orbital is the 3π molecular orbital.

The bonding in nitrous oxide has been discussed in terms of the distribution of the valence electrons into simple delocalised orbitals but this does not give the correct bond orders for the molecule and so localised orbitals have been proposed.[27,33] Green[27] has suggested several ways in

which these localised molecular orbitals may be constructed. From these suggestions the following description of the molecular orbitals in nitrous oxide is proposed. In the 4σ and 5σ molecular orbitals the electrons are considered to be localised on the oxygen and *exo* nitrogen atoms respectively (due to the higher electronegativity of the oxygen atom compared with the nitrogen atom, the orbital involving the oxygen atom is assigned the lower energy). In the 6σ and 7σ molecular orbitals, the electrons are localised mainly along the nitrogen-oxygen and nitrogen-nitrogen bonds respectively. However, in each case there must also be some electron density on the other terminal atom (*i.e.* the nitrogen and oxygen atom respectively). Green[27] has suggested that the filled π molecular orbitals can be combined to give a pair of symmetric orbitals and a pair of asymmetric orbitals, but he does not indicate which pair will be the more stable. In the asymmetric orbitals the electrons are localised on the oxygen atom and in a nitrogen-nitrogen π bond, while the symmetric pair consists of two lopsided equivalent orbitals which extend from the *exo* nitrogen atom to the oxygen atom. A symmetric orbital would be expected to be more stable than an asymmetric orbital but in this case there are electrons localised on the oxygen atom in the asymmetric orbitals which may make them the more stable. However, from the decomposition of nitrous oxide and the nitrous oxide ion (N_2O^+), Coleman *et al.*[34] have concluded that, in the 2π molecular orbital of nitrous oxide, the electrons are localised more on the oxygen end of the molecule than on the nitrogen end. Also, as the 1π molecular orbital is strongly bonding whereas the 2π molecular orbital is almost non bonding,[30] the asymmetric

orbital is assigned as the 2π molecular orbital and the symmetric orbital is assigned as the 1π molecular orbital. In the 3π molecular orbital (the lowest energy, unfilled molecular orbital), the electrons are localised mainly on the central nitrogen atom and it is antibonding toward the nitrogen-nitrogen and nitrogen-oxygen bonds.

4:10:2. Co-ordinated nitrous oxide.—

The infrared spectra of the nitrous oxide complexes are very similar to those of the corresponding dinitrogen and carbonyl complexes (Tables 3:6 and 4:2) indicating that there is back-bonding from the metal to the nitrous oxide in its complexes. That this back-bonding occurs is also indicated by the strength of the ruthenium-nitrous oxide bond which is very similar to that of the ruthenium-dinitrogen bond in the analogous dinitrogen complex (section 3:9). Thus, a bonding scheme for co-ordinated nitrous oxide will have to take into account that both the oxygen and the *exo* nitrogen atoms can co-ordinate, and so an orbital capable of σ-donation to the metal must be available for both of these atoms. Also a π-orbital is required to accept the electrons involved in the bonding from the metal to the ligand.

In nitrous oxide the two molecular orbitals which will be capable of bonding the nitrous oxide to the metal are the 7σ and 3π molecular orbitals. The metal-ligand σ-bond could be formed by donation of electrons from the 7σ molecular orbital while the 3π molecular orbital has an energy which will allow it to accept electrons from the metal and form the π-bond. Although

the electron density of the 7σ molecular orbital is localised mainly along the nitrogen-nitrogen bond, there must also be some electron density on the oxygen atom. Hence, both oxygen and nitrogen linkage isomers of nitrous oxide can be formed with this bonding scheme, and the nitrous oxide will be linearly co-ordinated in both isomers.

In both the linkage isomers, the overlap between the metal d orbitals and the 7σ molecular orbital of nitrous oxide will not be very great. This is because the electron density on the oxygen and *exo* nitrogen atoms is small and also because the 7σ molecular orbital has an energy (-16.38 eV[29]) which is probably too low to give an effective overlap with the orbitals on the metal (it is even lower in energy than the σ-donor orbital of dinitrogen[35]). Consequently, the metal-ligand σ-bond will be weak and this could be the reason for the complexes being so unstable with respect to loss of co-ordinated nitrous oxide.

The calculated force constants for the oxygen linked isomer (Tables 4:10 and 4:11) indicate that on co-ordination of the nitrous oxide, the nitrogen-nitrogen bond is strengthened slightly and the nitrogen-oxygen bond is weakened. These changes indicate that the 7σ molecular orbital is weakly antibonding, so that both bonds are strengthened on σ-donation from this orbital, and that the nitrogen-oxygen bond is weakened much more than the nitrogen-nitrogen bond on back-donation into the 3π molecular orbital. The variation of the calculated force constants with the anion in the complex also supports this latter conclusion. The weakest nitrogen-oxygen bond was

found with the smallest anion, which produces the greatest delocalisation of electrons into the ligand 3π molecular orbital, whereas the strength of the nitrogen-nitrogen bond was not affected much as the anion became smaller. By comparison with the oxygen linked isomer where the bond nearer the metal (*i.e.* the nitrogen-oxygen bond) is weakened more than the other bond, back-bonding into the 3π molecular orbital in the nitrogen linked isomer should weaken the nitrogen-nitrogen bond more than the nitrogen-oxygen bond. Hence the changes in the force constants in the nitrogen linked isomer may be expected to be similar to those observed in the oxygen linked isomer except that the nitrogen-nitrogen bond may be weakened instead of the nitrogen-oxygen bond as the anion becomes smaller.

Although, on energy considerations, the 2π molecular orbital of nitrous oxide corresponds more closely with the metal 4d orbitals than does the 7σ molecular orbital (the energy of 2π molecular orbital is -12.89 eV whereas the energy of 7σ molecular orbital is -16.38 eV[29]), donation of electrons from the 2π molecular orbital to the metal is excluded since the empty metal orbitals all have σ-symmetry.

4:11. Conclusion.—

The work presented here, and that of Armor and Taube, has shown that both linkage isomers of nitrous oxide are formed when nitrous oxide reacts with $[RuA_5(OH_2)]^{2+}$. Although neither isomer is very stable, the oxygen linked isomer appears to be more stable than the nitrogen linked isomer.

Consequently, under the equilibrium conditions in which they are formed, there is probably a higher concentration of the oxygen linked isomer than the nitrogen linked isomer. Hence, on the addition of an excess of a precipitating agent, only the oxygen linked isomer was isolated, except when ammonium hexafluorophosphate was used, and then the nitrogen linked isomer was also precipitated. However, the nitrogen linked isomer is more susceptible to reduction than the oxygen linked isomer and in the presence of an external reducing agent an equilibrium solution of the nitrous oxide complex is reduced quantitatively to the dinitrogen complex, in which the *endo* nitrogen atom is the *exo* nitrogen atom of the nitrous oxide.

Attempts have been made to isolate other ruthenium(II)-ammine complexes containing co-ordinated nitrous oxide. Bellen[36] and Zotti[37] have observed that $[Ru(en)_2(OH_2)_2]^{2+}$ reacts with nitrous oxide in the presence of an external reducing agent to give $[Ru(en)_2(OH_2)N_2]^{2+}$. In the absence of an external reducing agent they observed an absorption around 240 nm which was attributed to $[Ru(en)_2(OH_2)(N_2O)]^{2+}$. However attempts to isolate the nitrous oxide complex, even under forty atmospheres pressure of nitrous oxide, were unsuccessful. Apparently, either the complex is too soluble or its concentration in solution during the reaction is too low, and so no precipitate was obtained.

After the nitrous oxide complexes were first prepared, Bottomley and Crawford[38] reported the isolation of the chloride and iodide salts from the

reaction of hydroxylamine with the nitrosyl complex, $[RuA_5NO]X_3$. The chloride, bromide and iodide salts were also prepared by the reaction of hydrazine hydrate with the nitrosyl complex. However in this reaction the dinitrogen complex, $[RuA_5N_2]X_2$ (X = Cl, Br, I), was also produced.

TABLE 4:21

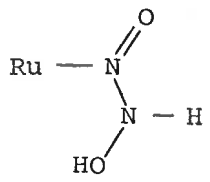
Infrared absorptions of co-ordinated nitrous oxide in the complexes $[RuA_5(N_2O)]X_2$ prepared by Bottomley and Crawford[38]

anion (X)	ν_3 (cm^{-1})	ν_1 (cm^{-1})
chloride	1150	2240
bromide	1160	2260
iodide	1175	2250

The nitrous oxide complex was proposed to form *via* a nucleophilic attack of hydroxylamine or hydrazine on the nitrogen atom of the nitrosyl group and a rearrangement in a manner analogous to the formation of isocyanate complexes from the reaction of hydrazine or azide ion with carbonyl complexes.[39] If this is the case then the nitrogen linked isomer of nitrous oxide would be expected to be isolated. However, the infrared absorptions due to the co-ordinated nitrous oxide in the complexes (Table 4:21) are in good agreement with the corresponding absorptions in the oxygen linked isomer (although the position of the ν_3 absorption for the bromide salt appears to

be too high). If the complexes did contain nitrous oxide linked through the nitrogen atom, then ν_3 would be expected to be lower than 2222 cm^{-1} which is the position of ν_3 in the hexafluorophosphate salt for the nitrogen linked isomer.

The oxygen linked isomer could not have formed by the decomposition of the nitrogen linked isomer, followed by recombination of nitrous oxide and $[RuA_5(OH_2)]^{2+}$ to form an equilibrium mixture of the nitrogen and oxygen linked isomers, because the reaction was carried out in the air and so the ruthenium(II) complex would have been oxidised and the released nitrous oxide would have escaped from the solution. However, the oxygen linked isomer of the nitrous oxide complex could be formed by the migration of the metal to the oxygen atom (and not the nitrogen atom) during the rearrangement of the intermediate, V.



V

The isolation of the oxygen linked isomer from this reaction is further evidence that it is more stable than the nitrogen linked isomer.

Recently, Armor and Taube[40] have isolated another nitrous oxide complex from the reaction of $[RuA_5(OH_2)]^{2+}$ and nitrous oxide (at one or five

atmospheres pressure). This complex was formulated as $[A_5Ru(N_2O)RuA_5]X_4$ ($X = Br^-$ or BF_4^-) where the nitrous oxide is bridging between two ruthenium atoms (the tetrafluoroborate salt was contaminated with the dinitrogen complex, $[RuA_5N_2](BF_4)_2$). In air-saturated water, the solids had an absorption at 238 nm, and within two minutes it decayed and gave a new absorption at 298 nm (characteristic of $[RuA_5OH]^{2+}$). The infrared spectra of both solids were recorded as Nujol mulls and as potassium bromide discs. In a potassium bromide disc, the bromide salt had absorptions at 2110 and 1160 cm^{-1} and the tetrafluoroborate salt had absorptions at 2105 and 1155 cm^{-1}, which were assigned to the co-ordinated nitrous oxide (the position of the lower absorption in the tetrafluoroborate salt was difficult to determine because of the absorption of the anion in the region). The nitrous oxide content of the solid was determined by dissolving it in water or oxidising it with ferric ions. The yield of nitrous oxide was 43-59% of the value expected for a $Ru:N_2O$ ratio of 1:1. Equivalent yields of dinitrogen were obtained when the solid was added to a solution containing excess chromium(II) (to reduce the co-ordinated nitrous oxide to co-ordinated dinitrogen) followed by the addition of excess ferric ions to the resulting solution. The ruthenium(II) content of the solids was less than 100% of the expected value (61-73% for the bromide salt and 83-97% for the tetrafluoroborate salt). This low value is due to the presence of ruthenium(III) oxidation products or the dinitrogen complex, $[RuA_5N_2]^{2+}$, (as this was not detected by the method used) in the solids.[40]

The properties of the solids isolated by Armor and Taube can be rationalised in terms of their being a mixture of the mono-nuclear nitrous oxide complex, $[RuA_5(N_2O)]X_2$, and the dinitrogen complex, $[RuA_5N_2]X_2$. The electronic spectral properties of the solid obtained by Armor and Taube are the same as those of $[RuA_5(N_2O)]^{2+}$. It would be expected that the di-nuclear complex would have a different absorption frequency from that of the mono-nuclear complex, as is observed in the analogous dinitrogen complexes.[41] As mentioned earlier (section 4:4) $[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$ decomposed during the preparation of potassium bromide discs, and the spectrum observed was similar to that of the bromide salt. As ν_{N_2} for $[RuA_5N_2]Br_2$ is observed at 2110 cm^{-1}, and ν_3 and ν_1 for $[RuA_5(N_2O)]Br_2$ occur at 2239 and 1161 cm^{-1} respectively (Table 4:3), the infrared spectra of the solids are consistent with the higher frequency absorption being ν_{N_2} of $[RuA_5N_2]Br_2$ and the lower one being ν_1 of co-ordinated nitrous oxide in $[RuA_5(N_2O)]Br_2$. In the bromide salt, the ν_3 absorption of co-ordinated nitrous oxide is very weak and would not be easily observed. However, it is not clear why similar spectra were obtained for both the bromide and tetrafluoroborate salts in Nujol mulls.

Armor and Taube[40] suggested that their microanalyses, which repeatedly showed less than seven nitrogen atoms for each ruthenium atom, were very good evidence for their solid being a di-nuclear complex. However, it was difficult to obtain good microanalyses for the mono-nuclear complex due to the loss of co-ordinated nitrous oxide from the complex, and the nitrogen analyses were always low (section 3:6:1). Also the yields of nitrous oxide

obtained by Armor and Taube on oxidising their solid with ferric ion are similar to those obtained when $[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$ was oxidised with ferric sulphate (section 3:6:3). Although the dinitrogen complex was formed when the mono-nuclear nitrous oxide complex was added to a solution containing excess chromium(II), the yields were very low. Thus, it may be coincidence that the yields of nitrous oxide obtained by Armor and Taube when they oxidised their solid with ferric ions were similar to the yields of dinitrogen obtained when they first reduced their solid with chromium(II). Most of this dinitrogen may have been released from the dinitrogen complex which is present as an impurity in the solid. There may be up to 40% of this impurity in the bromide salt and 20% in the tetrafluoroborate salt.

Hence it appears that a di-nuclear complex of nitrous oxide has not been isolated. The instability of the nitrogen linked isomer of the mono-nuclear nitrous oxide complex suggests that a di-nuclear nitrous oxide complex would not be very stable.

The similarity of the bonding of nitrous oxide to that of dinitrogen in their complexes suggests that metals which are able to form stable dinitrogen complexes may also form nitrous oxide complexes. The formation of these complexes requires that the metal be in a low oxidation state so that it can participate in back-bonding to the ligand (nitrous oxide or dinitrogen). However, to obtain a stable nitrous oxide complex, the metal must be stable with respect to oxidation, or the nitrous oxide will be

reduced to dinitrogen. For this reason it is unlikely that many transition metals will form stable nitrous oxide complexes. For example, it is unlikely that it will be possible to isolate ammine(dinitrogen oxide)-osmium(II) complexes analogous to the ruthenium(II) complexes. Although several complexes have been observed to react with nitrous oxide (see section 2:4), only the penta-ammine(dinitrogen oxide)ruthenium(II) complexes have been isolated up to date. Attempts are now being made to isolate a nitrous oxide complex from the reaction of $[RuA_4(OH_2)_2]^{2+}$ with nitrous oxide.[14] Rhenium complexes may offer the best opportunity to synthesise further nitrous oxide complexes as it appears to be stable in its +1 (and +3) oxidation states.

The source of nitrous oxide may also determine whether or not the complex will be isolated. Using gaseous nitrous oxide low conversions to the complex may make it difficult to isolate. However, a reaction similar to that of Bottomley and Crawford[38] in which the nitrous oxide is synthesised by the reaction of a co-ordinated ligand should give better conversions, and this method may also offer the metal less opportunity of reducing the nitrous oxide. As reactions of co-ordinated ligands are being investigated extensively at the moment, this type of reaction offers the best chance of isolating further nitrous oxide complexes.

Although the reduction of the co-ordinated nitrous oxide may prevent the isolation of many more nitrous oxide complexes, this property of the ligand

makes it a good source of co-ordinated dinitrogen and it may be possible to prepare new dinitrogen complexes using nitrous oxide as a source of the dinitrogen.

TABLE 4:1

Infrared absorptions of adsorbed nitrous oxide

Adsorbed on alkali halide films

alkali halide film		ν_3	ν_1	ν_2
NaCl		2240	1252	571
		2225	1265	582
	($^{14}N^{15}N^{16}O$)	2193		
NaBr		2235	1247	567
		2222	1261	579
			1274	
NaI		2250 (sh)	1248	568
		2232	1257	578
			1272	582
CsCl		2235	1272	575 (sh)
			1288	582
CsBr		2241	1263	580
		2233	1284	
CsI		2238	1260	570 (sh)
		2227	(1275)	576
			1287	

TABLE 4:1 (cont'd)

Adsorbed on Y-type zeolites

zeolite	ν_3	ν_1	ν_2
Na Y	2240	1260	
Ca Y	2250		
Decationated Y	2240		
H Y	2200		

TABLE 4:2

Ligand stretching frequencies

anion/complex	$[RuA_5CO]X_2$[7]	$[RuA_5N_2]X_2$[8]	$[RuA_5(N_2O)]X_2$		
	ν_{CO}	ν_{N_2}	ν_3	ν_1	$2\nu_1$
chloride	1931, 1870 (sh)	2105			
bromide	1936, 1887 (sh)	2114	2239	1161	2315 (w)
iodide	1945	2129	2252	1180	
tetrafluoroborate*	1972, 1960, 1913 (sh)	2144	2270	1209	2415 (w)
hexafluorophosphate*	1990, 1955 (sh)	2167	2280, 2222	1222	

*Values for tetrafluoroborate and hexafluorophosphate salts taken from Table 6:1 for $[RuA_5CO]X_2$.

TABLE 4:3

Infrared absorptions of isotopically labelled, co-ordinated nitrous oxide in the complexes $[RuA_5(N_2O)]X_2$

Stretching frequencies ν_3 and ν_1

anion (X)	isotope*	ν_1	ν_3	ν_3'	ν_{N_2}
chloride	1				2076.8
	2				2036.3
	3				2036.3
bromide	1	1160.8	2239.3		2110.2
	2	1150.0	2217.4		2075.1
	3	1161.0	2203.0		2076.2
iodide	1	1180.4	2252.0		2128.1
	2	1167.3	2227.2		2089.2
	3	1178.3	2213.8		2093.4
tetrafluoroborate†	1	1209.3	2269.8	2145.6	
	2	1195.3	2246.1	2146.6	2110 (sh)
	3	1206.7	2228.6	2145.4	2110 (w)
hexafluorophosphate†	1	1221.7	2279.9	2221.9 2253.2 (w)	2165.5
	2	1206.5	2255.9	2199.4 2231.1 (w)	
	3	1218.5	2235.7	2175.1 2278.1 (w) 2211.5 (w)	

*1 = $^{14}N^{14}N^{16}O$; 2 = $^{15}N^{14}N^{16}O$; 3 = $^{14}N^{15}N^{16}O$.

†This salt also contains one molecule of lattice water.

TABLE 4:4

Isotopic shifts of co-ordinated nitrous oxide

ν_3 absorption

anion/isotope	$^{14}N^{14}N^{16}O$	$^{15}N^{14}N^{16}O$	$\Delta\nu^{\dagger}$ (cm^{-1})	$^{14}N^{15}N^{16}O$	$\Delta\nu^{\dagger}$ (cm^{-1})
bromide	2239.3	2217.4	-21.9	2203.0	-36.3
iodide	2252.0	2227.2	-24.8	2213.8	-38.2
tetrafluoroborate	2269.8	2246.1	-23.7	2228.6	-41.2
hexafluorophosphate	2279.9	2255.9	-24.0	2235.7	-44.2
nitrous oxide$_{(g)}$ **	2223.9	2202.5	-21.4	2177.6	-46.3

ν_1 absorption

anion/isotope	$^{14}N^{14}N^{16}O$	$^{15}N^{14}N^{16}O$	$\Delta\nu^{\dagger}$ (cm^{-1})	$^{14}N^{15}N^{16}O$	$\Delta\nu^{\dagger}$ (cm^{-1})
bromide	1160.8	1150.0	-10.8	1161.0	+0.2
iodide	1180.4	1167.3	-13.1	1178.3	-2.1
tetrafluoroborate	1209.3	1195.3	-14.0	1206.7	-2.6
hexafluorophosphate	1221.7	1206.5	-15.2	1218.5	-3.2
nitrous oxide$_{(g)}$ **	1285.5	1270.6	-14.9	1281.0	-4.5

$^{\dagger}\Delta\nu = \nu_{*N_2O} - \nu_{N_2O}$

** These values are taken from reference 13.

TABLE 4:5

Irradiation of the hexafluorophosphate salt

isotope	initially	after irradiation	assignment
$^{14}N^{14}N^{16}O$	2280	2280 (unchanged)	ν_3
	2222		ν_3'
		2165 (weak)	ν_{N_2}*
	1222	1222 (unchanged)	ν_1
		1160 (medium)	$\nu^*_{Ru\equiv N}$
$^{15}N^{14}N^{16}O$	2256	2256 (unchanged)	ν_3
	2199		ν_3'
		2080 (weak)	ν_{N_2}*
	1206.5	1206.5 (unchanged)	ν_1
		1154 (medium)	$\nu^*_{Ru\equiv N}$
$^{14}N^{15}N^{16}O$	2236	2236 (unchanged)	ν_3
	2175		ν_3'
		not observed	ν_{N_2}*
	1218.5	1218.5 (unchanged)	ν_1
		1164 (medium)	$\nu^*_{Ru\equiv N}$

*tentative assignment

TABLE 4:7

Infrared absorptions of isotopically labelled, co-ordinated nitrous oxide in the complexes $[RuA_5(N_2O)]X_2$

600-250 cm^{-1}

frequencies in italics refer to shoulders

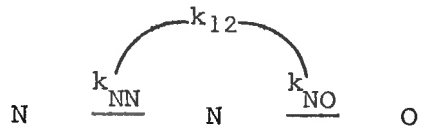
anion (X)	isotope*	region under consideration					
		605-595	575-500	490-465	460-400	350-250	
Cl^-	1	598.2	574.2	485.6	*458.0*, 452.9, *418.3*, 404.9	340	306, *284*, 258
Br^-	1	605.1	500.2	476.4	445.0, *428.4*	336	301
	2	602.5		477.3	*458.1*, 446.4, 426.0	334	301
	3	605.8		478.2	*455.3*, 446.4, 426.1	334	298
I^-	1	599.7		(489.1)	424.3	321	301
	2	598.5		467.0	448.3 424.0, *405.9*	321	301
	3	604.0		468.5	*448.6*, *439.1*, 425.6	320	301
BF_4^- †	1	599.1			459.5 423.5, 404.9	313	305
	2	601.2	574.0		450.4, 431.4	310	302
	3		575.4,494.6	(476.8)	433.9	310	303
PF_6^- †	1	a		469.9	*459.6* 415.6	*308*	301
	2	a		469.7	427.4, 413.0, 401.7		298
	3	a		469.8	423.0, 416.6	*310*	303

*1 = $^{14}N^{14}N^{16}O$; 2 = $^{15}N^{14}N^{16}O$; 3 = $^{14}N^{15}N^{16}O$.

†This salt also contains one molecule of lattice water.

TABLE 4:8

Calculated force constants for co-ordinated nitrous oxide in the complexes $[RuA_5(N_2O)]X_2$ from the model XYZ



interaction constant, $k_{12} = 1.36 \times 10^5$ dyne cm^{-1}

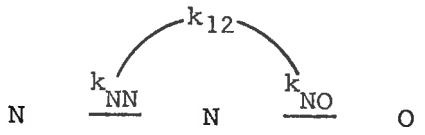
anion (X)	isotope*	k_{NN} ($\times 10^{-5}$) (dyne cm^{-1})	k_{NO} ($\times 10^{-5}$) (dyne cm^{-1})
bromide	1	19.4_5	8.6_9
	2	19.5_8	8.7_0
	3	19.5_7	8.7_5
iodide	1	19.5_4	9.0_4
	2	19.6_4	9.0_1
	3	19.6_5	9.0_6
tetrafluoroborate†	1	19.6_6	9.5_7
	2	19.7_6	9.5_4
	3	19.7_4	9.5_8
hexafluorophosphate†	1	19.7_5	9.8_0
	2	19.8_6	9.7_5
	3	19.8_1	9.8_0

*1 = $^{14}N^{14}N^{16}O$; 2 = $^{15}N^{14}N^{16}O$; 3 = $^{14}N^{15}N^{16}O$.

†This salt also contains one molecule of lattice water.

TABLE 4:9

Effect of the force constants on the stretching frequencies of nitrous oxide using the model XYZ



Variation of the bond force constants, k_{NN} and k_{NO}

k_{NN}			k_{NO}		
$k_{NO} = 11.5 \times 10^5$ dyne cm^{-1}			$k_{NN} = 18.0 \times 10^5$ dyne cm^{-1}		
$k_{12} = 1.36 \times 10^5$ dyne cm^{-1}			$k_{12} = 1.36 \times 10^5$ dyne cm^{-1}		
k_{NN} ($\times 10^{-5}$) (dyne cm^{-1})	ν_3 (cm^{-1})	ν_1 (cm^{-1})	k_{NO} ($\times 10^{-5}$) (dyne cm^{-1})	ν_3 (cm^{-1})	ν_1 (cm^{-1})
16.0	2132.0	1273.2			
16.5	2157.5	1277.9	10.0	2193.9	1223.6
17.0	2182.9	1282.2	10.5	2206.7	1246.9
17.5	2208.2	1286.2	11.0	2219.8	1269.0
18.0	2233.3	1289.9	11.5	2233.3	1289.9
18.5	2258.3	1293.4	12.0	2247.2	1309.8
19.0	2283.2	1296.6	12.5	2261.3	1328.6
19.5	2307.9	1299.6	13.0	2275.9	1346.5
20.0	2332.4	1302.5			
	$\Delta\nu$ 200.4	29.3		$\Delta\nu$ 82.0	122.9

TABLE 4:9 (cont'd)

Variation of the interaction constant, k_{12}

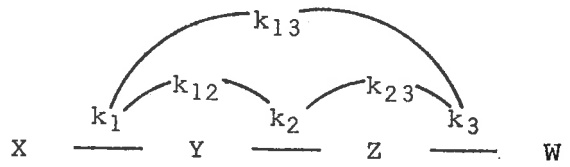
$$k_{NN} = 17.8_8 \times 10^5 \text{ dyne cm}^{-1}$$
$$k_{NO} = 11.3_9 \times 10^5 \text{ dyne cm}^{-1}$$

k_{12} ($\times 10^{-5}$) (dyne cm^{-1})	ν_3 (cm^{-1})	ν_1 (cm^{-1})
0.6	2280.4	1257.5
0.8	2265.7	1264.8
1.0	2250.9	1272.0
1.2	2236.1	1279.0
1.4	2221.3	1285.9
1.6	2206.4	1292.7
1.8	2191.5	1299.3
2.0	2176.5	1305.7
2.2	2161.6	1312.0
2.4	2146.6	1318.1
	$\Delta\nu$ -133.8	+60.6

TABLE 4:10

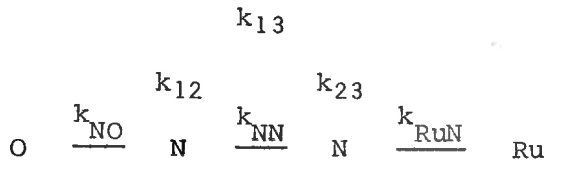
Calculated force constants for co-ordinated nitrous oxide

in the complexes $[RuA_5(N_2O)]X_2$ from the model XYZW



Mass W = 101 $k_{12} = 1.36 \times 10^5$ dyne cm^{-1} $k_{23} = k_{13} = 0$

Co-ordination through the nitrogen atom

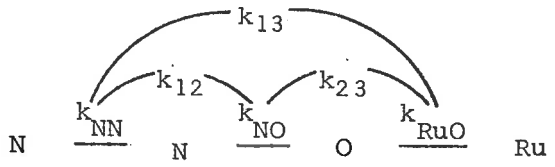


anion	k_{NO} ($\times 10^{-5}$) (dyne cm^{-1})	k_{NN} ($\times 10^{-5}$) (dyne cm^{-1})	k_{RuN} ($\times 10^{-5}$) (dyne cm^{-1})
bromide	18.7_3	5.1_9	11.0_3
iodide	16.1_4	9.5_9	8.8_9
tetrafluoroborate†	15.6_7	11.6_8	6.5_0
hexafluorophosphate†	13.9_6	14.5_4	3.9_5

†This salt also contains one molecule of lattice water.

TABLE 4:10 (cont'd)

Co-ordination through the oxygen atom

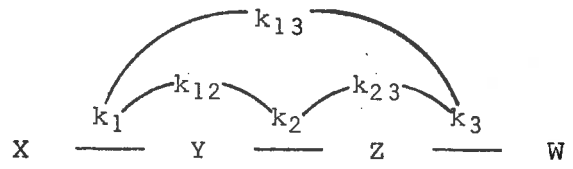


anion	k_{NN} ($\times 10^{-5}$) (dyne cm^{-1})	k_{NO} ($\times 10^{-5}$) (dyne cm^{-1})	k_{RuO} ($\times 10^{-5}$) (dyne cm^{-1})
bromide	16.5_6	7.7_9	11.1_6
iodide	18.3_3	7.2_0	8.7_2
tetrafluoroborate†	18.0_9	9.1_5	6.3_7
hexafluorophosphate†	18.4_3	10.0_1	3.8_8

†This salt also contains one molecule of lattice water.

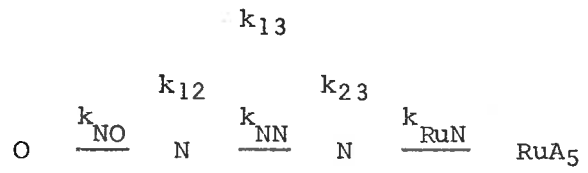
TABLE 4:11

Calculated force constants for co-ordinated nitrous oxide in the complexes $[RuA_5(N_2O)]X_2$ from the model XYZW



Mass W = 186 $k_{12} = 1.36 \times 10^5$ dyne cm^{-1} $k_{23} = k_{13} = 0$

Co-ordination through the nitrogen atom

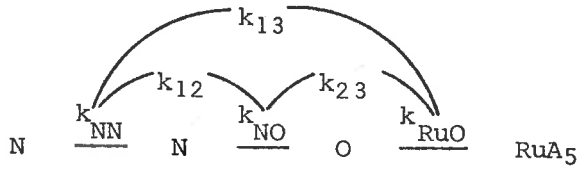


anion	k_{NO} ($\times 10^{-5}$) (dyne cm^{-1})	k_{NN} ($\times 10^{-5}$) (dyne cm^{-1})	k_{RuN} ($\times 10^{-5}$) (dyne cm^{-1})
bromide	19.1_6	4.6_1	11.5_0
iodide	16.3_1	9.3_8	9.1_0
tetrafluoroborate†	15.7_4	11.5_9	6.5_9
hexafluorophosphate†	13.9_6	14.5_4	3.9_5

†This salt also contains one molecule of lattice water.

TABLE 4:11 (cont'd)

Co-ordination through the oxygen atom



anion	k_{NN} ($\times 10^{-5}$) (dyne cm^{-1})	k_{NO} ($\times 10^{-5}$) (dyne cm^{-1})	k_{RuO} ($\times 10^{-5}$) (dyne cm^{-1})
bromide	16.5_4	7.7_5	11.5_8
iodide	18.3_1	7.4_4	8.4_2
tetrafluoroborate†	18.0_9	9.1_4	6.5_0
hexafluorophosphate†	18.4_3	10.0_0	3.9_2

†This salt also contains one molecule of lattice water.

TABLE 4:12

Stretching frequencies, ν_4, calculated with the force constants from the model XYZW

Co-ordination through the nitrogen atom

anion/isotope	$^{14}N^{14}N^{16}O$	$^{15}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$
Mass W = 101			
bromide	590.3	583.4	581.6
iodide	656.8	651.0	648.9
tetrafluoroborate†	591.7	586.5	585.5
hexafluorophosphate†	478.7	474.9	474.3
Mass W = 186			
bromide	533.1	526.1	524.6
iodide	612.8	606.7	604.7
tetrafluoroborate†	551.9	546.3	545.4
hexafluorophosphate†	446.8	440.7	440.2

Co-ordination through the oxygen atom

anion/isotope	$^{14}N^{14}N^{16}O$	$^{15}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$
Mass W = 101			
bromide	686.3	678.2	676.2
iodide	599.7	594.4	592.4
tetrafluoroborate†	557.4	552.5	551.6
hexafluorophosphate†	452.6	449.0	448.5
Mass W = 186			
bromide	646.5	638.1	636.2
iodide	563.9	558.3	556.4
tetrafluoroborate†	521.9	516.6	515.8
hexafluorophosphate†	421.9	418.1	417.6

†This salt also contains one molecule of lattice water.

TABLE 4:13

Solution of the cubic equation for the tetrafluoroborate salt

Observed frequencies: $\nu_3 = 2269.8$ $\nu_1 = 1209.3$

Co-ordination through the nitrogen atom

Force constants* ($\times 10^{-5}$) (dyne cm^{-1})	Calculated frequencies (cm^{-1})
Mass W = 101	
$k_{NO} = 15.6_7$	$\nu_3 = 2123.3$
$k_{NN} = 11.6_8$	$\nu_1 = 1479.3$
$k_{RuN} = 6.5_0$	$\nu_4 = 517.2$
Mass W = 186	
$k_{NO} = 15.7_4$	$\nu_3 = 2122.2$
$k_{NN} = 11.5_8$	$\nu_1 = 1476.7$
$k_{RuN} = 6.5_9$	$\nu_4 = 483.4$

Co-ordination through the oxygen atom

Force constants* ($\times 10^{-5}$) (dyne cm^{-1})	Calculated frequencies (cm^{-1})
Mass W = 101	
$k_{NN} = 18.0_9$	$\nu_3 = 2182.9$
$k_{NO} = 9.1_5$	$\nu_1 = 1379.2$
$k_{RuO} = 6.3_7$	$\nu_4 = 508.4$
Mass W = 186	
$k_{NN} = 18.0_9$	$\nu_3 = 2182.4$
$k_{NO} = 9.1_4$	$\nu_1 = 1376.8$
$k_{RuO} = 6.5_0$	$\nu_4 = 476.7$

*The force constants are taken from Tables 4:10 and 4:11.

TABLE 4:14

Effect of the force constants on the stretching frequencies of co-ordinated nitrous oxide in the complexes $[RuA_5(N_2O)]X_2$ from the model XYZW

Co-ordination through the oxygen atom

Mass W = 186 $k_{12} = 1.36 \times 10^5$ dyne cm^{-1} $k_{23} = k_{13} = 0$

force constants ($\times 10^{-5}$) (dyne cm^{-1})			calculated frequencies (cm^{-1})		
k_{NN}	k_{NO}	k_{RuO}	ν_3	ν_1	ν_4
18.43	10.80	1.00	2237.4	1288.4	214.0
18.60	10.80	1.00	2246.0	1289.4	214.0
18.30	8.50	2.00	2175.1	1206.4	293.6
18.50	8.50	2.00	2185.8	1207.1	293.6
18.43	10.50	2.00	2230.6	1302.1	296.2
18.60	10.50	2.00	2239.3	1303.1	296.2
18.00	8.00	2.50	2147.6	1194.7	322.8
18.45	8.00	2.50	2172.2	1195.9	322.8
18.10	9.80	2.50	2196.1	1283.6	326.5
18.00	8.00	3.00	2147.9	1210.9	348.8
18.45	8.00	3.00	2172.4	1212.2	348.9
18.40	8.50	3.00	2181.0	1238.0	350.4
18.10	9.80	3.00	2196.6	1298.1	353.6

TABLE 4:15

Effect of the interaction constants on the stretching frequencies of co-ordinated nitrous oxide in the complexes $[RuA_5(N_2O)]X_2$ from the model XYZW

Mass W = 186

Frequencies used initially: $\nu_3 = 2269.8$, $\nu_1 = 1209.3$, $\nu_4 = 0$.

interaction constant			solutions from K AND V				solutions from CUBIC		
k_{12}	k_{23}	k_{13}	k_{NN}	k_{NO}	k_{RuO}	ν_4	ν_3	ν_1	ν_4
0.0	0.0	0.0	18.0_8	6.4_2	8.9_9	517	2215.0	1318.9	485.9
0.4	0.0	0.0	18.1_0	7.2_2	8.2_8	526	2206.5	1334.9	490.6
0.0	0.5	0.0	18.1_6	6.4_3	10.0_0	546	2216.2	1318.9	512.7
0.4	0.5	0.0	18.1_9	7.2_4	9.3_0	559	2208.3	1334.3	520.5
1.0	0.5	0.0	18.2_1	8.4_4	8.2_1	566	2194.6	1359.5	520.7
1.5	0.5	0.0	18.2_0	9.4_4	7.2_8	562	2181.6	1382.0	511.0
1.0	1.5	0.0	18.4_3	8.4_8	10.2_9	639	2200.0	1357.8	579.9
1.5	1.5	0.0	18.4_5	9.4_8	9.3_8	644	2189.0	1379.6	577.9
0.4	0.0	0.0	18.1_0	7.2_2	8.2_8	526	2206.5	1334.9	490.6
0.4	0.5	0.0	18.1_9	7.2_4	9.3_0	559	2208.3	1334.3	520.5
1.0	0.5	0.0	18.2_1	8.4_4	8.2_1	566	2194.6	1359.5	520.7
1.0	1.5	0.0	18.4_3	8.4_8	10.2_9	639	2200.0	1357.8	579.9

TABLE 4:15 (cont'd)

interaction constant			solutions from K AND V				solutions from CUBIC		
k_{12}	k_{23}	k_{13}	k_{NN}	k_{NO}	k_{RuO}	ν_4	ν_3	ν_1	ν_4
1.5	0.5	0.0	18.2_0	9.4_4	7.2_8	562	2181.6	1382.0	511.0
1.5	1.5	0.0	18.4_5	9.4_8	9.3_8	644	2189.0	1379.6	577.9

All force constants are $\times 10^{-5}$ dyne cm^{-1} and frequencies are in cm^{-1}.

TABLE 4:16

Solution of the cubic equation

Co-ordination through the oxygen atom

Mass W = 186

Force Constants used: $k_{NN} = 18.50 \times 10^5$ dyne cm^{-1}

$k_{NO} = 10.50 \times 10^5$ dyne cm^{-1}

$k_{RuO} = 2.00 \times 10^5$ dyne cm^{-1}

$k_{12} = 1.36 \times 10^5$ dyne cm^{-1}

$k_{23} = k_{13} = 0$

isotope	calculated frequencies (cm^{-1})					
	ν_3	$\Delta\nu_3$	ν_1	$\Delta\nu_1$	ν_4	$\Delta\nu_4$
$^{14}N^{14}N^{16}O$	2234.2		1302.5		296.2	
$^{15}N^{14}N^{16}O$	2208.9	-25.3	1288.8	-13.7	293.1	-3.1
$^{14}N^{15}N^{16}O$	2187.7	-46.5	1300.6	- 1.9	293.3	-2.9

TABLE 4:17

Calculation of ν_1 and ν_2 for penta-amminedinitrogenruthenium(II) bromide from the model XYZ

$[RuA_5N_2]Br_2$

isotope	calculated frequency (cm^{-1})			
	ν_1	$\Delta\nu_1$	ν_2	$\Delta\nu_2$
Mass X = 101				
$Ru^{14}N^{14}N$	507.7		507.7	
$Ru^{15}N^{14}N$	500.7	-7.0	495.8	-11.9
$Ru^{14}N^{15}N$	500.2	-7.5	502.7	- 5.0
Mass X = 186				
$A_5Ru^{14}N^{14}N$	507.7		507.7	
$A_5Ru^{15}N^{14}N$	500.0	-7.7	495.8	-11.9
$A_5Ru^{14}N^{15}N$	499.5	-8.2	502.6	- 5.1

Observed[17] for $[RuA_5N_2]Br_2$

complex	frequency (cm^{-1})	
		$\Delta\nu$
$A_5Ru^{14}N^{14}N$	507.7	
$A_5Ru^{15}N^{14}N$	493.4	-14.3
$A_5Ru^{14}N^{15}N$	500.6	- 7.1

TABLE 4:18

XYZ systems in which ν_1 and ν_2 have been assigned unambiguously

$Ni(CO)_4$[22]

isotope	frequency (cm^{-1})			
	ν_7*	$\Delta\nu_7$	ν_6**	$\Delta\nu_6$
$Ni(^{12}C^{16}O)_4$	423.1		458.9	
$Ni(^{13}C^{16}O)_4$	417.3	-5.8	442.7	-16.2
$Ni(^{12}C^{18}O)_4$	416.6	-6.5	453.8	- 5.1

Nitrous oxide[1]

isotope	frequency (cm^{-1})			
	ν_1	$\Delta\nu_1$	ν_2	$\Delta\nu_2$
$^{14}N^{14}N^{16}O$	1285.5		588.8	
$^{14}N^{15}N^{16}O$	1281.0	- 4.5	575.6	-13.2
$^{15}N^{14}N^{16}O$	1270.6	-14.9	585.6	- 3.2

*ν_7 is essentially the Ni-C stretch *i.e.* ν_1.

**ν_6 is essentially the ligand deformation *i.e.* ν_2.

TABLE 4:19

Calculation of ν_1 and ν_2 for penta-amminedinitrogenosmium(II) bromide from the model XYZ

Observed frequencies[15]

$[OsA_5{}^{14}N{}^{14}N]Br_2$	515.5 cm^{-1}
$[OsA_5{}^{15}N{}^{15}N]Br_2$	501.5 cm^{-1}

Calculated frequencies for $[OsA_5{}^{15}N{}^{15}N]Br_2$

ν_1

ν_1 = 498.1 cm^{-1}

For ν_3, ν_3' and ν_1 the values of 2018, 1949 and 515.5 cm^{-1}, respectively, were used.[15]

ν_2

ν_2 = 498.0	Mass X = 190	$l_1{}^*$ = 2.11 Å
ν_2 = 498.1	Mass X = 275	$l_1{}^*$ = 2.11 Å
ν_2 = 504.4	Mass X = 190	$l_1{}^*$ = 2.21 Å
ν_2 = 504.4	Mass X = 275	$l_1{}^*$ = 2.21 Å

*l_1 is the osmium-nitrogen bond length.

TABLE 4:20

Calculation of ν_1 and ν_2 for aquotetra-amminedinitrogenruthenium(II) chloride from the model XYZ

$[RuA_4(OH_2)N_2]Cl_2$

isotope	calculated frequencies (cm^{-1})			
	ν_1	$\Delta\nu_1$	ν_2	$\Delta\nu_2$
Mass X = 101				
$Ru^{14}N^{14}N$	515		515	
$Ru^{15}N^{14}N$	509.4	-5.6	502.9	-12.1
$Ru^{14}N^{15}N$	509.4	-5.6	509.9	- 5.1
Mass X = 187				
$A_4(OH_2)Ru^{14}N^{14}N$	515		515	
$A_4(OH_2)Ru^{15}N^{14}N$	508.6	-6.4	502.9	-12.1
$A_4(OH_2)Ru^{14}N^{15}N$	508.6	-6.4	509.9	- 5.1

Observed[14] for $[RuA_4(OH_2)N_2]Cl_2$

complex	frequency (cm^{-1})	
		$\Delta\nu$
$A_4(OH_2)Ru^{14}N^{14}N$	515	
$A_4(OH_2)Ru^{15}N^{14}N$	505	-10
$A_4(OH_2)Ru^{14}N^{15}N$	513	- 2

FIGURE 4:1

Effect on ν_3 of isotopic labelling in the complexes $[RuA_5(N_2O)]X_2$

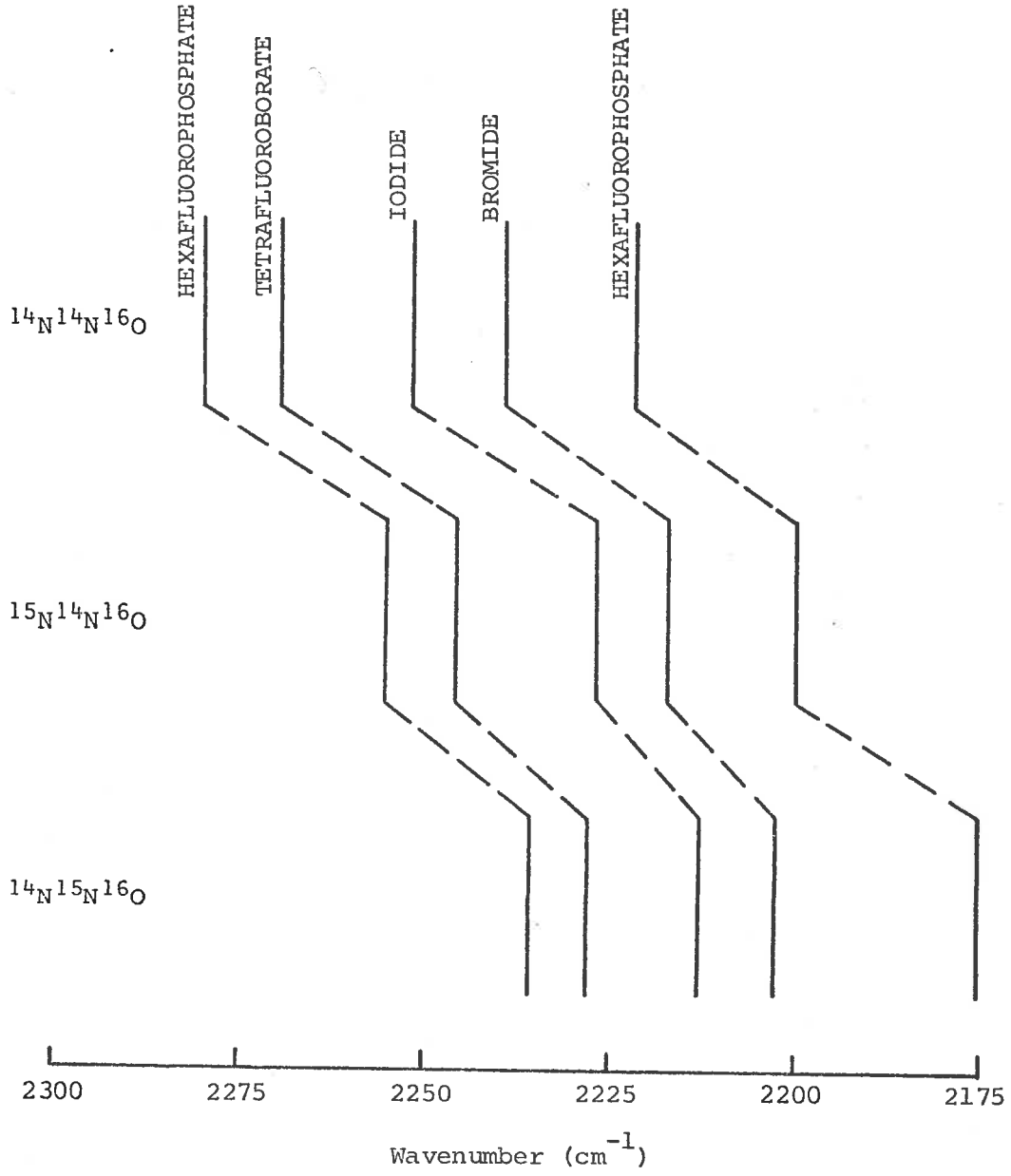
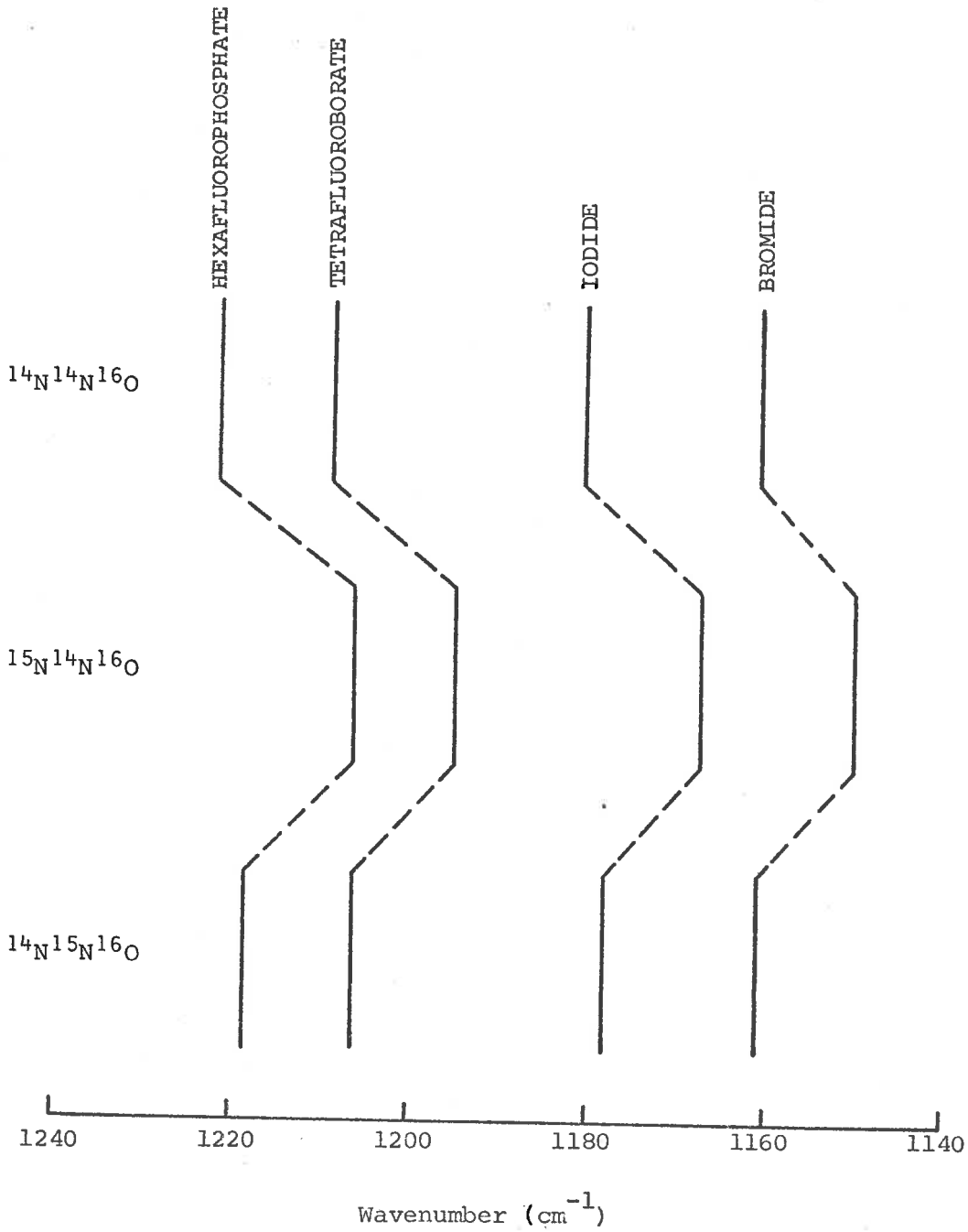


FIGURE 4:2

Effect on ν_1 of isotopic labelling in the complexes $[RuA_5(N_2O)]X_2$



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CHAPTER 5

ISOLATION AND CHARACTERISATION OF AQUOPENTA-AMMINERUTHENIUM(II) COMPLEXES

5:1. Introduction.—

The reduction of chloropenta-ammineruthenium(III) chloride with amalgamated zinc or zinc amalgam in the presence of excess of a ligand L, has been used as a convenient preparative route to ruthenium(II) complexes of the type $[RuA_5L]X_2$, where L = aromatic nitrogen heterocycles[1,2] (pyridine, substituted pyridines and azines), organonitriles[2-4] (benzonitrile and acetonitrile), dinitrogen,[5] carbon monoxide,[6] methylisocyanide[7] and hydrogen cyanide.[8] In many cases the corresponding ruthenium(III) complex can be prepared by oxidising the ruthenium(II) complex.[1,3,4] The reduced species which reacts with the ligand L in these reactions is considered to be $[RuA_5(OH_2)]^{2+}$.

In 1962 Endicott and Taube[9] found that the ruthenium containing products from the reduction of $[RuA_5(OH_2)]^{3+}$ and $[RuA_5Cl]^{2+}$ with chromium(II) were identical (reactions 1 and 2).

$$[RuA_5(OH_2)]^{3+} + Cr^{2+} \longrightarrow [RuA_5]^{2+} + Cr^{3+} + H_2O \qquad 1$$

$$[RuA_5Cl]^{2+} + Cr^{2+} \longrightarrow [RuA_5]^{2+} + CrCl^{2+} \qquad 2$$

Although the product was formulated as $[RuA_5]^{2+}$, it was thought to be $[RuA_5(OH_2)]^{2+}$. However evidence for the aquo-ligand was not obtained.

Itzkovitch and Page[10] formulated the species formed by the electrolytic reduction of $[RuA_5Cl]^{2+}$ in a sulphate medium as $[RuA_5X]$ and Harrison *et al.*[11] considered the possibility that reduction with amalgamated zinc under similar conditions may also yield the sulphato-complex, $[RuA_5(SO_4)]$, as well as the aquo-complex. Page and co-workers[12] have found since, that the electronic absorption spectra of the reduced species were identical, whether generated electrolytically in a sulphate medium, at pH 2-11, or in a sodium tetrafluoroborate solution. These spectra were reported to be identical with those of the reduced species obtained by Armor and Taube,[13] who used $Pt(H_2)$, chromium(II) or zinc amalgam as the reducing agent in an aqueous chloride solution. The similarity of these spectra, produced under these different conditions, is good evidence that the same complex is obtained in all reductions. Assuming that the metal is hexa co-ordinated, the complex is $[RuA_5(OH_2)]^{2+}$ because it is independent of any anions present in the solution.

This evidence is really only indirect, and unambiguous confirmation of whether or not an aquo-ligand is present in the co-ordination sphere could only be made if the complex were isolated. There have been no reports in the literature of its isolation, and as it was the reactant for nitrous oxide in the system discussed in Chapter 2, attempts were made to isolate and characterise this ruthenium(II) complex.

5:2. Isolation of the Complexes.—

$[RuA_5Cl]Cl_2$ was reduced in an aqueous solution with $Pt(H_2)$, or electrolytically at a mercury pool cathode (using the sodium or potassium salt of the required counteranion as the electrolyte). Although the reduced complex was very soluble, it could be precipitated by adding excess of the precipitating agent. The bromide, iodide, tetrafluoroborate and hexafluorophosphate salts were isolated. The chloride salt was too soluble to isolate. The iodide salt was precipitated from a yellow solution but it was always isolated as a pale-green yellow solid. The green colour may be due to a small amount of an iodo-complex formed on the addition of excess potassium iodide to the solution. As no violet colour, characteristic of $[RuA_5I]I_2$,[14] was observed in the solution, it is likely that the impurity is of the type, $[RuA_5I]I$. Such a ruthenium(II)-iodo complex has not been reported and so the properties of this complex are not known. The hexafluorophosphate salt was the most convenient to prepare.

The complexes were unstable in contact with air, showing visible signs of decomposition after several hours. The most unstable complex was the tetrafluoroborate salt. It decomposed to a brown solid in only two to three hours. Except for the tetrafluoroborate salt, the complexes could be stored at -5°C over silica gel for several days, with no apparent decomposition. In solution they were stable under oxygen-free conditions but were rapidly oxidised to ruthenium(III) complexes in contact with air.

5:3. Characterisation of the Complexes.—

The complexes are formulated as $[RuA_5(OH_2)]Br_2$, $[RuA_5(OH_2)]I_2$ and $[RuA_5(OH_2)](PF_6)_2 \cdot H_2O$ on the basis of their microanalyses and electronic absorption spectra. The tetrafluoroborate salt was so unstable that satisfactory analytical data could not be obtained for it. However, its infrared spectrum indicated that it contained lattice water and so it is tentatively formulated as $[RuA_5(OH_2)](BF_4)_2 \cdot H_2O$.

The hexafluorophosphate salt was diamagnetic as expected for an octahedral ruthenium(II) complex.

5:3:1. Microanalyses.—

Microanalyses of these complexes, just as with the nitrous oxide complexes, could not be carried out until three days after their preparation. A microanalysis of the hexafluorophosphate salt in Melbourne resulted in a very high value for the fluoride content of the complex. This indicated that decomposition of the complex had occured before it was analysed. Consequently, analyses of the complexes were carried out as soon as possible after their preparation, but these were limited to determinations of the halogen (bromide and iodide) and ruthenium content of the complexes.

Ruthenium analyses of the hexafluorophosphate complex did not give satisfactory results due to a reaction with the porcelain and platinum combustion boats used in the determinations. This reaction is probably due to the formation of hydrogen fluoride under the ignition conditions. Allen

et al.[15] also appear to have had difficulties in their ruthenium analysis of $[RuA_5N_2](BF_4)_2$ (calc. = 20.04%) and obtained a value of only 18.63%. If the complexes are fumed with concentrated sulphuric and nitric acids before heating, it may be possible to remove the fluorine and obtain more accurate results. There are several solution techniques which have been used to analyse for ruthenium,[16,17] but as the complex had a satisfactory extinction coefficient and infrared spectrum, no further attempts were made to analyse for ruthenium.

5:3:2. Solution properties.—

(a). Extinction coefficient of $[RuA_5(OH_2)]^{2+}$. The electronic absorption spectrum of the aquo-complex has been reported by Ford *et al.*[16] to have two maxima. One, a very broad absorption, is centred at 267 nm with an extinction coefficient of approximately 530 $M^{-1}cm^{-1}$, and the other is at 410 nm with an extinction coefficient of 44 $M^{-1}sec^{-1}$. The position of the more intense absorption is anion dependent. Page and co-workers[12] have observed a broad, weak band centred at 260 nm. The extinction coefficient near the maximum was 550 $M^{-1}cm^{-1}$. From the zinc amalgam reduction of $[RuA_5(OH_2)]^{3+}$ in *p*-trifluoromethylbenzenesulphonic acid, Broomhead[18] formed $[RuA_5(OH_2)]^{2+}$ with an absorption maximum at 270 nm. As the reduction was never complete, the extent of the reduction was measured using the pyridine method of Ford *et al.*,[16] and allowing for the ruthenium(III) complex remaining, an extinction coefficient of 598 ± 60 $M^{-1}cm^{-1}$ was estimated for $[RuA_5(OH_2)]^{2+}$ in the solution. All these extinction coefficients

have been measured on the aquo-complex generated in solution and not on a solution prepared from the solid.

The spectra of the solid aquo-complexes prepared above, were recorded in 0.1 M methanesulphonic acid. The bromide salt had a broad absorption centred at 271 nm whereas the absorption maximum was at 268 nm in the hexafluorophosphate salt, and occured as a shoulder at 267 nm (on the strong absorption of the iodide ion) in the iodide salt.

The extinction coefficient of $[RuA_5(OH_2)]^{2+}$ determined for the bromide and hexafluorophosphate salts was 570 ± 5 $M^{-1}cm^{-1}$. The value for the iodide salt was higher than this because of the absorption of the iodide ion in this region. The tetrafluoroborate salt had its absorption maximum at 268 nm but reproducible extinction coefficients could not be obtained from it. The extinction coefficients for the salts are tabulated in Table 5:1. The extinction coefficients are similar to those previously determined, but they may be considered to be more reliable because the solutions were prepared from the solid.

All the salts had another maximum at 410 nm but an accurate measurement of the low extinction coefficient (< 50 $M^{-1}cm^{-1}$) was not attempted.

(b). Conversion to $[RuA_5Cl]^{2+}$. In 1 M hydrochloric acid, aerial oxidation of $[RuA_5(OH_2)]^{2+}$ resulted in the formation of an absorption at

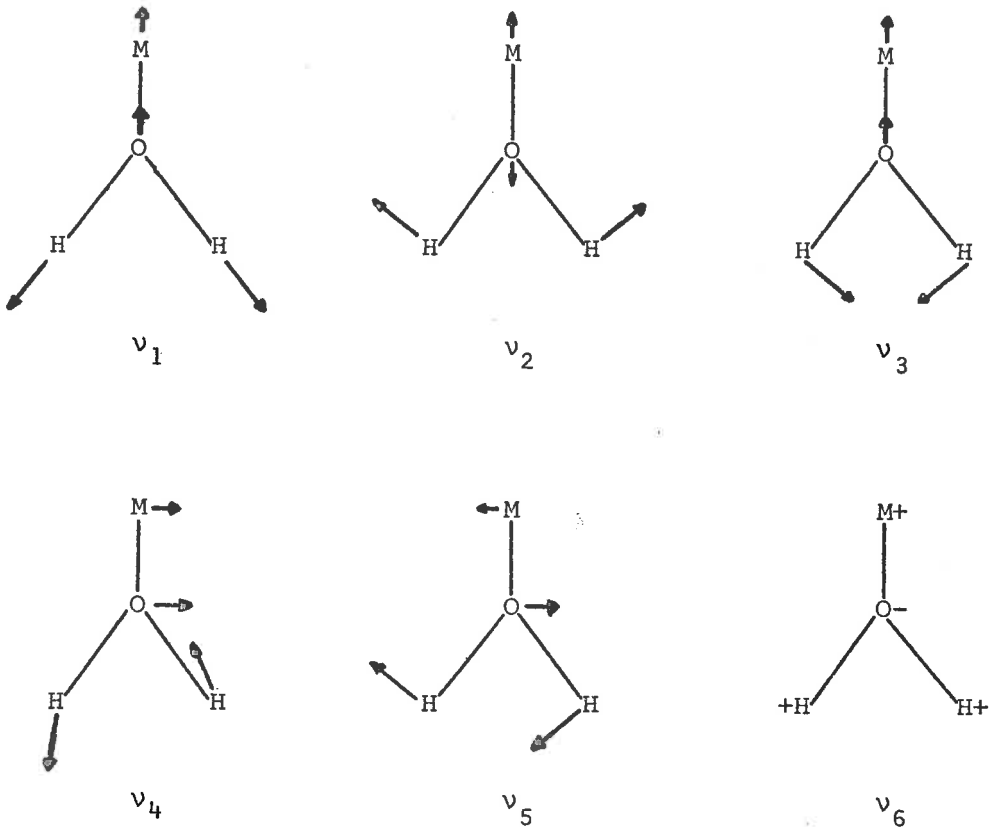
327 nm characteristic[14] of $[RuA_5Cl]^{2+}$. Almost quantitative conversion, as estimated by the extinction coefficient of this absorption, was achieved with the hexafluorophosphate salt after 30-60 minutes (Table 5:1). However quantitative conversion was not achieved with the bromide or iodide salts. In the presence of these anions the bromo- and iodo-penta-ammineruthenium-(III) complexes, respectively, were also formed. These were detected by their visible absorptions; $[RuA_5Br]^{2+}$ at 398 nm[14] and $[RuA_5I]^{2+}$ at 540 nm.[14]

5:4. Infrared Spectra of the Complexes.—

The infrared spectra were recorded as Nujol mulls or as potassium bromide discs. The complexes decomposed during the recording of the spectra and absorptions due to ruthenium(III) complexes could be observed as weak shoulders on some of the absorptions (especially in spectra recorded as potassium bromide discs because some decomposition also occured during the preparation of the disc). The absorptions observed are tabulated in Table 5:2.

The positions of the ammonia vibrations in the complexes were very similar to those in the corresponding hexa-ammineruthenium(II) complexes.[19] As well as these absorptions, there were others which were assigned to the water in the complex.

Using planar $M\text{-}O\begin{smallmatrix}H\\H\end{smallmatrix}$ as a model for water co-ordinated to a metal, six fundamental vibrations will be expected. These are[20]



Essentially, the ν_1, ν_4 and ν_3 vibrations are the symmetric and asymmetric stretching and the bending fundamentals, respectively, of the water molecule. The metal-ligand stretching vibration for the co-ordinated water is the ν_2 vibration and ν_5 and ν_6 are the rocking and wagging modes, respectively, of the M-CH_2 grouping.

Satori *et al.*[21] have made a normal co-ordinate analysis of co-ordinated water using the above model, and they have calculated that the frequencies of the rocking, wagging and metal-ligand stretching vibrations should be around 900, 768 and 673 cm^{-1} respectively. However, it has been found that

the positions of these absorptions are very dependent on the other ligands present in the complex and on the oxidation state of the metal.[20,22] Thus these calculated values give only a general indication of where the absorptions associated with each vibration may be.

In the aquopenta-ammineruthenium(II) complexes the absorptions associated with the co-ordinated water were weak and below 1100 cm^{-1} only two vibrations associated with the metal-oxygen bond were observed. The rocking mode was observed around 1030 cm^{-1} and the other absorption was around 600 cm^{-1}. The latter absorption is probably the wagging mode because it is at a higher frequency than is normally observed for ruthenium(II)-ligand stretches. The metal-ammine stretches in ruthenium(II) complexes are observed at 400-450 cm^{-1} and in $[RuA_5CO]X_2$,[6] the metal-carbonyl stretching vibration is around 525 cm^{-1}. Hence, it is not expected that the ruthenium-(II)-aquo stretching frequency would be as high as 600 cm^{-1}. There were no other absorptions below 600 cm^{-1} which could be assigned to the metal-aquo stretching vibration. The only other absorption which could not be assigned was around 1400 cm^{-1}. It was of medium intensity in the hexafluorophosphate salt but very weak in the bromide and iodide salts.

In the hexafluorophosphate salt two medium absorptions were present at 3580 and 3645 cm^{-1} as well as a shoulder at 1700 cm^{-1} on the ammonia absorption at 1632 cm^{-1}. Similar absorptions were observed in the tetra-fluoroborate and hexafluorophosphate salts of the nitrous oxide complexes

(section 3:7) in which they were assigned as lattice water vibrations. Hence, they are similarly assigned in this aquo-complex. The tetrafluoroborate salt also had similar absorptions, and so it must also contain lattice water and it is probably $[RuA_5(OH_2)](BF_4)_2 \cdot H_2O$.

5:5. Conclusion.—

The analytical data, electronic absorption spectra, and infrared spectra of these complexes confirm that there is an aquo-ligand present in the complexes. However, there is still no direct evidence that the complex remains hexaco-ordinated in solution.

Evidence for this can be obtained from the proton magnetic resonance spectrum of the complex. If it is hexaco-ordinated then two signals due to the ammonia protons should be observed. The area of these absorptions should be in the ratio 4:1 with the less intense absorption (due to the ammonia group *trans* to the aquo-ligand) at higher field. This is expected because in cobalt penta-ammine complexes it has been observed that if the sixth ligand has a lower ligand field strength than ammonia, then the *cis*-ammine protons occur at a lower field than the *trans*-ammine protons.[23] Two absorptions would also be observed if the complex was only five co-ordinate with the ammonia ligands in a square pyramidal arrangement about the ruthenium atom. However this structure is not likely for a ruthenium(II) complex. If only one absorption is observed, then it is not possible to make any conclusion concerning the structure of the complex in solution because it may be that

all five ammonia groups are equivalent in a five co-ordinate complex, or that the *trans*-ammonia to the aquo-ligand has become so labile that its signal cannot be detected. The only way to distinguish in this situation would be to use an internal calibrant to see if there are four or five ammonia groups contributing to the signal.

Some attempts were made to record the spectrum but reproducible results could not be obtained. Usually a very broad absorption at about $\tau = 2.5$ was observed, although once, three absorptions at $\tau = 1.9$, 2.3 and 2.7 were observed. The absorptions were not very stable and they decreased and shifted to higher τ values on standing as the solution became an intense blue colour. The main difficulties in obtaining the spectra were to exclude air from the samples and to get high concentrations of $[RuA_5(OH_2)]^{2+}$ (usually about 0.1 M were used). The first attempts to measure the proton magnetic resonance spectrum of $[RuA_5(OH_2)]^{2+}$ were made by electrolytically reducing a suspension of $[RuA_5Cl]Cl_2$ in 0.1 M sulphuric acid/D_2O and then transferring the solution to the sample tube and recording the spectrum. Using this method it was not possible to rigorously exclude air and this is why the spectra were not reproducible.

The isolation of the complex has made it possible to prepare the solutions *in vacuo* and to seal them in the sample tube. Only the hexafluorophosphate salt has been used in this way and it was too insoluble to obtain a concentrated solution. A more soluble salt, *e.g.* the bromide salt,

will need to be used to achieve the high concentrations, but it may be difficult to obtain the large amounts of complex which are required.

TABLE 5:1

Solution properties of $[RuA_5(OH_2)]X_2$

Extinction Coefficient

Spectrum in 0.1 M methanesulphonic acid.

	λ_{max} (nm)	$\varepsilon^{\dagger}$ ($M^{-1}cm^{-1}$)
$[RuA_5(OH_2)]Br_2$	271	567.3, 572.7
$[RuA_5(OH_2)]I_2$	267 (sh)	649.9, 644.2, 638.2
$[RuA_5(OH_2)](BF_4)_2 \cdot H_2O$*	268	481.6, 537.1, 590.5
$[RuA_5(OH_2)](PF_6)_2 \cdot H_2O$	268	566.0, 571.2, 571.3

†From several preparations.

*The presence of water in the complex was indicated by its infrared spectrum.

Conversion to $[Ru^{III}A_5Cl]^{2+}$

Spectra in 1 M hydrochloric acid after aerial oxidation, the extinction coefficient was measured at 327 nm.

	ε ($\times 10^{-3}$) ($M^{-1}cm^{-1}$)
$[RuA_5(OH_2)]Br_2$	1.20
$[RuA_5(OH_2)]I_2$	1.40, 1.60
$[RuA_5(OH_2)](PF_6)_2 \cdot H_2O$	1.78, 1.81

lit.[14] for $[RuA_5Cl]^{2+}$; λ_{max} = 327 nm; $\varepsilon = 1.9_3 \times 10^3$ $M^{-1}cm^{-1}$.

TABLE 5:2

Infrared spectra of the aquopenta-ammineruthenium(II) complexes

assignment/anion	Br^-	I^-	BF_4^-	PF_6^-
ν_{OH} (lattice water)			3605, 3535	3645, 3580
ν_{OH} (co-ordinated water)	3500-3300 (br)	3500-3300 (br)	*	*
ν_{NH}	3300 (br)	3285 (br)	3370, 3295	3375, 3305, 3220
δ_{OH_2}	1700 (sh)	1700 (sh)	1700 (sh)	1700 (sh)
δ_{NH_3} asym	1608	1600	1628	1632
δ_{NH_3} sym	1234	1246	1273	1275
$\rho_{rock}(Ru\text{-}OH_2)$	1032	1035	a	1030
ρ_{NH_3}	762	753	747	743
$\rho_{wag}(Ru\text{-}OH_2)$	608, 590 (sh)	605	600	
$\nu_{Ru\text{-}NH_3}$	450 (br)	468 (w), 435		
ν_3 BF_4^-, PF_6^-			1100-1000	850 (br)
ν_4 BF_4^-, PF_6^-			525	560
other absorptions	1385 (w)	1383 (w)		1430, 475 (w)

*Covered by the absorptions due to lattice water.

CHAPTER 5

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CHAPTER 6

PREPARATION OF RUTHENIUM(II)-CARBONYL COMPLEXES

6:1. Carbon Dioxide as the Source of the Carbonyl Ligand.—

Chloropenta-ammineruthenium(II) chloride, prepared from $RuCl_3$[1] or $[RuA_6]Cl_3$,[2] was used as the starting material for the preparation of the aquo-complex, $[RuA_5(OH_2)]^{2+}$, in this work. Occasionally in the preparation from $RuCl_3$, the chloro-complex had an absorption at 1930 cm^{-1} in its infrared spectrum due to an impurity. A complex with an infrared absorption in this region was of interest, especially as the dinitrogen complex, $[RuA_5N_2]^{2+}$, is an intermediate in the reaction. Hence, attempts were made to isolate and characterise the impurity.

Using ruthenium trichloride, the first step is to form the dinitrogen complex, $[RuA_5N_2]^{2+}$, by the reaction of the trichloride with hydrazine hydrate. The dinitrogen complex is not isolated but is refluxed with excess hydrochloric acid to form the chloro-complex. It was found that if insufficient acid were added and the solution was still basic when it was refluxed, then the product isolated on the addition of excess acid to the refluxed solution was impure, and it had an absorption at 1930 cm^{-1} in its infrared spectrum due to the impurity.

The impurity was very soluble in water, and could be separated from the less soluble chloro-complex by adding the precipitate to a small volume of water and filtering off the undissolved chloro-complex. The solid which

had dissolved was reprecipitated by the addition of excess anion. Repetition of this process several times removed most of the chloro-complex. The impurity isolated in this way was found to contain ruthenium red.[3] However, the visible spectrum of the solid had only a weak absorption due to ruthenium red, and as this has a very high extinction coefficient, it was concluded that there was not much present in the solid.

A microanalysis of the solid indicated that carbon was present in the complex. This was not expected because at no stage of the reaction had a carbon containing complex been used. The most likely source of carbon in this reaction would be carbon dioxide in the atmosphere. This was confirmed to be the source of the carbon by refluxing an alkaline solution of the dinitrogen complex under carbon dioxide. Samples were taken from this reaction every 15 minutes and the products were precipitated by the addition of excess hydrochloric acid. The infrared spectra of these solids showed that the strong absorption of the dinitrogen complex decreased during the reaction, and after one hour the absorption had disappeared completely. Corresponding to this decrease, an absorption at 1930 cm^{-1} began to increase, and after one hour it was very strong. Two further absorptions at 1990 and 2070 cm^{-1} were observed when the solution was refluxed for more than one hour. The latter absorptions increased in intensity on heating longer.

The reaction product obtained after 90 minutes was recrystallised three times, from dilute ammonia. A pale yellow solid was obtained. Its infrared spectrum, in the region 1900-2200 cm^{-1}, had only an absorption at 1930 cm^{-1}.

Elemental analyses were consitent with the formulation $[RuA_5CO]Cl_2$.

The bromide and iodide salts were similarly prepared by adding potassium bromide or potassium iodide respectively to the refluxed solution. The tetrafluoroborate and hexafluorophosphate salts were isolated as colourless solids from the chloride salt by metathesis. The infrared spectra of these carbonyl complexes (Table 6:1) were in good agreement with the previously reported spectra.[4]

Although there are not many examples to date, carbon dioxide has been reported to react with transition metal complexes. It will insert into the metal-hydride bond of $[Os(CO)HClL_3]$,[5] $[IrH_3L_3]$,[5] $[PtHClL_2]$[5] and $[CoH(N_2)L_3]$[6] ($L = PPh_3$) to form formato complexes. It is also known to react with the co-ordinately unsaturated complex, $Pt(PPh_3)_3$, in the presence of oxygen to form the carbonato complex, $[(PPh_3)_2Pt(CO_3)]$,[7] with the peroxycarbonate, $[(PPh_3)_2Pt(OCO_3)]$,[8] as an intermediate.

However in the reaction with ruthenium the reactant complex is probably $[RuA_5Cl]^{2+}$, formed from the decomposition of the dinitrogen complex by the acid. As this complex does not have any high energy bonds (*e.g.* a metal-hydride bond) and it is not co-ordinately unsaturated, it is not likely that there is a direct reaction of carbon dioxide with the complex.

Stollé and Hofmann[9] found that hydrazine will react with carbon dioxide and they have isolated hydrazine carboxylic acid, $NH_2NHCOOH$, from the reaction. Gogorishivili *et al.*[10-13] have shown that hydrazine and carbon

dioxide in the presence of cobalt and nickel complexes (*e.g.*, $[CoA_5Cl]Cl_2$,[10] $[CoA_4(CO_3)]NO_3$[11,12] and $NiCl_2 \cdot 6H_2O$[13]) react to give complexes which contain the anion of hydrazine carboxylic acid as a ligand.

If in the preparation of $[RuA_5Cl]Cl_2$, insufficient acid is added to the solution containing $[RuA_5N_2]^{2+}$ before it is refluxed, then unprotonated hydrazine (pKa *ca.* 6.1)[14] will be present in the solution when it is refluxed. Hence, especially under carbon dioxide, hydrazine carboxylate anion will be formed in the solution and the ruthenium-carbonyl complex is probably formed by the abstraction of the carbonyl group from this anion. Presumably cobalt[10-12] and nickel[13] complexes do not abstract the carbonyl group because their carbonyl complexes are not as stable as those of ruthenium.

Many transition metal complexes are known to be able to decarbonylate aldehydes,[15,16] amides[17] and acids[18] with the formation of a carbonyl complex. Several examples are:-

$$[RhCl(PPh_3)_3] + RCH_2CH_2CHO \longrightarrow [Rh(CO)Cl(PPh_3)_2] + RCH_2CH_3 + PPh_3 \quad 1$$

$$[Ru_2Cl_3(Et_2PhP)_6]Cl + 4C_3H_7CHO \longrightarrow 2[Ru(CO)Cl_2(Et_2PhP)_3] + 2C_3H_6 + 2C_3H_7CH_2OH \quad 2$$

$$RhCl_3 \xrightarrow{PPh_3/\text{dimethylformamide}} [Rh(CO)Cl(PPh_3)_2] \quad 3$$

$$[IrCl_6]^{3-} + HCO_2H \longrightarrow [Ir(CO)Cl_5]^{2-} + \text{formato-derivatives} \quad 4$$

Colton and Farthing[19] have made a detailed investigation of the reaction of ruthenium trichloride and formic acid. They have found that formic acid, in the presence of a halo acid, is able to both reduce and carbonylate the ruthenium complex. After one hour of refluxing, the initial product is the monocarbonyl, $[Ru(CO)Cl_5]^{2-}$, but on heating for a further four hours the dicarbonyl complex $[Ru(CO)_2Cl_4]^{2-}$ is obtained. Further heating gives a tricarbonyl complex. In dilute hydrochloric acid, the monocarbonyl is characterised by a single absorption at 2055 cm^{-1} in the carbonyl region of its infrared spectrum. The dicarbonyl has two absorptions, at 2070 and 2003 cm^{-1}, in this region.

This suggests that in the reaction from which $[RuA_5CO]Cl_2$ was isolated, the two additional bands which appeared on refluxing for over one hour are due to a dicarbonyl complex formed by further reaction of the monocarbonyl. Because the absorptions were observed to increase at the same rate, they suggest that only one new complex is being formed. As two absorptions were observed the dicarbonyl is probably *cis*-$[RuA_4(CO)_2]^{2+}$. This dicarbonyl has not been reported before.

It has been suggested[15,20] that decarbonylation reactions involve the co-ordination of the carbonyl containing compound to the metal and then it is decarbonylated with the formation of the metal carbonyl. Hence, in this case, it would mean that the anion of hydrazine carboxylic acid becomes co-ordinated. Although the nitrogen-nitrogen stretching frequency of the

co-ordinated hydrazine carboxylate anion has been observed around 1000 cm^{-1} in its complexes,[21] there was no evidence for this absorption in the infrared spectra of any samples taken during the reaction. However this does not exclude the possibility that the hydrazine carboxylate anion is co-ordinated to the metal before the abstraction of the carbonyl group.

The ability of ruthenium trichloride to be carbonylated by formic acid may mean that it is not necessary to form the dinitrogen complex first, and that stirring ruthenium trichloride and hydrazine hydrate under carbon dioxide may be a better preparative route to $[RuA_5CO]Cl_2$.

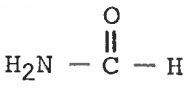
6:2. Formamide as the Source of the Carbonyl Ligand.—

It has been shown that $[RuA_5(OH_2)]^{2+}$ is a very good starting material for the synthesis of ruthenium(II)-ammine complexes in aqueous solutions. In the hope that it would be possible to extend its reactions into non-aqueous solvents, its solubility in several solvents was investigated. However, it was insoluble in all the solvents which were tried except formamide, dimethylformamide and dimethylsulphoxide.

When $[RuA_5(OH_2)]I_2$ was added to formamide it dissolved rapidly, but at high concentrations (10^{-1} M) a yellow precipitate formed within minutes of the aquo-complex dissolving. The infrared spectrum of this yellow solid had absorptions characteristic of a ruthenium(II)-ammine complex and also an absorption at 1948 cm^{-1} and a shoulder at about 1670 cm^{-1} on the asymmetric

ammonia deformation. An iodide analysis of 51.9$_3$% was obtained for this solid. This is very close to that calculated for the formamide complex $[RuA_5(HCONH_2)]I_2$ (calc. = 52.3$_2$%) and suggests that the yellow solid is $[RuA_5(HCONH_2)]I_2$ with $[RuA_5CO]I_2$ present as an impurity. Warming the reaction solution increased the carbonyl content of the precipitate.

Formamide may be considered to be a resonance hybrid of structures I and II. When it is co-ordinated to a metal it has two potential



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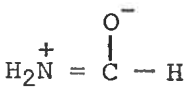

II

co-ordination sites — the nitrogen atom or the oxygen atom. Co-ordination through the oxygen atom would be expected to increase the contribution of structure II to the ground state of the ligand, while co-ordination through the nitrogen atom would favour structure I. Thus oxygen co-ordination would be expected to decrease the frequency of the carbonyl stretching vibration (ν_{CO}), and increase the frequency of the carbon-nitrogen stretch (ν_{CN}), relative to those in the unco-ordinated ligand. Bonding through the nitrogen atom would have the opposite effects on the position of these vibrations (*i.e.* ν_{CO} will be increased, ν_{CN} will be decreased).[22,23] Complexes containing amides (*e.g.* formamide,[24] dimethylformamide,[23] and dimethylacetamide[22]) are known, and in all these complexes the amide is co-ordinated through the oxygen atom.

Although the formamide complex was always contaminated with the carbonyl complex, it was possible to pick out some of its absorptions in the infrared spectrum of the product. They are tabulated in Table 6:2. The assignments for the complex are based on those of Randall *et al.*[23] for dimethylformamide complexes. The shifts in ν_{CO} (1683 to 1670 cm^{-1}) and ν_{CN} (1312 to 1385 cm^{-1}) show that the formamide is co-ordinated through the oxygen atom also.[24]

TABLE 6:2

Infrared absorptions of $[RuA_5(HCONH_2)]I_2$

ammonia vibrations	cm^{-1}	formamide vibrations	cm^{-1}
δ_{NH_3} asym	1605	ν_{CO}	1670 (sh)
δ_{NH_3} sym	1246	ν_{CN}	1385
ρ_{NH_3}	750	δ_{CH}	1127
ν_{Ru-NH_3}	465		621

When slightly oxidised samples of $[RuA_5(OH_2)]I_2$ were added to formamide, the green colour rapidly disappeared and the yellow solid was obtained. This indicated that the ruthenium(III) impurities had been reduced in the reaction and so the more readily available $[RuA_5Cl]Cl_2$ was used instead of $[RuA_5(OH_2)]I_2$ in an attempt to isolate the carbonyl complex.

$[RuA_5Cl]Cl_2$ dissolved in a formamide-water mixture (1:1) to give a

yellow solution, but no solid could be isolated from the solution. When the solution was heated it became colourless and then an intense yellow. Samples from the reaction indicated that these colour changes were associated with the formation of a monocarbonyl complex (ν_{CO} = 1945 cm^{-1} for the iodide salt) which reacted further to give a more soluble dicarbonyl complex (ν_{CO} = 1995 and 2083 cm^{-1} for the iodide salt). It was difficult to control this reaction and the monocarbonyl, $[RuA_5CO]I_2$, could not be obtained pure.

$[RuA_5(OH_2)]I_2$ also dissolved readily in dimethylformamide and dimethylsulphoxide. From the dimethylformamide solution, a solid was isolated which had an absorption at 1650 cm^{-1} in its infrared spectrum. This infrared absorption suggests that dimethylformamide, co-ordinated through the oxygen atom, is present in the complex. No solid could be isolated from dimethylsulphoxide, but it is likely that a complex with the solvent is also formed. The dinitrogen complex, $[RuA_5N_2]X_2$, dissolves in dimethylsulphoxide to form $[RuA_5(DMSO)]X_2$ (DMSO = dimethylsulphoxide).[1]

Solutions of $[RuA_5(OH_2)]^{2+}$ in formamide, dimethylformamide and dimethylsulphoxide were exposed to dinitrogen at 60 atmospheres pressure to see if the dinitrogen complex could be isolated. A solid was isolated from the formamide and dimethylformamide solutions, but none could be obtained from dimethylsulphoxide. The infrared spectra of these solids had the absorption characteristic of the dinitrogen complex, but the solids were not pure. The

solid isolated from formamide was contaminated with the carbonyl complex while the solid isolated from dimethylformamide was contaminated with a complex containing dimethylformamide.

Although this has not been a very critical study, it is apparent that these solvents will not be useful in extending the reactions of $[RuA_5(OH_2)]^{2+}$ into non-aqueous media.

6:3. Conclusion.—

Although the carbonyl complex, $[RuA_5CO]X_2$, has been prepared by the reaction of carbon monoxide[4] with $[RuA_5(OH_2)]^{2+}$, and by the ammination[25] of the carbonyl halide anion, $[Ru(CO)(H_2O)Cl_4]^{2-}$, the abstraction reactions discussed in this chapter may also become a useful preparative route to this complex if a suitable source of the carbonyl group can be found. For example, the carbonyl group may be abstracted from an aldehyde more easily than it is from formamide. The problem with using hydrazine carboxylic acid as the source of the carbonyl ligand is the formation of biproducts from the reaction of hydrazine with the starting complexes.

TABLE 6:1

Infrared spectra of the carbonyl complexes

assignment/anion	Cl^-	Br^-	I^-	BF_4^-	PF_6^-
ν_{NH}	3305 3185 (sh)	3295 3177 (sh)	3290 3230 (sh) 3180 (sh)	3375 3305 3215 (sh)	3380 3310 (sh)
ν_{CO}	1931 1870 (sh)	1936 1887 (sh)	1945	1972 1960 1913 (sh)	1990 1955 (sh)
δ_{NH_3} asym	1627	1622	1612	1637	1632
δ_{NH_3} sym	1280 1232	1279 1250 (sh)	1286 1270 (sh)	1313 1288 (sh)	1306 1290 (sh)
ρ_{NH_3}	806	795	783	787 775	a
δ_{CO}	590	586	579	581	
ν_{Ru-C}	547	536	526	494 (w) 483 (w)	512 483
ν_{Ru-NH_3}	450	442	437	434 358	429

CHAPTER 6

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CHAPTER 7

EXPERIMENTAL

7:1. Analyses.—

Microanalyses. Carbon, hydrogen, nitrogen, fluorine, chlorine and bromine determinations were performed by C.S.I.R.O. Melbourne. Samples of the nitrous oxide and aquo-complexes were sealed under nitrous oxide and argon, respectively, over silica gel, before being sent to Melbourne.

Chloride, Bromide and Iodide determinations in Adelaide were performed using the expanded scale of a Horiba Model F 5 pH meter to follow the changes in potential.

Ruthenium was determined by heating the sample, in a porcelain or platinum boat, to 600°C in the air for one hour and then in a stream of dihydrogen at 600°C for a further hour. It was cooled in a stream of dihydrogen and the residue was weighed as ruthenium metal. This method was unsatisfactory for the tetrafluoroborate and hexafluorophosphate salts because there was a reaction with the combustion boats during the ignition of the sample.

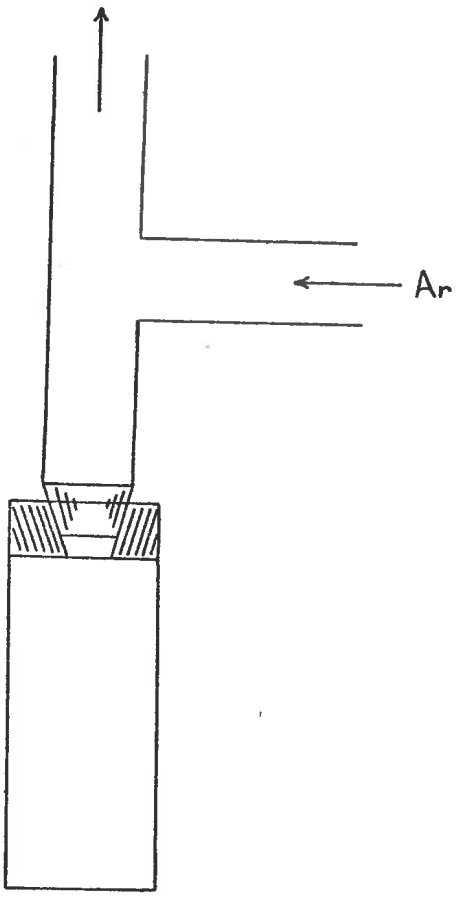
7:2. Physical Measurements.—

7:2:1. Electronic absorption spectra.—

All spectra were recorded on a Unicam SP 700 Spectrophotometer. The

extinction coefficients of the complexes were measured on a Shimadzu Model QR-50 manual spectrophotometer which was calibrated with potassium chromate solution.[1] The decomposition of $[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$ was followed on an external recorder (60 mm/min.; 12.5 mm = 0.20 OD units) connected to a Unicam SP 800 spectrophotometer in the time scan mode (two minute scanning time).

As most of the solutions were air sensitive, the spectra were recorded under an inert atmosphere (dinitrogen or argon). The spectrophotometer cell was first flushed with the particular gas and then the solution was added with a Pasteur pipette against a counterstream of gas using the T-piece as shown.



The cell was sealed with a lightly greased stopper in a stream of gas from the T-piece and then the spectrum was recorded.

7:2:2. Infrared spectra.—

Infrared spectra were recorded in the range 4000-250 cm^{-1} on a Perkin Elmer 457 grating infrared spectrophotometer. Spectra were recorded as Nujol mulls between potassium bromide (4000-400 cm^{-1}) or Polyethylene (600-250 cm^{-1}) plates. Spectra were also recorded as potassium bromide discs for the complexes which did not decompose during the preparation of the disc.

Absorptions due to nitrous oxide in the isotopically labelled nitrous oxide complexes were recorded on the x10 expanded wavenumber scale (1" = 25 cm^{-1} above 2000 cm^{-1}, and 1" = 12.5 cm^{-1} below 2000 cm^{-1}). The positions of the absorptions were measured using carbon monoxide[2] (2500-2000 cm^{-1}), ammonia vapour[2] (1250-1100 cm^{-1}) and atmospheric water vapour[3] (400-250 cm^{-1}) to calibrate the ranges indicated. The accuracy of the frequencies is better than ±0.5 cm^{-1}.

7:2:3. Magnetic susceptibilities.—

Magnetic susceptibilities of the solids were measured at room temperature under nitrous oxide or argon using the Gouy technique.

7:2:4. Mass spectra.—

Gas samples were analysed for dihydrogen, dinitrogen, argon, nitrous oxide and water vapour using an Associated Electrical Industries MS 10 mass spectrometer fitted with a gas handling inlet system.

At an ionisation potential of 70 eV, nitrous oxide was observed to have fragments at m/e values of 14 (N^+), 16 (O^+), 28 (N_2^+), 30 (NO^+) and 44 (N_2O^+). (It is not likely that there is much N_2^{2+} contributing to the m/e = 14 fragment.) The cracking pattern of nitrous oxide was observed to depend on the pressure of the gas in the ionisation chamber, and the variance of the intensity of the peaks due to N^+ and N_2^+ on the total pressure of nitrous oxide (plotted as the peak height of the N_2O^+ fragment) is given in Figure 7:1. Due to adsorption of the nitrous oxide on the inside of the ionisation chamber, it was necessary to equilibrate the samples for one hour before recording the values.

Dinitrogen has fragments at m/e values of 14 (N^+) and 28 (N_2^+) and so it was not possible to determine directly if samples of nitrous oxide contained dinitrogen. The calibration curve for nitrous oxide (Figure 7:1) was used to detect dinitrogen in nitrous oxide. By comparing the intensity of the peaks at m/e values of 14, 28 and 44, 20% dinitrogen in a sample of nitrous oxide could be detected. When the dinitrogen content was expected to be lower than this, the sample tube was cooled in liquid nitrogen to condense the nitrous oxide and then the non-condensable gas was introduced

into the ionisation chamber using a Toepler pump. In this way 1-2% dinitrogen in the nitrous oxide could be detected.

Dihydrogen, water vapour and argon were detected at m/e values of 2, 18 and 40 respectively.

The mass spectra of the isotopically labelled nitrous oxides (Table 7:1) were recorded on a Hitachi Perkin Elmer Model RMU-6D mass spectrometer.

7:2:5. Proton magnetic resonance spectra.—

The proton magnetic resonance spectra were recorded on a Varian Model T 60 nuclear magnetic resonance spectrometer. Tetramethylsilane was used as an external reference.

7:2:6. Powder photographs.—

The powder photographs were recorded using Cu Kα/Ni f radiation (λ = 1.5418 Å), generated by a Phillips PW 1008/80 X-ray spectrometer, and a Nomis powder camera whose radius was 28.65 mm. The samples were mounted in 0.3 mm diameter glass capillaries. Although the film was used in its packet, no allowance was made for this in the calculations.

7:2:7. Manometric measurements.—

Manometric measurements were made using the apparatus in Figure 7:2, which was thermostated to room temperature before each reading.

During measurements at atmospheric pressure, the tap H was open to the atmosphere and the levelling of the two arms of the manometer was achieved with a screw levelling device. The two arms were judged to be level with a cathetometer using black shading on the mercury meniscus. Measurements against a vacuum were made by opening the tap H to the pumps. The head of mercury was measured using the cathetometer. Using a vernier scale the positions of the meniscus could be read to 0.001 cm.

Volume changes (at STP) during a reaction were calculated using the equation,

$$V = \left\{\frac{P_f}{T_f}(V_o + B_f) - \frac{P_i}{T_i}(V_o + B_i)\right\}\frac{T_{273\cdot16}}{P_{760}} \qquad 1$$

where P_i, T_i, B_i are the initial values and P_f, T_f, B_f are the final values of the pressure, temperature and left-hand side burette reading respectively. Values of P_i and P_f were corrected for the solvent vapour pressure. (P_i, $P_f = P_{measured}$ - solvent vapour pressure). V_o is the volume of the apparatus to the zero line of the burette. This was calibrated by trapping a small volume of air in the apparatus and measuring the pressure and volume changes produced on it by changing the position of the mercury reservoir.

As $$P(V_o + B) = \text{constant} \qquad 2$$

the volume of the apparatus, V_o, was obtained from a least squares calculation of the burette reading, B, and the reciprocal of the pressure, 1/P.

Gas samples for mass spectral analyses were collected in the sample tube through taps E and F, or *via* the trap T if this was required, using a Toepler pump.

7:2:8. Balances.—

Solids for analyses or for the determination of extinction coefficients were weighed on a Cahn Model G2 Electrobalance. All other weighings were made on a Mettler H 16 balance weighing to 0.01 mg. The latter weighings were made in a glass weighing tube whose capacity was 100 mg. It was sealed with a ground glass stopper. A thin glass rod was attached to the base of the weighing tube and this was used to manipulate the tube.

7:3. Gases.—

All gases were obtained from Commercial Industrial Gases (Australia) Limited. *Dinitrogen* (oxygen free) and *argon* were used as received. *Nitrous oxide* was passed through a chromous chloride bubbler to remove oxygen, and then through phosphorus pentoxide drying towers before being used.

7:3:1. Deoxygenated nitrous oxide at 40 atmospheres was obtained by collecting the dried, deoxygenated nitrous oxide in a meteorological balloon (volume: 45 litres) and then condensing the filled balloon into a small gas cylinder (volume: *ca.* 100 cc) which was immersed in liquid nitrogen. Three cycles were necessary to fill the small cylinder and a

pressure of 40 atmospheres (the vapour pressure of nitrous oxide at room temperature) was maintained for three to five preparations of the nitrous oxide complexes.

7:3:2. Preparation of isotopically labelled nitrous oxide.—

$^{15}NH_4Cl$ (96.55% enriched) and $^{14}NH_4{}^{15}NO_3$ (96.47% enriched) were obtained from ONIA, Office National Industriel de l'azote.

(a). $^{15}N^{14}N^{16}O$.— $^{15}NH_4Cl$ was converted to $^{15}NH_4{}^{14}NO_3$ by eluting a concentrated solution of the ammonium chloride down a column of Amberlite IRA 400 ion-exchange resin in the nitrate form. The eluent was evaporated to dryness and the ammonium nitrate, free of chloride ion, was dried over phosphorus pentoxide.

The dried ammonium nitrate was decomposed by a method similar to those of Friedman and Bigeleisen[4] and Armor and Taube.[5] The reaction vessel was a glass tube (150 cc) which had a brake seal at one end and a quickfit joint, with a constriction just below it, at the other end.

$^{15}NH_4{}^{14}NO_3$ (0.3 g) was added to the tube and the system was evacuated on the vacuum line. It was exposed to degassed water for two minutes and then sealed at the constriction. The ammonium nitrate was decomposed in an oven at 220-240°C until no ammonium nitrate crystallised on cooling the tube. The nitrous oxide was condensed in liquid nitrogen and the reaction tube was opened on the vacuum line (Figure 7:2). The non-condensables were pumped

off and the nitrous oxide was dried by distilling it from the reaction tube, cooled to -30 — -40°C, into the trap T which was cooled in liquid nitrogen. The reaction tube was removed and the nitrous oxide was redistilled, using the same temperatures, into a clean flask and then back into the trap T in which it was stored. About 100 cc of dry $^{15}N^{14}N^{16}O$ were collected from two decompositions.

(b). $^{14}N^{15}N^{16}O$.— $^{14}NH_4{}^{15}NO_3$, as supplied, was dried over phosphorus pentoxide. $^{14}N^{15}N^{16}O$ was prepared in the same way as $^{15}N^{14}N^{16}O$ and similar yields were obtained.

The isotopic composition of the gases was confirmed by their mass spectra (Table 7:1).

7:4. Preparation of the Complexes.—

$RuCl_3$ and $[RuA_6]Cl_3$ were obtained from Johnson Matthey and Company Limited. AnalaR reagents were used for the precipitating agents wherever possible. Solutions of sodium tetrafluoroborate and ammonium hexafluorophosphate were filtered before being added to the reactions.

Air sensitive complexes were manipulated using standard Schlenk tube techniques.[6]

7:4:1. Preparation of chloropenta-ammineruthenium(III) chloride.—

$[RuA_5Cl]Cl_2$ was prepared by the literature methods from $RuCl_3$[7] or

$[RuA_6]Cl_3$.[8] The samples to be used for the kinetic studies were crystallised from 0.1 M hydrochloric acid.[9] Otherwise they were recrystallised by the method of Allen and Senoff.[7]

Found: Cl, 36.5_8; Ru, 34.6_2.

$H_{15}Cl_3N_5Ru$ requires: Cl, 36.39; Ru, 34.56.

The extinction coefficients of the preparations were between $(1.85\text{-}1.92) \times 10^3$ $M^{-1}cm^{-1}$ (lit.[10] = 1.93×10^3 $M^{-1}cm^{-1}$).

7:4:2. Reduction of chloropenta-ammineruthenium(III) chloride.—

$[RuA_5Cl]Cl_2$ was reduced to $[RuA_5(OH_2)]^{2+}$ with Zn/Hg, $Pt(H_2)$ or electrolytically.

Reduction with Zn/Hg was used to generate $[RuA_5(OH_2)]^{2+}$ for the kinetic studies in Chapter 2. Excess Zn/Hg was added from a bent side tube to a degassed solution of $[RuA_5Cl]Cl_2$ under the appropriate atmosphere. The reduction was usually complete within ten minutes.

Electrolytic reduction was carried out in a glass electrolysis vessel using a mercury pool of about 10 sq cms as the cathode. The electrolysis vessel was a Schlenk tube which had a piece of platinum wire sealed into the glass near the bottom, and a side tube fitted with a B 10 joint half way up the tube. The anode compartment was a glass tube fitted with a B 24 joint and a sintered disc. The platinum foil anode was inside this tube resting

on the sintered disc. During the electrolysis the system was sealed and a slow stream of gas (argon) was passed over the cathode solution and out the anode compartment. The electrolyte solution containing the $[RuA_5Cl]Cl_2$ (15 ml) was pipetted on to the mercury pool and degassed with a stream of argon through the side arm. The anode compartment was fitted in a counterstream of argon. Electrical contact was made by adding a more concentrated solution of the electrolyte to the anode compartment before it was fitted, or by allowing the cathode solution to diffuse into the anode compartment. The former method was used in the preparation of the nitrous oxide complexes and the latter in the kinetic studies. The electrolyte for the preparations was a 0.1 M solution of the precipitating agent to be used. A 0.5 M solution of the precipitating agent was used in the anode compartment to make electrical contact. This concentration was used so that excess ions were present to carry the charge during the reduction and so prevent a decrease in the pH of the cathode solution due to hydrogen ion migration during the reduction.

The $[RuA_5Cl]^{2+}$ was reduced at 0.6 V relative to a saturated calomel electrode under argon. With practice, it was possible to maintain the desired potential without using a reference electrode. Reduction was complete when the current remained constant over ten minutes. (The final background current was usually around 50-100 μA.) The ruthenium(II) solution was removed through the side arm in a stream of argon.

Electrolytic reduction was not used often to produce $[RuA_5(OH_2)]^{2+}$ for the preparations because the volume required to make electrical contact in the cell meant that large amounts of $[RuA_5Cl]Cl_2$ were required to obtain the concentrations used in the preparations. $Pt(H_2)$ reduction was more generally used for this, because of the smaller volumes which could be reduced.

$Pt(H_2)$ *reductions* were carried out in a Schlenk tube which had a second joint fitted near the bottom of the tube. The aqueous solution (or suspension) of $[RuA_5Cl]Cl_2$ was added through this second joint and degassed with argon. Dihydrogen was passed into the solution through a tube which was centrally positioned in the Schlenk tube. The platinum black surface was wrapped around this tube. There were several small holes in the bottom of this tube to give a fine stream of gas over the platinum black. This also stirred the solution. The solutions were reduced for about an hour and then removed through the second joint under a stream of dihydrogen. Reaction vessels of various sizes were used and volumes of 2-10 ml could be reduced by this method. $Pt(H_2)$ reduction was very convenient for the preparation of the ruthenium(II) complexes because concentrated solutions could be obtained without using large amounts of $[RuA_5Cl]Cl_2$.

7:4:3. Preparation of penta-ammine(dinitrogen oxide)ruthenium(II) complexes.—

These complexes were prepared in the presence of excess precipitating

agent using deoxygenated nitrous oxide at forty atmospheres pressure. The reasons for the choice of these reaction conditions were discussed in Chapter 3. The reaction vessel was a glass test tube with a quickfit joint and the pressures were obtained using the larger pressure vessel in Figure 7:3.

While $[RuA_5Cl]Cl_2$ (70-90 mg) was being reduced electrolytically (15 ml, 0.1 M in precipitating agent) or with $Pt(H_2)$ (10 ml of water), the bottom of the pressure vessel containing the reaction vessel was connected to a vacuum line, evacuated and filled with argon several times. When the reduction was complete, the degassed solution of the precipitating agent and then the ruthenium(II) solution were added to the reaction vessel under argon. The top of the pressure vessel was flushed with argon and the vessel was rapidly sealed while a stream of argon was maintained over the solution (in at tap A and out at tap B). The deoxygenated nitrous oxide cylinder was connected at tap A making sure that the connecting brass tubing had been flushed with nitrous oxide. The solution was pressurised and the pressure vessel was allowed to stand in ice for thirty minutes.

The pressure was released, and with a stream of nitrous oxide from the cylinder over the solution, the top of the pressure vessel was removed and the test tube quickly stoppered. It was transferred to a wooden glove box, which was filled with deoxygenated nitrous oxide, and the solid was collected. As the solid collected at the bottom of the test tube during the

reaction it was possible to remove most of the supernatent solution with a Pasteur pipette and then collect the precipitate.

The solid was washed several times with small quantities (1-3 ml) of cold water and then with ethanol. It was dried *in vacuo*, over phosphorus pentoxide, in the absence of light for 1-2 hours.

In this way the bromide, iodide, tetrafluoroborate and hexafluorophosphate salts were isolated. They could be stored at -5°C in the absence of moisture for several weeks without noticeable decomposition.

$[RuA_5(N_2O)]Br_2$ was obtained as a brown-yellow solid (50-60 mg; 45-50%) using potassium bromide (2 g in 5 ml water) as the precipitating agent. Its infrared spectrum indicated that it was usually contaminated with the dinitrogen complex, $[RuA_5N_2]Br_2$.

Found: H, 4.0_1; N, 23.8_0; Br, 42.0*, 41.7_2†.

$H_{15}Br_2N_7ORu$ requires: H, 3.88; N, 25.15; Br, 40.98.

$[RuA_5(N_2O)]I_2$ was obtained as a yellow solid (30 mg, 27%) using potassium iodide (0.75 g in 5 ml water) as the precipitating agent. It was necessary to wash the precipitate a number of times with water to remove a green impurity.

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*microanalysis in Melbourne.

†potentiometrically in Adelaide.

Found: I, 52.0_6†.

$H_{15}I_2N_7ORu$ requires: I, 52.43.

$[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$ was obtained as a pale yellow solid (43-56 mg, 34-45%) using sodium tetrafluoroborate (1 g in 5 ml water) as the precipitating agent.

Found: H, 4.0_2; N, 22.2_2; F, 36.8 .

$H_{17}B_2F_8N_7O_2Ru$ requires: H, 4.06; N, 23.25; F, 36.02.

The hexafluorophosphate salt prepared in this way was contaminated with the aquopenta-ammineruthenium(II) complex which precipitated when the ruthenium(II) solution was added to the ammonium hexafluorophosphate solution, so the preparation was modified. Ammonium hexafluorophosphate (1.0 g in 1 ml water) was added to the ruthenium(II) solution, under argon, to precipitate the aquo-complex. The supernatent solution was removed with a Pasteur pipette and the solid was redissolved in degassed water (5 ml) and then transferred to the reaction vessel under argon. It was pressurised and the product collected in the same way as for the other complexes.

$[RuA_5(N_2O)](PF_6)_2 \cdot H_2O$ was isolated as a yellow solid (46 mg, 35%). An analysis of this complex has not been performed and its formulation is based on its solution properties.

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†potentiometrically in Adelaide.

Attempts to prepare the chloride salt were unsuccessful. Solid hydrated lithium chloride (3 g) was added to the ruthenium(II) solution but only a brown solid, heavily contaminated with a dinitrogen complex, was obtained when the pressure of nitrous oxide was released.

The analytical data and the solution properties of the complexes are tabulated in Tables 3:2 and 3:3.

7:4:4. Preparation of isotopically labelled penta-ammine(dinitrogen oxide)-ruthenium(II) complexes.—

Only 100 cc of the labelled gases were prepared but the pressure of nitrous oxide required for the preparations was achieved by condensing the gas into the smaller pressure vessel in Figure 7:3 the volume of which was 3-4 cc. In this way a pressure of at least twenty atmospheres was obtained and this was sufficient to prepare the complexes.

$[RuA_5Cl]Cl_2$ (15-20 mg) in water (2 ml) was reduced with $Pt(H_2)$. During the reduction a large Schlenk tube containing the lower half of the pressure vessel and a round bottom glass reaction vessel was evacuated and filled with argon several times, on a vacuum line. When the reduction was complete, solid precipitating agent (1.0 g hydrated lithium chloride, 0.3 g potassium bromide, 0.25 g potassium iodide or 0.7 g sodium tetrafluoroborate) was added to the solution and it was transferred under argon to the reaction vessel. In the preparation of the hexafluorophosphate salt, the aquo-complex was

precipitated with solid ammonium hexafluorophosphate (0.3 g), redissolved in degassed water (2 ml) and then transferred to the reaction vessel. With argon passing through the tap, the top half of the pressure vessel was connected to the bottom half and sealed.

It was connected by rubber tubing to the vacuum line at the joint J (Figure 7:2) and gradually immersed in liquid nitrogen to the top of the grooves. This had to be done slowly to avoid breaking the reaction vessel. While the pressure vessel was in the liquid nitrogen, hot air was directed on to the tap to ensure that it did not become frozen or develop a leak. When the solution was frozen, the argon was pumped out and the labelled nitrous oxide was condensed in from the trap T where it was stored. The pressure vessel was warmed to room temperature and after five minutes it was cooled in ice for thirty minutes.

After the reaction was complete the pressure was released and the gas recollected in the trap T. The pressure vessel was opened and the solid was filtered rapidly in the air. In this way 8-12 mg of the complexes were isolated, except for the chloride salt which was too soluble to obtain sufficient solid for an infrared spectrum. Although the solids obtained were not pure, the infrared absorptions of the co-ordinated nitrous oxide could be assigned.

7:4:5. Preparation of aquopenta-ammineruthenium(II) complexes.—

$[RuA_5Cl]Cl_2$ (60-70 mg) in water (3-5 ml) was reduced with $Pt(H_2)$ and

after an hour the platinum surface was removed and the precipitating agent added. The solution was cooled in ice until precipitation was complete and then the precipitate was filtered in the glove box under argon. It was washed with cold water and ethanol and dried *in vacuo* over phosphorus pentoxide in the absence of light. The solids were stored at -5°C over silica gel.

$[RuA_5(OH_2)]Br_2$ was isolated as a yellow solid (15 mg, 15%) by the addition of either solid potassium bromide (3 g) or a saturated solution of potassium bromide (3 ml) to the reduced solution.

Found: Br, 44.3_1.

$H_{17}Br_2N_5ORu$ requires: Br, 43.91.

$[RuA_5(OH_2)]I_2$ was isolated as a green-yellow solid (40 mg, 40%) using solid potassium iodide (2 g) as the precipitating agent. The green colour is due to an impurity (possibly $[RuA_5I]I$) which could not be removed completely. The analytical figures indicate that there is not much of the impurity present.

Found: I, 55.3_5; Ru, 22.4_6.

$H_{17}I_2N_5ORu$ requires: I, 55.41; Ru, 22.05.

$[RuA_5(OH_2)](PF_6)_2 \cdot H_2O$ was isolated as a yellow solid (40-60 mg, 40-50%) by the addition of ammonium hexafluorophosphate (0.75 g in 3 ml water) to the reduced solution. Analytical data for this complex were not very

satisfactory. The high fluoride content indicates that decomposition had occured before the analyses were performed. However, the solution properties and infrared spectrum of the complex were in good agreement with the above formulation.

Found: H, 3.1_6; F, 49.9 ; N, 13.3_7; Ru, 24.9_1, 17.3_0.

$H_{19}F_{12}N_5O_2P_2Ru$ requires: H, 3.74; F, 44.52; N, 13.68; Ru, 19.74.

A tetrafluoroborate salt was isolated as a yellow solid (10 mg, 10%) by the addition of solid sodium tetrafluoroborate (2.5 g) to the reduced solution. Consistent analytical data for this complex could not be obtained. The infrared spectrum of the complex indicated that it contained lattice water and so it may be formulated as $[RuA_5(OH_2)](BF_4)_2 \cdot H_2O$.

The extinction coefficients of these complexes and their solution properties are tabulated in Table 5:1.

7:4:6. Preparation of penta-amminecarbonylruthenium(II) complexes.—

(a). Carbon dioxide as the source of the carbonyl group. $RuCl_3$ (1 g) was dissolved in water (6 ml) and hydrazine hydrate (85%, 10 ml) was added slowly with stirring. The solution was stirred for 18 hours and then filtered several times under gravity. Hydrochloric acid (4 M, *ca.* 10 ml) was added to the filtrate until its pH was nine. The solution was refluxed under carbon dioxide for one to two hours and then allowed to cool. The solid was filtered, washed with water and ethanol and dried *in vacuo* over

phosphorus pentoxide. It was recrystallised three times from dilute ammonia to remove the dicarbonyl complex which was also formed during the reaction.

$[RuA_5CO]Cl_2$ was isolated as a pale yellow solid (0.33 g, 25%).

Found: C, 4.3_6; H, 5.2_4; Cl, 24.6 ; Ru, 35.8_8.

$CH_{15}Cl_2N_5ORu$ requires: C, 4.21; H, 5.30; Cl, 24.57; Ru, 35.44.

It was possible to obtain a second crop of crystals by the addition of hydrochloric acid to the alkaline solution. However, this was more difficult to purify.

During the refluxing under carbon dioxide, dense white fumes were formed. These were probably hydrazine carboxylic acid, but this was not confirmed.

The bromide, iodide, tetrafluoroborate and hexafluorophosphate salts were prepared also. The infrared spectra of the complexes are tabulated in Table 6:1, and are in good agreement with those published.[11,12]

(b). Abstraction of the carbonyl group from formamide. When $[RuA_5(OH_2)]I_2$ (21 mg) was added under argon to degassed, dry formamide (2 ml) a yellow precipitate immediately formed. After heating the solution at 50°C for five minutes, the solid was filtered. Its iodide analysis indicated that it was $[RuA_5(HCONH_2)]I_2$ but the infrared spectrum showed that $[RuA_5CO]I_2$ was also present. The carbonyl complex became the major product

when the solution was heated for longer.

Found: I, 51.9_3.

$CH_{18}I_2N_6ORu$ requires: I, 52.32.

$[RuA_5Cl]Cl_2$ was also found to form the carbonyl complex when it was gently refluxed in aqueous formamide (1:1, 2 ml) for two hours. The complex was precipitated by the addition of the appropriate anion. The products were identified by their infrared spectra which are tabulated in Table 6:1.

7:5. Characterisation of the Complexes.—

7:5:1. Solution properties.—

Extinction coefficients and the conversions to $[RuA_5(OH_2)]^{2+}$ were recorded by pipetting the required volume of 0.1 M methanesulphonic acid (5 or 10 ml) on to the weighed solids in a Schlenk tube under argon, and transferring the solution to the spectrophotometer cell under argon.

Conversion to $[RuA_5Cl]^{2+}$ was achieved by dissolving the weighed solids in 1 M hydrochloric acid (20 ml) and stirring the solution in the air for 30-60 minutes.

Conversion to $[RuA_5OH]^{2+}$ was carried out by adding ferric sulphate (10^{-2} M) in 0.1 M sulphuric acid (10 ml) to the solids under argon. The solution was stirred for 30 minutes to ensure complete oxidation and then dilute ammonia was added in the air. The solution was centrifuged and

removed from the iron hydroxides. The spectrum was recorded immediately and repeated again after 1-2 hours. The spectra were recorded against a blank solution of ferric sulphate which had been treated in the same way as the sample.

7:5:2. Release of nitrous oxide from $[RuA_5(N_2O)](BF_4)_2 \cdot H_2O$.—

The nitrous oxide content of the complex was determined on the vacuum line shown in Figure 7:2. The oxidising agent, cerium(IV) sulphate or ferric sulphate (10^{-2} M, 5 ml), was degassed by the freeze-thaw method in a two necked flask, the volume of which was known. The nitrous oxide complex was added from the weighing tube, through the second neck, on to the frozen solution in the air. The flask was evacuated and the solution thawed as rapidly as possible. It was stirred for one hour. When dioxygen was used as the oxidising agent the complex was dissolved in water and the oxidation was carried out in an atmosphere of dioxygen.

When oxidation was complete (after one hour) the pressure and volume of the system were recorded. The solution was frozen in liquid nitrogen and the non condensable gas (dinitrogen) was pumped off. The nitrous oxide was then distilled over to the trap T. This was achieved by cooling the trap in liquid nitrogen, and cooling the reaction solution to -30 — -40°C. The solution was then allowed to thaw and the dissolved nitrous oxide was collected using the same temperatures. Several blank runs showed that two more cycles ensured that all the nitrous oxide had been collected.

Distillation of the nitrous oxide from the trap, at -40°C, to another vessel which was cooled in liquid nitrogen (two cycles), gave dry nitrous oxide.

After the nitrous oxide had been removed, the vapour pressure of the solution was determined by degassing the solution until a constant pressure was obtained. The reaction flask was then removed and the nitrous oxide was distilled from the trap T, at -30 — -40°C, into a calibrated cap (cooled in liquid nitrogen) at joint J. The pressure and the burette reading were recorded.

From the initial readings and the vapour pressure of the solution, the total gas evolved (dinitrogen and nitrous oxide) was calculated. The volume of nitrous oxide was calculated from the final readings. Results obtained are tabulated in Table 3:4.

7:6. Reaction between $[RuA_5(OH_2)]^{2+}$ *and Nitrous Oxide.*—

7:6:1. Kinetic studies.—

During the reactions, 0.25 or 0.10 ml samples were taken under argon and added to argon saturated water or 0.1 M sulphuric acid.

Zn/Hg reduction. The solution of $[RuA_5Cl]Cl_2$, in a two necked flask fitted with a side arm as shown in Figure 7:2, was degassed by the freeze-thaw method and then Zn/Hg in the side arm was added by up-ending the side arm. When the reductions were under nitrous oxide the reaction commenced immediately. If the reductions were carried out under argon, then the

solution was frozen and the argon replaced with nitrous oxide after the reduction was complete. The reaction commenced when the solution was thawed. Samples were taken through the side joint.

Reaction in the absence of Zn/Hg. The $[RuA_5Cl]Cl_2$ solution was reduced under argon and then transferred to a second reaction vessel under argon. This was achieved by using a pipette which was filled with argon, or by having the second flask connected to the first by a short filter stick and filtering the solution under argon. The second flask was then attached to the vacuum line. The reaction was initiated by replacing the argon with nitrous oxide.

Electrolytic reduction. The electrolysis apparatus described previously was used for these studies. Electrical contact was made by allowing the cathode solution to diffuse into the anode compartment. $[RuA_5Cl]Cl_2$ was reduced under argon, which was then replaced with nitrous oxide, and the reaction was followed while a constant potential of 0.6 V relative to a standard calomel electrode was maintained in the cell. Samples were taken through the side arm against a counterstream of nitrous oxide.

$Pt(H_2)$ *reductions.* These studies were made using the apparatus described in section 7:4:2. $[RuA_5Cl]Cl_2$ was reduced and then nitrous oxide was mixed with the dihydrogen to initiate the reaction. Samples were taken through the side joint under a stream of argon. The gas mixture was saturated with water vapour before it was bubbled through the reaction

solution so that a constant volume was maintained during the reaction.

Variations of the nitrous oxide pressure. Reduced pressures of nitrous oxide were achieved by admitting the required volume of nitrous oxide to the flask. Samples were taken in a counterstream of argon after the flask had been filled with argon. The reaction was continued after the pressure of nitrous oxide had been re-established. This was done by freezing the solution, evacuating the flask, re-admitting the required volume of nitrous oxide, and then thawing the solution.

The kinetic results are tabulated in Tables 2:5, 2:6, 2:8, 2:9a and 2:9b.

7:6:2. Uptake of nitrous oxide.—

The uptake of nitrous oxide during the reaction was measured on the vacuum line shown in Figure 7:2. Nitrous oxide was trapped above the tap A and its volume measured. The solution of $[RuA_5Cl]Cl_2$ was added to the flask and then the side arm containing the Zn/Hg was fitted. The flask was evacuated and then the nitrous oxide was admitted. The reaction was initiated by adding the Zn/Hg to the solution. When the reaction was complete the nitrous oxide was removed into the trap T from the reaction vessel using the technique described in section 7:5:2. A sample of the solution was taken and the concentrations of the monomer and dimer in the solution were determined spectrophotometrically. The nitrous oxide was then

distilled from the trap T, at -40°C, into a calibrated cap at the joint J and its volume determined.

The results obtained are tabulated in Table 2:7 (page 28).

7:6:3. Release of dinitrogen from the reaction solution.—

A sample of a completed reaction solution, in which the concentrations of the monomer and dimer had been measured, was transferred to a two necked flask on the vacuum line. Cerium(IV) sulphate (10^{-2} M, 5 ml) in a second flask was fitted by a U bend to the first flask and the system was degassed by the freeze-thaw method. Cerium(IV) sulphate was then added to the solution containing the dinitrogen complexes and the solution was stirred for an hour.

The volume of dinitrogen evolved was measured taking into account the partial pressure of the solution which was determined in the same way as in section 7:5:2.

7:7. Computer Calculations.—

The analysis of the infrared spectra, structure factor, kinetic and least square calculations were performed on the University of Adelaide's CDC 6400 computer.

The programmes developed for the analysis of the infrared data are given in Appendix III. The structure factors for $[RuA_5(N_2O)]Br_2$ were

calculated using the programme of Dr. M.R. Snow. The kinetic results were processed using the programme of Mr. N. Van der Hoek.

TABLE 7:1

Mass spectra of isotopically labelled nitrous oxide

Relative peak heights (as % of the strongest peak)

m/e	45	44	31	30	29	28	16	15	14
Species	$^{*}N_2O^{+}$	N_2O^{+}	$^{*}NO^{+}$	NO^{+}	$^{*}N_2^{+}$	N_2^{+}	O^{+}	$^{*}N^{+}$	N^{+}
$^{14}N^{14}N^{16}O$	0.9	100		13		8	0.3		0.5
$^{15}N^{14}N^{16}O$	100	4		13	5	1	0.5_5	0.5	0.4
$^{14}N^{15}N^{16}O$	100	5	12.5	1.8_5	5		0.4	0.3_5	0.3

FIGURE 7:1

Mass spectral calibration curve for nitrous oxide

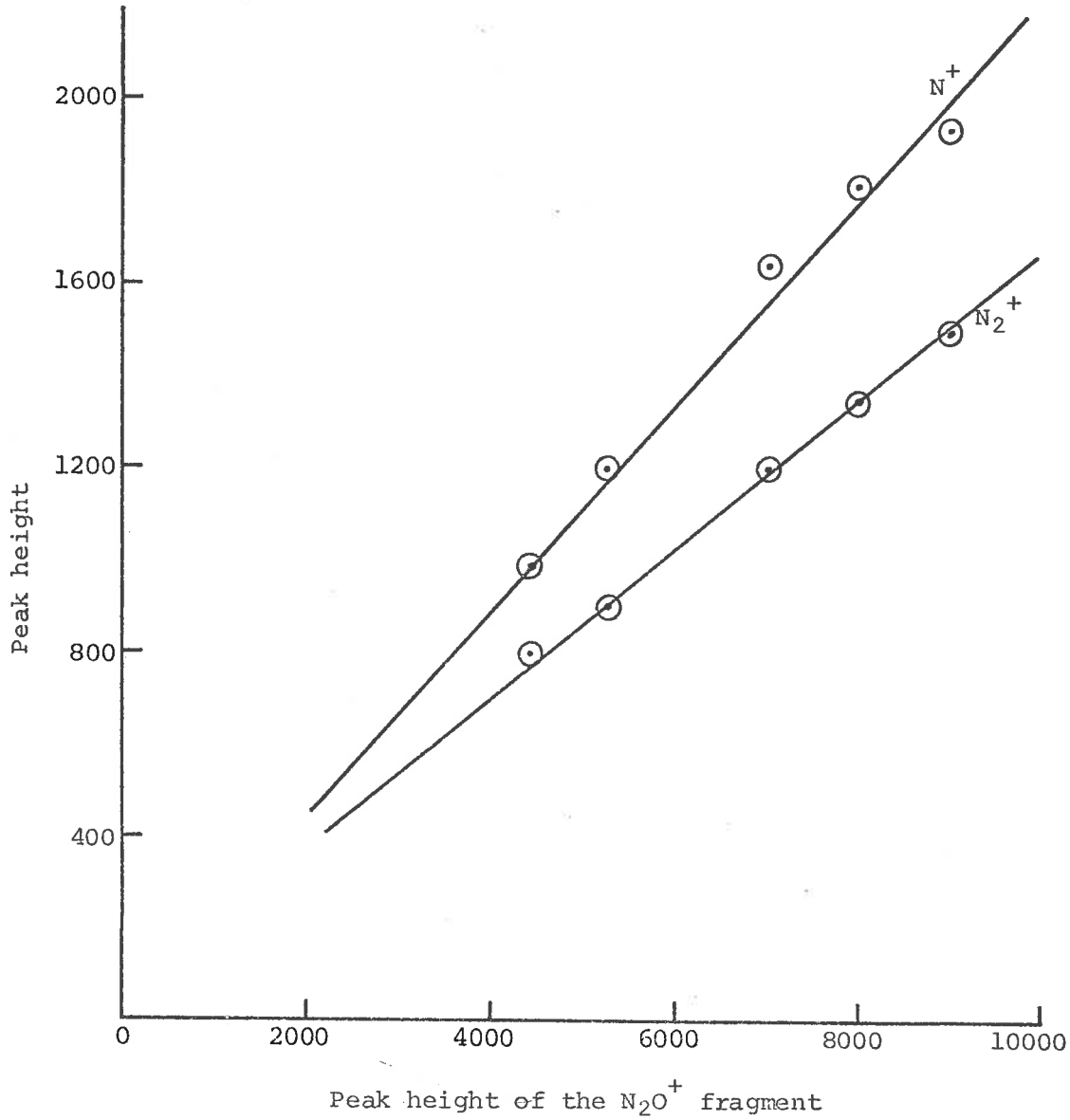


FIGURE 7:2. Vacuum Line

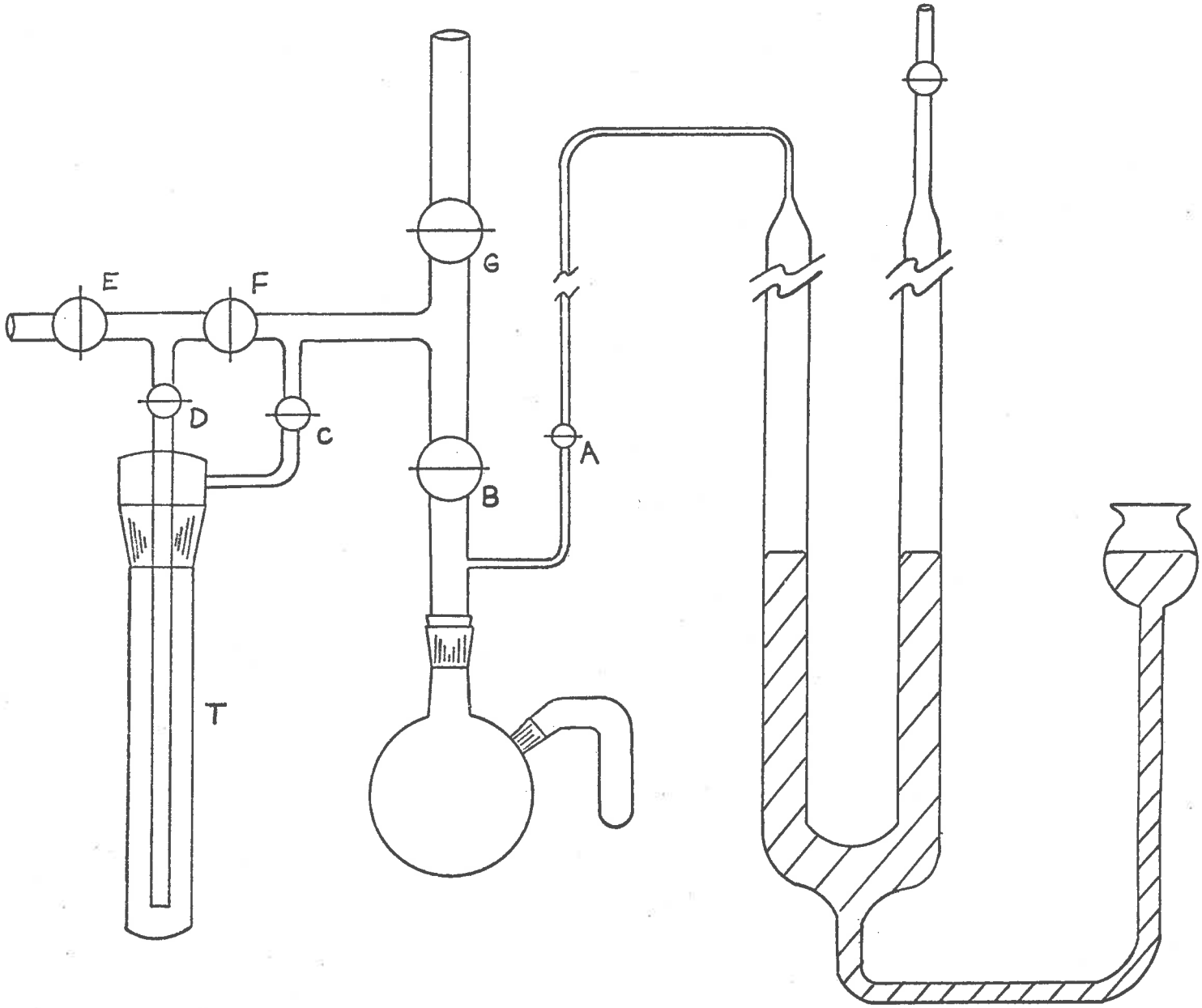
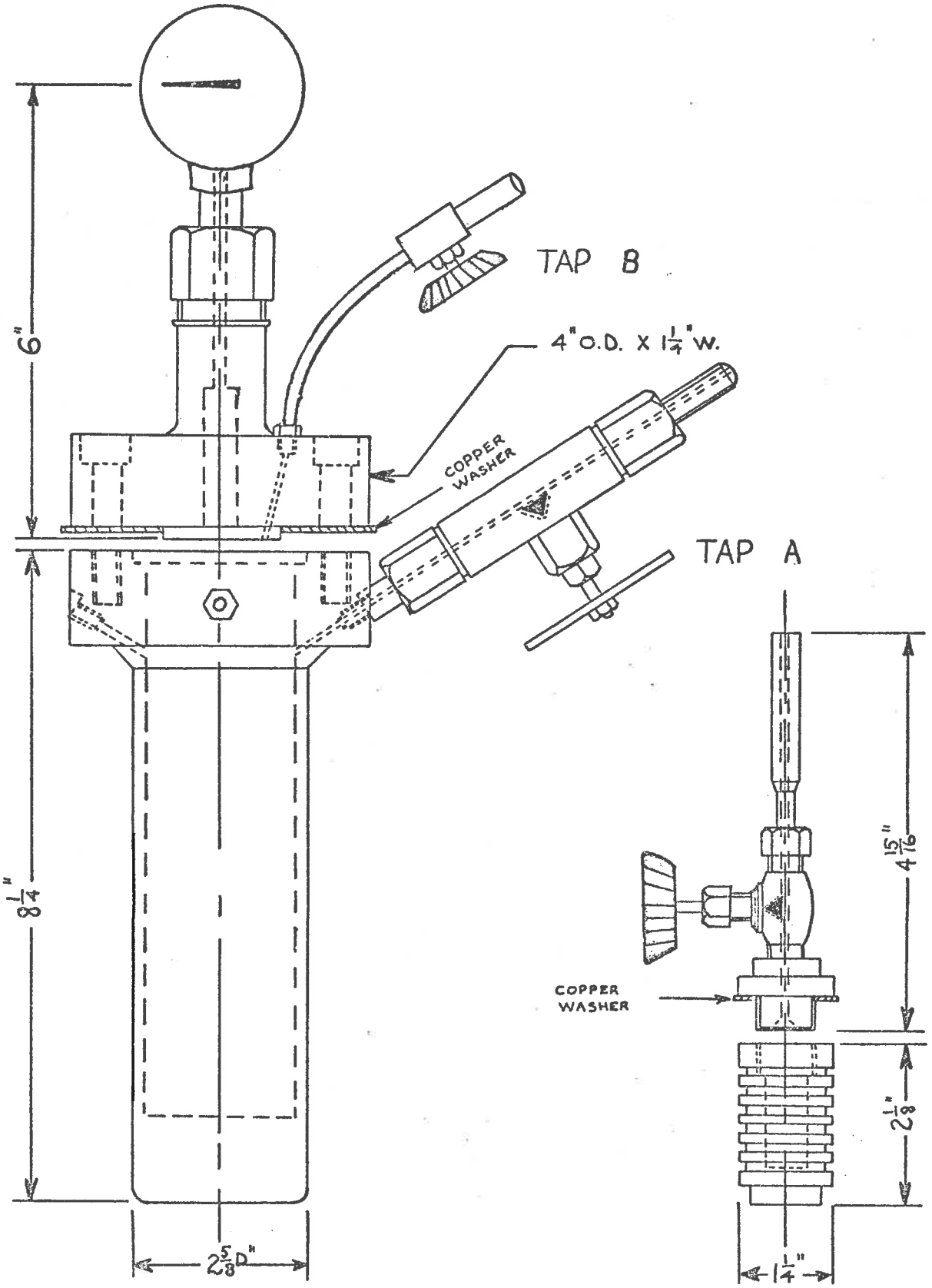


FIGURE 7:3. Pressure Vessels



CHAPTER 7

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APPENDIX I

METHOD USED FOR THE NORMAL CO-ORDINATE ANALYSIS OF THE INFRARED SPECTRA

Although it is not the method generally used for normal co-ordinate analyses, the method used here follows that given by Herzberg*. (The equation numbers in brackets refer to the corresponding equation in Herzberg.)

(a). Derivation of the secular equation. For any particle i carrying out simple harmonic motion of frequency ν_i the displacement S_i is given by

$$S_i = S_i^\circ \cos(2\pi\nu_i t + \Psi) \qquad 1 \text{ (II,2)}$$

where S_i° is the amplitude, t the time and Ψ a phase constant.

The acceleration of the particle will be

$$a_i = \frac{d^2S_i}{dt^2} = -4\pi^2\nu_i^2 S_i^\circ \cos(2\pi\nu_i t + \Psi)$$

$$= -4\pi^2\nu_i^2 S_i \qquad 2 \text{ (II,3)}$$

The restoring force under whose action the simple harmonic motion is carried out is

$$F_i = m_i a_i = -4\pi^2\nu_i^2 m_i S_i \qquad 3 \text{ (II,4)}$$

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* G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, 1945, Chapter II.

where m_i is the mass of the particle i.

Now $$F_i = -\frac{d(V_i)}{dS_i} \qquad 4$$

so the potential energy, V_i, for the simple harmonic oscillator is

$$V_i = 2\pi^2\nu_i^2 m_i S_i^2$$

$$= 1/2 k_i S_i^2 \qquad 5 \text{ (II,21)}$$

where $$k_i = 4\pi^2\nu_i^2 m_i \qquad 6 \text{ (II,22)}$$

is the force constant of the harmonic oscillation. At the equilibrium position, $S_i = 0$, the potential energy is taken to be zero.

The kinetic energy is

$$T_i = 1/2 m_i \nu_i^2 = 1/2 m_i \dot{S}_i^2 \qquad 7 \text{ (II,23)}$$

where $$\dot{S}_i = \frac{dS_i}{dt}$$

Thus the total energy is

$$H_i = V_i + T_i = 1/2(k_i S_i^2 + m_i \dot{S}_i^2) \qquad 8 \text{ (II,24)}$$

For small displacements, the potential energy of the nucleii in a molecule, referred to the equilibrium position as V = 0, may be given as a first approximation by

$$V = 1/2 \sum_{ij} a_{ij} q_i q_j \qquad 9 \text{ (II,94; II,106)}$$

where q, the displacement, may be in any co-ordinate system (*e.g.*, cartesian, internal or normal) and a_{ij} is a function of the force constants in the system.

The kinetic energy of the nucleii is given by

$$T = 1/2 \sum_{ij} b_{ij}\dot{q}_i\dot{q}_j \qquad 10 \text{ (II,95; II,107)}$$

If new co-ordinates n_1, n_2, ... n_N (N is the number of degrees of freedom in the molecule) are introduced by means of linear equations

$$q_i = C_{i1}n_1 + C_{i2}n_2 + ... + C_{iN}n_N \qquad 11 \text{ (II, 31)}$$

then the correct choice of the coefficients C_{ik} will allow V and T to be written as

$$V = 1/2(\lambda_1 n_1^2 + \lambda_2 n_2^2 + ... + \lambda_N n_N^2) \qquad 12 \text{ (II,32)}$$

$$\text{and } T = 1/2(\dot{n}_1^2 + \dot{n}_2^2 + ... + \dot{n}_N^2) \qquad 13 \text{ (II,33)}$$

then λ_i can be shown to be the roots of the *secular equation* of the problem:-

$$\begin{vmatrix} b_{11}\lambda - a_{11} & b_{12}\lambda - a_{12} & b_{13}\lambda - a_{13} \cdots \\ b_{21}\lambda - a_{21} & b_{22}\lambda - a_{22} & b_{23}\lambda - a_{23} \cdots \\ b_{31}\lambda - a_{31} & b_{32}\lambda - a_{32} & b_{33}\lambda - a_{33} \cdots \\ \vdots \quad \vdots & \vdots \quad \vdots & \vdots \quad \vdots \end{vmatrix} = 0 \qquad 14 \text{ (II,96)}$$

where a_{ij} and b_{ij} are the coefficients of the equations 9 and 10 respectively.

(b). A solution of the secular equation can be achieved by expanding the determinant and solving the function which is obtained. The high degree of this function permits only simple systems to be solved this way. When symmetry co-ordinates are used as the co-ordinate system then the secular equation obtained consists of the product of several smaller determinants. There is a determinant for each vibrational symmetry type in the molecule and the degree of the determinant in each case is determined by the number of vibrations which have that particular symmetry. As each of these determinants can be solved independently, solving the complete secular equation for the molecule is easier.

The roots of the secular equation are usually written in the form

$$\Sigma\lambda_i = f_1(k,m) \qquad 15$$

$$\Sigma\lambda_i\lambda_j = f_2(k,m) \qquad i\neq j \qquad 16$$

$$\Sigma\lambda_i\lambda_j\lambda_l = f_3(k,m) \qquad i\neq j\neq l \qquad 17$$

where $f_n(k,m)$ are functions of the force constants and the masses of the atoms. The functions are the coefficients of the various powers of λ in the expanded form of the secular equation.

In nitrous oxide the stretching vibrations (ν_1 and ν_3) have Σ^+ symmetry and can be considered separately from the bending vibration (ν_2) which has Π symmetry.

APPENDIX II

NORMAL CO-ORDINATE ANALYSIS OF LINEAR XYZ AND LINEAR XYZW

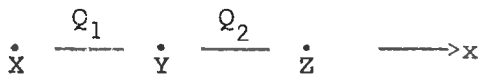
The normal co-ordinate analysis of linear XYZ and linear XYZW given here follows the method given in Appendix I. (The equations are numbered the same as in Herzberg.[1])

(a). Normal co-ordinate analysis of linear XYZ. The calculations were made using internal symmetry co-ordinates[2,3] because:-

(i) it was possible to consider the stretching vibrations, which have Σ^+ symmetry, separate from the bending vibration which has Π symmetry. This was advantageous because only relations between the stretching vibrations was required and the degree of the resulting secular equation was only two.

(ii) the form of the potential energy function for this co-ordinate system is simple no matter how many interaction constants are considered.

and (iii) it would be easy to extend the calculations to the second model, linear XYZW.



For linear XYZ, the internal symmetry co-ordinates Q_1 and Q_2 are as shown. The force constants k_1 and k_2 are the force constants for the bonds XY and YZ respectively and k_{12} is the interaction constant. The cartesian displacement co-ordinates are x_1, x_2 and x_3 for X, Y and Z, respectively, in the direction shown.

The potential energy of the system is given by

$$2V = \sum_{ij} a_{ij} Q_i Q_j \qquad a_{ij} = a_{ji} \qquad \text{II,94; II,106}$$

thus, $$2V = a_{11}Q_1^2 + a_{22}Q_2^2 + 2a_{12}Q_1Q_2$$

where $a_{11} = k_1$, $a_{22} = k_2$ and $a_{12} = k_{12}$.

In Cartesian co-ordinates, the kinetic energy is

$$2T = \sum_i m_i(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \qquad \text{II,28}$$

i.e., $$2T = (m_1\dot{x}_1^2 + m_2\dot{x}_2^2 + m_3\dot{x}_3^2)$$

for this system where $\dot{y}_i = \dot{z}_i = 0$.

Written in the internal symmetry co-ordinates the kinetic energy is

$$2T = \sum_{ij} b_{ij}\dot{Q}_i\dot{Q}_j \qquad \text{where } b_{ij} = b_{ji} \qquad \text{II,95; II,107}$$

thus, $$2T = b_{11}\dot{Q}_1^2 + b_{22}\dot{Q}_2^2 + 2b_{12}\dot{Q}_1\dot{Q}_2$$

Using the relations,

$$Q_1 = x_2 - x_1$$

$$Q_2 = x_3 - x_2$$

and $$0 = m_1x_1 + m_2x_2 + m_3x_3$$

and the equations II,101, the Cartesian co-ordinates expressed in terms of the internal symmetry co-ordinates are,

$$x_1 = -1/M((m_2 + m_3)Q_1 + m_3Q_2)$$

$$x_2 = -1/M(-m_1Q_1 + m_3Q_2)$$

and $$x_3 = -1/M(-m_1Q_1 - (m_1 + m_2)Q_2)$$

where $M = m_1 + m_2 + m_3$.

These relations are also valid for the time derivatives, so on substituting for $\dot{x}_1$, $\dot{x}_2$ and $\dot{x}_3$ in equation II,28, and evaluating the coefficients with those in equation II,95 we have

$$b_{11} = \frac{m_1}{M}(m_2 + m_3)$$

$$b_{22} = \frac{m_3}{M}(m_1 + m_2)$$

and $$b_{12} = \frac{m_1 \cdot m_3}{M}$$

where $M = m_1 + m_2 + m_3$.

The secular equation for the system is of the form,

$$\begin{vmatrix} b_{11}\lambda - a_{11} & b_{12}\lambda - a_{12} \\ b_{21}\lambda - a_{21} & b_{22}\lambda - a_{22} \end{vmatrix} = 0 \qquad \text{II,96}$$

which on expansion gives,

$$(b_{11}b_{22} - b_{12}^2)\lambda^2 - (a_{22}b_{11} + a_{11}b_{22} - 2a_{12}b_{12})\lambda + (a_{11}a_{22} - a_{12}^2) = 0$$

where $a_{12} = a_{21}$ and $b_{12} = b_{21}$.

Hence,[4]

$$\lambda_1 + \lambda_2 = \frac{a_{22}b_{11} + a_{11}b_{22} - 2a_{12}b_{12}}{b_{11}b_{22} - b_{12}^2}$$

and $$\lambda_1\lambda_2 = \frac{a_{11}a_{22} - a_{12}^2}{b_{11}b_{22} - b_{12}^2}$$

Where λ_1 and λ_2 are the roots of the quadratic equation (compare these equations with II,117 and II,118).

Substituting for a_{ij} and b_{ij} we have,

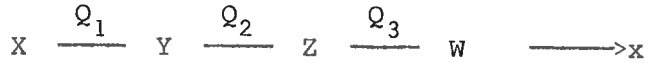
$$\lambda_1 + \lambda_2 = k_1\left(\frac{m_1 + m_2}{m_1 \cdot m_2}\right) + k_2\left(\frac{m_2 + m_3}{m_2 \cdot m_3}\right) - \frac{2k_{12}}{m_2}$$

and $$\lambda_1\lambda_2 = \frac{m_1 + m_2 + m_3}{m_1 \cdot m_2 \cdot m_3}\left(k_1k_2 - k_{12}^2\right)$$

As $$\lambda_i = 4\pi^2\nu_i^2, \qquad \text{II,37}$$

where ν_i is a fundamental vibration of the system, the roots for nitrous oxide were written as λ_1 and λ_3 so that a direct comparison with the fundamental vibrations of nitrous oxide, ν_1 and ν_3, could be made.

(b). Normal co-ordinate analysis of linear XYZW.



For linear XYZW, the internal symmetry co-ordinates Q_1, Q_2 and Q_3 are as shown. The force constants k_1, k_2 and k_3 are the force constants of the bonds XY,YZ and ZW, respectively. The interaction constants between the bond XY and YZ, YZ and ZW, and XY and ZW are k_{12}, k_{23} and k_{13} respectively. The Cartesian displacement co-ordinates are x_1, x_2, x_3 and x_4 for the atoms X, Y, Z and W respectively in the direction shown.

As the working for linear XYZW is similar, but more complicated, than that for linear XYZ above, only the final equations for each step will be given.

For linear XYZW the potential energy is

$$2V = a_{11}Q_1^2 + a_{22}Q_2^2 + a_{33}Q_3^2 + 2a_{12}Q_1Q_2 + 2a_{23}Q_2Q_3 + 2a_{13}Q_1Q_3$$

where $a_{11} = k_1$, $a_{22} = k_2$, $a_{33} = k_3$, $a_{12} = k_{12}$, $a_{23} = k_{23}$ and $a_{13} = k_{13}$

The kinetic energy expressions are,

$$2T = m_1\dot{x}_1^2 + m_2\dot{x}_2^2 + m_3\dot{x}_3^2 + m_4\dot{x}_4^2$$

and $$2T = b_{11}\dot{Q}_1^2 + b_{22}\dot{Q}_2^2 + b_{33}\dot{Q}_3^2 + 2b_{12}\dot{Q}_1\dot{Q}_2 + 2b_{23}\dot{Q}_2\dot{Q}_3 + 2b_{13}\dot{Q}_1\dot{Q}_3$$

The equations,

$$Q_1 = x_2 - x_1$$

$$Q_2 = x_3 - x_2$$

$$Q_3 = x_4 - x_3$$

and $$0 = m_1x_1 + m_2x_2 + m_3x_3 + m_4x_4$$

were used to express the Cartesian co-ordinates in terms of the internal symmetry co-ordinates, and it was found that,

$$x_1 = -1/M((m_2 + m_3 + m_4)Q_1 + (m_3 + m_4)Q_2 + m_4Q_3)$$

$$x_2 = -1/M(-m_1Q_1 + (m_3 + m_4)Q_2 + m_4Q_3)$$

$$x_3 = -1/M(-m_1Q_1 - (m_1 + m_2)Q_2 + m_4Q_3)$$

and $$x_4 = -1/M(-m_1Q_1 - (m_1 + m_2)Q_2 - (m_1 + m_2 + m_3)Q_3)$$

where $M = m_1 + m_2 + m_3 + m_4$

Substituting into the kinetic energy expression and equating the coefficients as for linear XYZ we have,

$$b_{11} = \frac{m_1}{M}(m_2 + m_3 + m_4)$$

$$b_{22} = \frac{(m_1 + m_2)(m_3 + m_4)}{M}$$

$$b_{33} = \frac{m_4}{M}(m_1 + m_2 + m_3)$$

$$b_{12} = \frac{2m_1}{M}(m_3 + m_4)$$

$$b_{23} = \frac{2m_4}{M}(m_1 + m_2)$$

and $$b_{13} = \frac{2m_1 \cdot m_4}{M}$$

where $M = m_1 + m_2 + m_3 + m_4$

The secular equation for this system is of the form,

$$\begin{vmatrix} b_{11}\lambda - a_{11} & b_{12}\lambda - a_{12} & b_{13}\lambda - a_{13} \\ b_{21}\lambda - a_{21} & b_{22}\lambda - a_{22} & b_{23}\lambda - a_{23} \\ b_{31}\lambda - a_{31} & b_{32}\lambda - a_{32} & b_{33}\lambda - a_{33} \end{vmatrix} = 0$$

Expansion of this determinant gives a cubic equation whose coefficients are functions of a_{ij} and b_{ij}. Substituting for a_{ij} and b_{ij} in these coefficients, simplifying and using the relationships between the coefficients of a polynomial[4] we have,

$$\lambda_1 + \lambda_2 + \lambda_3 = k_1\left(\frac{m_1 + m_2}{m_1 \cdot m_2}\right) + k_2\left(\frac{m_2 + m_3}{m_2 \cdot m_3}\right) + k_3\left(\frac{m_3 + m_4}{m_3 \cdot m_4}\right) - \frac{2k_{12}}{m_2}$$

$$- \frac{2k_{23}}{m_3} - 2k_{13}(0)$$

$$\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3 = \frac{m_2 + m_3 + m_4}{m_2 \cdot m_3 \cdot m_4}(k_2k_3 - k_{23}^2) + \frac{m_1 + m_2 + m_3}{m_1 \cdot m_2 \cdot m_3}(k_1k_2 - k_{12}^2)$$

$$+ \frac{(m_1 + m_2)(m_3 + m_4)}{m_1 \cdot m_2 \cdot m_3 \cdot m_4}(k_1k_3 - k_{13}^2) + \frac{2}{m_3}\left(\frac{m_1 + m_2}{m_1 \cdot m_2}\right)(k_{13}k_{12} - k_1k_{23})$$

$$+ \frac{2}{m_2}\left(\frac{m_3 + m_4}{m_3 \cdot m_4}\right)(k_{13}k_{23} - k_3k_{12}) + \frac{2}{m_2 \cdot m_3}(k_{12}k_{23} - k_2k_{13})$$

and $$\lambda_1\lambda_2\lambda_3 = \frac{m_1 + m_2 + m_3 + m_4}{m_1 \cdot m_2 \cdot m_3 \cdot m_4}(k_1k_2k_3 + 2k_{12}k_{13}k_{23} - k_1k_{23}^2 - k_2k_{13}^2 - k_3k_{12}^2)$$

The roots were written as λ_1, λ_3 and λ_4 so that direct comparison with the fundamental vibrations of the co-ordinated nitrous oxide, ν_1, ν_3 and ν_4, could be made.

1. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, 1945, Chapter II.

2. Reference 1, pp. 142-148.

3. E.B. Wilson Jr., J.C. Decius, and P.C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955, p. 117.

4. For a polynomial

$$A(x) = a_o x^n + a_1 x^{n-1} + \ldots . a_{n-1} x + a_n \qquad a_o \neq o$$

having n roots $x_1, x_2 \ldots . , x_n$.

then,
$$\sum_i x_i = -\frac{a_1}{a_o}$$

$$\sum_{ij} x_i x_j = +\frac{a_2}{a_o} \qquad i \neq j$$

$$\sum_{ijk} x_i x_j x_k = -\frac{a_3}{a_o} \qquad i \neq j \neq k$$

etc.

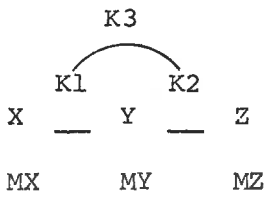
see, L. Weisner, "Introduction to the Theory of Equations", MacMillan, New York, 1938, p. 42.

APPENDIX III

COMPUTER PROGRAMMES

1. F CONST.—

This programme was used to calculate the vibrational frequencies for a set of force constants, which could be varied, using the model linear XYZ.




```
      PROGRAM F CONST(INPUT, OUTPUT)
      REAL K3
      DATA MX,MY,MZ,K3,H/14,14,16,13.6,5.8894E-02/
C     K1 = K(XY)=I.  K2 = K(YZ)=J.  K3 = INTERACTION CONSTANT.
C     FORCE CONSTANT IS WRITTEN AS 150E+04 = 15.0E+05 K IS GIVEN 150
C        AND THE POWER IS INCORPORATED INTO THE CONSTANTS C,D ETC
      A = 1
      C = (MX + MY + MZ)/(MX*MY*MZ)*1E+08
      D = K3*K3
      E = (1./MX + 1./MY)*1E+04
      F = (1./MY + 1./MZ)*1E+04
      G = (2*K3/MY)*1E+04
    9 PRINT1,K3
    1 FORMAT(1H1,6X,* FORCE CONSTANTS FOR N(14)  N(14)  O(16) *, 10X,*
     *K3 =*F6.3//)
      PRINT8,A,C,D,E,F,G
    8 FORMAT(1HX,*A =*E10.4,5X,*C =*E10.4,5X,*D =*E10.4,5X,*E =*E10.4,
```

```
     *5X,*F =*E10.4,5X,*G =*E10.4,///)
      PRINT6
    6 FORMAT(1HX,17X,*K1*18X*K2*16X*V3*18X*V1*//)
C     U = ((MX+ MY+ MZ)/(MX*MY*MZ))*(K1*K2-K3*K3)*1E+08 = C(K1*K2-D)
C     W = (1/MX+1/MY)*K1*E+04  +  (1/MY+1/MZ)*K2*E+04  -  (2*K3/MY)*E+04.
C     W = E*K1 + F*K2 - G
   19 READ10,K,L,M,N
   10 FORMAT(4I5)
      IF(K.EQ.0)STOP
      DO 11 I=K,L
      DO 12 J=M,N
      U = C*((I*J) - D)
      W = ((E*I) + (F*J) - G)
      R = U*1E-10
      S = -W*1E-05
      CALL QUADRAT(A,S,R,X,Z)
      X = X*1E+05    $    Z = Z*1E+05
      IF(X.LT.0)2,3
    2 X = 0
    3 IF(Z.LT.0)4,5
    4 Z = 0
    5 V1 = SQRT(X/H)              $   V3 = SQRT(Z/H)
      PRINT7,I,J,V1,V3
    7 FORMAT(1HX,2(10X,I10),2(10X,F10.3),/)
   12 CONTINUE
   11 CONTINUE
      GO TO 19
      END OF F CONST
```

```
      SUBROUTINE QUADRAT(A,B,C,X,Z)
   26 IF(B*B.LT.(4*A*C))2,7
    2 X = 0  $  Z = 0
      RETURN
    7 DISC = B*B-(4*A*C)
      IF(DISC.EQ.0)GO TO 4
      DET = SQRT(DISC)
      GO TO 10
    4 DISC = DET
   10 X = (-B+DET)/(2*A)
      Z = (-B-DET)/(2*A)
      RETURN
      END
```

In this form, the programme was used to calculate frequencies for force constants over the ranges, (15.0-20.0) $\times 10^5$ and (8.0-10.0) $\times 10^5$ dyne cm^{-1}. (*i.e.* values read in for K,L, M and N were 150,200,80 and 100, respectively.) In this way an idea of the force constants which gave a particular set of frequencies was obtained.

By rewriting U and W as,

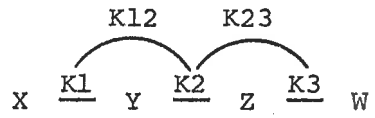
```
      U = C*((I*J/100) - D)
and   W = ((E*I/10) + (F*J/10) - G)
```

and using values for K,L,M and N such as 1950,1970,950 and 960 (for the hexafluorophosphate salt of the unlabelled complex) it was possible to find the combination of the force constants, K1 and K2, which gave a particular set of the frequencies, V3 and V1. Calculations involving a variation in K3 were carried out by including a read statement for K3 and incorporating K1 and K2 in the data statement. A series of K3 values were calculated by

modifying the do loops.

2. K AND V.—

For the model linear XYZW, force constants were calculated from the observed frequencies in the isotopically labelled complexes using this programme. V1, V2 and V3 are the frequencies for the complex whose masses are M1, M2, M3 and M4. Similarly V4, V5 and V6 are the frequencies for the complex with the masses M5, M6, M7 and M8, and V7, V8 and V9 are the frequencies for the complex with the masses M9, M10, M11 and M12. When the nitrous oxide is considered to be co-ordinated through the oxygen atom, the frequencies V1, V4 and V7 are those of the ν_3 absorption and the frequencies V2, V5 and V8 are those of the ν_1 absorption and *vica versa* when the nitrous oxide is bonded through the nitrogen atom. V3, V6 and V9 are the metal-ligand stretching vibration in the complexes. As this vibration was not known it was set to zero initially in the calculations and was evaluated after the initial set of force constants had been obtained. The interaction constants, K12 and K23, could be changed with each new set of data, or if they were to be kept constant for a series of calculations, they were defined in the data statement.




```
      PROGRAM K AND V (INPUT,OUTPUT)
      REAL M1,M2,M3,M4,M5,M6,M7,M8,M9,M10,M11,M12,K1,K2,K3,K12,K23
      DATA H/5.8894E-02/
   41 READ 5,M1,M2,M3,M4,M5,M6,M7,M8,M9,M10,M11,M12
    5 FORMAT(12(F5.0))
      IF(M1.EQ.0) STOP
      READ8,V1,V2,V3,V4,V5,V6,V7,V8,V9
    8 FORMAT(8(F10.0))
      READ 44,K12,K23
   44 FORMAT(2F10.4)
         K12 = K12*1E+05       $       K23 = K23*1E+05
      PRINT 1,M1,M2,M3,M4
    1 FORMAT(1H1,*SOLUTION FROM FREQUENCIES V1 AND V3 FOR* 2/
     * 20X,*  M1(*F2*)   M2(*F2*)   M3(*F2*)   M4(*F3*)*,2/ 40X,* ANION
     * IS   * ///)
      X = (M1+M2+M3+M4)/(M1*M2*M3*M4)
      Y = (M5+M6+M7+M8)/(M5*M6*M7*M8)
      Z = (M9+M10+M11+M12)/(M9*M10*M11*M12)
      I = 0
   11 A = V1*V1*H  +  V2*V2*H  +  V3*V3*H + 2*K12/M2 + 2*K23/M3
      B = V4*V4*H  +  V5*V5*H  +  V6*V6*H + 2*K12/M6 + 2*K23/M7
      C = V7*V7*H  +  V8*V8*H  +  V9*V9*H + 2*K12/M10+ 2*K23/M11
      A1 = ((M1+M2)/(M1*M2))     $     B1 = ((M2+M3)/(M2*M3))
      C1 = ((M3+M4)/(M3*M4))     $     A2 = ((M5+M6)/(M5*M6))
      B2 =  (M6+M7)/(M6*M7)      $     C2 = (M7+M8)/(M7*M8)     $     A3 = (M9+M10)
     */(M9*M10)     $     B3 = (M10+M11)/(M10*M11)   $  C3 = (M11+M12)/(M11*M12)
      D1 = B1 - B2*A1/A2      $      D2 = B1 - B3*A1/A3
      E1 = C1 - C2*A1/A2      $      E2 = C1 - C3*A1/A3
      F1 = A  - B*A1/A2       $      F2 = A - C*A1/A3
      PRINT6,A,A1,A2,A3,B,B1,B2,B3,C,C1,C2,C3,D1,D2,E1,E2,F1,F2
```

```
 6 FORMAT(1HX,4(* A = *E11.3,10X,)/4(* B = *E11.3,10X)/4(* C = *
  *E11.3,10X)/2(* D = *E11.3,10X)2(* E = *E11.3,10X)/2(* F = *E11.3,
  *10X))
    K3 = (F1-F2*D1/D2)/(E1-E2*D1/D2)
    K2 = (F1-K3*E1)/D1
    K1 = (A-K2*B1 - K3*C1)/A1
    R = (K1*K2*K3-K3*K12*K12)*X/(V1*V1*V2*V2*H*H*H)
    IF(R.LT.0)21,22
21  R = 0
22  V3 = SQRT(R)
    S = (K1*K2*K3-K3*K12*K12)*Y/(V4*V4*V5*V5*H*H*H)
    IF(S.LT.0)23,24
23  S = 0
24  V6 = SQRT(S)
    T = (K1*K2*K3-K3*K12*K12)*Z/(V7*V7*V8*V8*H*H*H)
    IF(T.LT.0)25,26
25  T = 0
26  V9 = SQRT(T)
    PRINT 3,K1,K2,K3,V3,V6,V9
 3  FORMAT(1HX,6X,3(*K = *E11.4,10X)//6X,3(*V = *E11.4,10X)//)
    I = I+1
    IF(I.EQ.5) 10,11
10  PRINT 2,K1,K2,K3,K12,K23,V1,V2,V3,V4,V5,V6,V7,V8,V9
 2  FORMAT(1HX,4/,3(* K = *E10.4,10X)//2(* K = *E10.4,10X)////
  *3(  * V = *F8.3,10X)// 3(  * V = *F8.3,10X)// 3(  * V = *F8.3,10X)//)
    GO TO 41
    END OF K AND V
```

3. CUBIC.—

This programme was used to calculate the three stretching frequencies for the complexes using a set of force constants (usually those obtained from K AND V).

```
      PROGRAM CUBIC(INPUT,OUTPUT)
      REAL K1,K2,K3,K12,K23,M1,M2,M3,M4
      DATA H/5.8894E-02/
   20 READ15,M1,M2,M3,M4
   15 FORMAT(4(F5.0))
      IF(M1.EQ.0) STOP
      READ 13,K1,K2,K3,K12,K23
   13 FORMAT(5(F10.0))
      PRINT 1,M1,M2,M3,M4,K1,K2,K3,K12,K23
    1 FORMAT(1H1,*SOLUTION OF CUBIC FOR M1(*F2*)-M2(*F2*)-M3(*F2*)--RU(
     **F3*)*////10X,3(*K = *F5.2,10X)//20X,2(*K = *F5.2,10X)////)
      I = 0
      A0 = 1
      A = K1*((M1+M2)/(M1*M2)) + K2*((M2+M3)/(M2*M3)) + K3*((M3+M4)/
     *(M3*M4)) - 2*K12/M2 - 2*K23/M3
      A1 = -A
      A2 = ((M2+M3+M4)/(M2*M3*M4))*(K2*K3 - K23*K23) + (((M1+M2)*(M3+M4)
     *)/(M1*M2*M3*M4))*(K1*K3) + ((M1+M2+M3)/(M1*M2*M3))*(K1*K2-K12*K12)
     * - 2/M2*((M3+M4)/(M3*M4))*(K3*K12) - 2/M3*((M1+M2)/(M1*M2))*(K1*K23)
     *) + 2/(M2*M3)*(K12*K23)
      A3 = ((M1+M2+M3+M4)/(M1*M2*M3*M4))*((K3*K12*K12)+(K1*K23*K23) -
     * (K1*K2*K3))
      PRINT4,A0,A1,A2,A3
    4 FORMAT(7X,4(*A = *E11.4,10X))
      PRINT 7.A0,A1,A2,A3
    7 FORMAT(1HX,4/,7X,4(E11.4,10X)//)
   10 I = I + 1
```

```
      X = A1*A1
      Y = A2*A2
      Z = A3*A3
      U = -2*A2
      V = -2*A1*A3
      A1 = X+U
      A2 = Y+V
      A3 = Z
      PRINT 5,A0,X.Y.Z,U,V,A0,A1,A2,A3
    5 FORMAT(7X,4(E11.4,10X)//27X,2(E11.4,10X)///7X,4(E11.4,10X)//)
      B = ABS(X/U)    $    C = ABS(Y/V)    $    D = 100000
   11 P = 2**I
      R = A1    $    S =A2    $    T = A3
      E = (1/P)*ALOG10(R)
      F = (1/P)*(ALOG10(S)-ALOG10(R))
      G = (1/P)*(ALOG10(T)-ALOG10(S))
      X1 = 10.**E
      X2 = 10.**F
      X3 = 10.**G
      V1 = SQRT(X1*1E+05/H)    $    V2 = SQRT(X2*1E+05/H)
      V3 = SQRT(X3*1E+05/H)
      PRINT 6,V1,V2,V3
    6 FORMAT(1HX,3/,*V3 = *F10.3,10X,*V1 = *F10.3,10X,*V4 = *F10.3///)
      IF(I.EQ.5)20,10
      END OF CUBIC
```