ASPECTS OF THE CO-ORDINATION CHEMISTRY
OF SOME TRANSITION METALS

PART A  Dinitrogen and Carbonyl Complexes.

PART B  The Nature of the Anion ReOCl$_5^{2-}$

A thesis presented for the degree of Doctor of Philosophy in Chemistry in the University of Canterbury, Christchurch, New Zealand.

by

J.L. Love

1971
ACKNOWLEDGEMENTS

The author is most grateful to Dr J. E. Fergusson for his guidance and encouragement. He also thanks Dr W. T. Robinson for his help in the crystallography section.

The award of a Nuffield Grant is acknowledged and Johnson Matthey and Co. Ltd. (London) are thanked for the loan of Ruthenium Trichloride.
<table>
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<th>Abbreviation</th>
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<tr>
<td>Me</td>
<td>Methyl ((\text{CH}_3^-))</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl ((\text{C}_6\text{H}_5^-))</td>
</tr>
<tr>
<td>en</td>
<td>Ethylenediamine ((\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2))</td>
</tr>
<tr>
<td>dtc</td>
<td>Diethylthiocarbamato ((\text{C}_2\text{H}_5)_2\text{NCS}^-)</td>
</tr>
<tr>
<td>R</td>
<td>Alkyl or aryl group</td>
</tr>
<tr>
<td>(\text{H} - \text{cp})</td>
<td>Cyclopentadienyl ((\text{C}_5\text{H}_5^-))</td>
</tr>
<tr>
<td>diphos</td>
<td>A bidentate phosphine</td>
</tr>
<tr>
<td>diars</td>
<td>A bidentate arsine</td>
</tr>
<tr>
<td>B.M.</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>esr</td>
<td>Electron spin resonance</td>
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The work reported in this thesis is divided into three parts. Part A is concerned with studies on stable complexes of dinitrogen, and related ligands, Part B details studies on the rhenium (V) oxo-complex $Cs_2ReOCl_5$, and part C outlines general experimental details.

Part A. Some reactions of the dinitrogen complex $[Ru(NH_3)_5(N_2)]Cl_2$ have been investigated and the oxidation potential of the $[Ru(NH_3)_5(N_2)]^{2+}$ ion in neutral conditions has been found to be approximately -0.95 volts. The reactions have demonstrated that $[Ru(NH_3)_5(N_2)]Cl_2$ prepared using hydrazine hydrate is impure, the impurity is probably $[Ru(NH_3)_5(N_2H_4)]Cl_2$. The dinitrogen of purified $[Ru(NH_3)_5(N_2)]Cl_2$ has not yet been reduced in aqueous conditions, contrary to a previous report.

The reactions of some ruthenium, osmium, iridium and rhodium complexes with hydrazine hydrate and with metal reductants (e.g. Zn) in concentrated ammonia were investigated. A number of products including $[M(NH_3)_5(N_2)]^{2+}$, $[M(NH_3)_4(N_2)_2]^{2+}$, $[M(NH_3)_5(CO)]^{2+}$ (M= Os, Ru), $[Ir(NH_3)_4(CO)Cl]^{2+}$ and $[Rh(NH_3)_5H]^{2+}$, together with hydrazine containing products, were formed. Possible mechanisms for some of these reactions are suggested.
The crystal structure of the osmium complex \([\text{Os}(\text{NH}_3)_5(\text{N}_2)_2] \text{Cl}_2\) has been determined by X-ray diffraction methods. The crystal belongs to the orthorhombic space group \(Pnma\) with \(a = 1357.5\), \(b = 1046.5\), \(c = 687.5\) pm and \(z = 4\). The cations lie on crystallographic mirror planes and the interatomic distances within the cation are \(\text{Os}-\text{N}_2 (184\text{pm})\); \(\text{N}-\text{N} (112\text{pm})\) and \(\text{Os}-\text{NH}_3 (212-215\text{pm})\).

The ruthenium complex \([\text{Ru}(\text{NH}_3)_5(\text{N}_2)_2] \text{Cl}_2\) was found to form solid solutions with \([\text{Ru}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2\) which are isomorphous with the above osmium complex. This corresponds to a change of crystal system for the ruthenium dinitrogen complex. The energy of the \(\nu(\text{NN})\) absorption in the solid solutions is up to 50 cm\(^{-1}\) lower than for pure \([\text{Ru}(\text{NH}_3)_5(\text{N}_2)_2] \text{Cl}_2\), and it is suggested that this observation is caused by steric interactions in the solid state.

Low frequency infrared spectra of a number of ammine complexes have been recorded. These spectra show coupling effects between vibration modes, and also that the two metals, osmium and iridium, form stronger bonds to halide and ammonia, than do the corresponding second row metals ruthenium and rhodium.

**Part B.** The reported paramagnetic rhenium (V) ions such as \(\text{ReOCl}_5^{2-}\) were studied in this section. This complex ion is reported as being different from most rhenium (V) complexes which are diamagnetic. The present study has demonstrated that \(\text{Cs}_2\text{ReOCl}_5\) is, in fact, only slightly paramagnetic, presumably due to temperature independent paramagnetism. The reason for the
high paramagnetism reported previously has been shown to be due to the presence of paramagnetic \( \text{Cs}_2\text{ReCl}_6 \) in samples of \( \text{Cs}_2\text{ReOCl}_5 \), owing to an equilibrium reaction.

\[
3\text{ReOCl}_5^2^- + \text{H}_2\text{O} \rightleftharpoons \text{ReO}_4^- + 2\text{ReCl}_6^{2-} + 2\text{H}^+ + 3\text{Cl}^- \]

occurring during the preparative procedures.
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PART A

Dinitrogen and Related Complexes
One of the most important processes for life, as we know it, is the biological fixation of atmospheric dinitrogen. It has been variously estimated\(^1\) that in the order of 100 to 1000 million tons of dinitrogen, of which man fixes about one tenth, are fixed annually on earth, yet the rate of dinitrogen fixation is probably the main limitation to increased agricultural production in many less developed countries\(^1\). In developed countries, biological fixation still accounts for about two thirds of the annually fixed dinitrogen.

The chemical problem, in increasing the amount of nonbiological fixed dinitrogen, is the great stability of the dinitrogen molecule. The energy of dissociation is \(940 \text{kJ.mole}^{-1}\)\(^3\), but the chemical stability is largely due to the high energy \((524 \text{kJ.mole}^{-1})^3\) required to break the first bond.

This energy far exceeds the corresponding bond dissociation energies of the isoelectronic cyanide ion \((276 \text{kJ.mole}^{-1})^3\) acetylene molecule \((252 \text{kJ.mole}^{-1})^3\) and carbon monoxide molecule \((298 \text{kJ.mole}^{-1})^3\).

(A more extensive comparison of Dinitrogen with Carbon Monoxide is shown in Table 1).
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<th>Carbon Monoxide*</th>
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<tr>
<td>Bond Dissociation Energy</td>
<td>945 kJ/mole</td>
<td>1073 kJ/mole</td>
</tr>
<tr>
<td>Dissociation Energy Corresp. Double Bond</td>
<td>421 kJ/mole</td>
<td>775 kJ/mole (3)</td>
</tr>
<tr>
<td>Difference</td>
<td>524 kJ/mole</td>
<td>298 kJ/mole (3)</td>
</tr>
<tr>
<td>1st Ionisation Potential</td>
<td>15.51 volts</td>
<td>14.1 volts</td>
</tr>
<tr>
<td>Bond Stretching Frequency</td>
<td>$2330 \text{ cm}^{-1}(125)$</td>
<td>$2160 \text{ cm}^{-1}(112)$</td>
</tr>
<tr>
<td>Force Constant</td>
<td>$22.2 \times 10^5 \text{ dynes/cm}(125)$</td>
<td>$18.6 \times 10^5 \text{ dynes/cm}(112)$</td>
</tr>
<tr>
<td>Bond length</td>
<td>108.9 pm (58)</td>
<td>112.8 pm (143)</td>
</tr>
<tr>
<td>Dipole Moment</td>
<td>0 esu</td>
<td>$0.11 \times 10^{-18}$ esu</td>
</tr>
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*References in Parenthesis, otherwise from reference 12
Dinitrogen first has to be activated by some mechanism before any reaction can occur. Exceptions occur with a few very reactive substrates such as the alkali metals, but these are unlikely to be useful for any commercial process for dinitrogen fixation.

Methods for Dinitrogen Activation

The methods of dinitrogen activation have been reviewed by Murray and Smith. Dinitrogen can be activated by four methods:

1. Interaction with metal surfaces
2. Interaction with the enzymes collectively called Nitrogenase
3. Interaction with transition metal complexes
4. Production of gas plasmas by various methods.

Only the first three methods of activation will be considered more fully. These methods are related in that they all probably involve the interaction of dinitrogen with metal atoms, or ions. A few organic compounds such as the \((\text{C}_6\text{H}_5\text{S})^+\) ion, also react with dinitrogen but the resulting products are of unknown formulation. Compounds in which the dinitrogen is bonded to sulphur rather than carbon as in a conventional diazonium salt, have been proposed. These organic systems will not be considered further.

1. Interactions with Metal Surfaces – The reduction of dinitrogen absorbed on metal surfaces forms the basis of the present industrial "Haber Process". This catalytic process requires high temperatures and pressures, but the actual "efficiency" of ammonia production is low.
The interaction of dinitrogen with a number of metal surfaces has been extensively studied. For example, three different chemisorption states ($\alpha$, $\beta$, $\gamma$) are known to be formed by interactions between dinitrogen and tungsten. The two low temperature states, called $\alpha$ and $\gamma$, involve interaction of molecular nitrogen while the high temperature $\beta$ state is probably a mixture of adsorbed atomic nitrogen and cyclic $N_4$ groups. Similar interactions occur with other metals. It has been proposed that ammonia production from these systems involves the interaction of adsorbed atomic nitrogen and atomic hydrogen on the metal surface.

(2) **Biological Fixation** - The same overall reaction ($N_2 + 3[H] \rightarrow 2[\text{NH}_3]$) occurs in biological fixation as in the major industrial process, but in the biological case, the reaction proceeds at full efficiency in an essentially aqueous medium* at room temperature with dinitrogen pressures as low as 0.1 atmospheres.

Until very recently the biological fixation of dinitrogen was unique in that this series of reactions involved the only known reaction of the dinitrogen molecule under mild conditions. Hence many attempts have been made to understand the action of nitrogenase. These attempts have not been completely successful, mainly because of the difficulties in studying isolated nitrogenase, together with the absence of model reactions of dinitrogen.

* Proteins have both hydrophobic and hydrophilic properties. The actual environment of the "fixation site" is unknown and will effect the medium present.
**TABLE 2**

**PROPERTIES OF THE FRACTIONS OF NITROGENASE FROM C. PASTEURIANUM**

<table>
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<th>Fraction</th>
<th>Molecular Wt.</th>
<th>Stability</th>
<th>Metal</th>
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<tr>
<td>Molybdoferrredoxin</td>
<td>100,000</td>
<td>Stable &lt; 60°</td>
<td>Mo:Fe* = 1:6</td>
</tr>
<tr>
<td>Azoferredoxin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IVs</td>
<td>45,000</td>
<td>Stable &gt; 0°</td>
<td></td>
</tr>
<tr>
<td>IVN</td>
<td>40,000</td>
<td>Stable</td>
<td>1 or 2 Fe* atoms</td>
</tr>
</tbody>
</table>

*Iron is present as non-heme iron*
In 1960 the first cell free extracts, with significant nitrogen fixing ability, were isolated from cultures of "Clostridium Pasteurianum". Some workers have attempted to elucidate the biological activity of nitrogenase by the purification and identification of the enzymes in extracts of the above C. pasteurianum or on extracts of "Azotobacter vinelandii", but other microbes have also been investigated. Nitrogenase from different sources appear to be similar. In a number of cases, the two major components of the active enzyme fractions, (molybdferredoxin and azoferredoxin), are interchangeable between extracts of different microbes.

Three proteins have been found to be directly involved in the fixation process in the C. pasteurianum enzyme system, but only the two major protein components, molybdferredoxin and azoferredoxin, have been reported for the lesser investigated systems. In these latter systems, the azoferredoxin component has some properties which suggests that this fraction is a mixture of two of the fractions detected in the C. pasteurianum extracts.

The properties of the three protein fractions identified within the nitrogenase of C. pasteurianum are shown in Table 2.

In all active nitrogenase extracts, an additional protein, ferredoxin, is required for electron transfer into the active reduction system. Further work is required on these enzyme extracts before the actual mechanism of biological dinitrogen fixation can
FIGURE 1

Periodic Table Showing the Transition Metals that React with Dinitrogen

- a) Metals that act as fixation catalysts
- b) Metals that react with (Ar-N₂⁺) in model reactions of Nitrogenase
- c) Metals that form stable Dinitrogen complexes
be positively determined\textsuperscript{2,15,16}, but iron and molybdenum metal atoms definitely appear to be involved.

(3) **Interactions with Transition Metal Complexes**

Simple reactions to reproduce biological dinitrogen fixation have been investigated with a number of transition metal complexes. The significant findings are:

(a) catalytic reduction of dinitrogen with complexes of the early transition metals, such as (\(\Pi\)-cpx)\(_2\)TiCl\(_2\).

(b) the preparation then reduction of model compounds, such as Ar-N\(_2^+\), using intermediate transition metal complexes of these molecules.

(c) the preparation of relatively stable transition metal dinitrogen complexes, but in this case reduction of the co-ordinated dinitrogen has not yet been achieved.

Figure 1, reproduced from Murray and Smith and updated, shows the transition metals which have been investigated for the three types of reaction above. These reactions will now be discussed in more detail.

(a) The most successful reactions in reproducing biological nitrogen fixation under mild conditions have involved complexes of the early transition metals acting as reduction catalysts\textsuperscript{4}. In these systems, the final reduced nitrogen product appears to be a metal nitride which is readily hydrolysed to ammonia. This reaction is probably different from biological systems\textsuperscript{17}. Complexes of the early transition metals appear to catalyse reduction systems which
are more similar to those involving dinitrogen interactions with metal surfaces.

The most thoroughly investigated system involves \((\pi^*\text{-cp})_2\text{TiCl}_2\)\(^{18,19}\), probably as this complex gives the greatest relative yields of reduced nitrogen. Two schools of thought exist as to the intermediate complexes involved in this titanium system. Much of this work has recently been reviewed by Henrici-Olivé and Olivé\(^{18}\).

The authors above\(^{18}\) consider that the reaction involves a dimeric hydride bridged Ti (III) - Ti (II) intermediate, but the type of bonding of the dinitrogen molecule, proposed to be co-ordinated to the titanium (II) ion, could not be determined from the esr spectral evidence they obtained.

Van Tamelen et al.\(^{20}\) disagree and suggest that no hydride intermediate is involved. They propose that in the \((\pi^*\text{-cp})_2\text{TiCl}_2\) system, the initial reaction involves the co-ordination of dinitrogen to titanocene \([\text{Ti}(\pi^*\text{-cp})_2]\), with the formation of the intermediate \([\text{Ti}(\text{N}_2)(\pi^*\text{-cp})_2]\)\(^2\). Van Tamelen et al.\(^{20}\) suggest that dimeric species such as those observed by Henrici-Olivé and Olivé\(^{18}\) are only formed in the absence of dinitrogen, but these dimers must dissociate back into titanocene before any reaction with dinitrogen occurs.

Franklin and Byrd\(^{21}\) have interpreted their potentiometric studies of the \(\text{TiCl}_4/\text{TiCl}_3\) system in dimethyl sulphoxide and in
propylene carbonate, as showing that both 1:1 and 1:2, dinitrogen:titanium complexes are possible, depending on the solvent used. Possibly this explains some of the problems in interpreting the titanium cyclopentadienyl system above.

Yamamoto et al. 22 have isolated a series of nitrogen containing complexes from reducing \([\text{TiCl}_3 (\text{THF})_3]\) with magnesium at room temperature in the presence of dinitrogen. The initial black product analysed as \([\text{TiNMg}_2\text{Cl}_2 (\text{THF})]_n\). Five moles of reductant are required (2.5 gm.atoms Mg/mole Ti) and the product gives no dinitrogen on pyrolysis at 200°C. Part of the magnesium chloride can be exchanged for aromatic amines such as pyridine. The authors consider the complex to be either a dinitrogen bridged system with a low NN bond order, or a nitride with a low TiN bond order.

Further work on the above titanium nitrogen complexes may positively identify the intermediates involved in the reduction of dinitrogen with the early transition metal complexes.

(b) Parshall 23 and others 24 have investigated the reduction of molecules, analogues to dinitrogen, such as \(\text{Ar-N}_2^+\). These molecules are co-ordinated to transition metal ions, then the triple bond in the ligand is reduced.

The mechanism of the reduction is proposed to be similar to that occurring in dinitrogen when in association with nitrogenase.
\[ p-\left[ \text{FC}_6\text{H}_4-N \equiv N \right] \text{BF}_4 + H\text{-Pt(PET}_3\text{)}_2\text{Cl} \]

\[ \rightarrow (p-\left[ \text{FC}_6\text{H}_4-N = NH \right] - \text{Pt(PET}_3\text{)}_2\text{Cl}) \text{BF}_4 \]

\[ [\text{H}] \rightarrow (p-\left[ \text{FC}_6\text{H}_4-NH-NH_2 \right] - \text{Pt(PET}_3\text{)}_2\text{Cl}) \text{BF}_4 \]

\[ [\text{H}] \rightarrow p-\left[ \text{FC}_6\text{H}_4-NH_2-NH_2 \right] + H\text{-Pt(PET}_3\text{)}_2\text{Cl} \]

\[ \rightarrow p-\left( \text{FC}_6\text{H}_4\text{NH}_2 \right) + \text{NH}_3 \]

**Figure 2**  
Model Reaction of the Reduction of N\(_2\)  
using Nitrogenase - Proposed by Parshall\(^\text{23}\)
Parshall* investigated the system composed of
\[ p- \left( \text{F}_6 \text{H}_4 \text{N}^\equiv \text{N} \right) \text{BF}_4 \] (as "dinitrogen") and \[ \text{Hpt(PF}_3)_2\text{Cl} \] (as "nitrogenase") (Figure 2). In this system some of the intermediates show similar "side reactions" to those observed with active nitrogenase\(^{25}\) for example both the imide intermediate and nitrogenase induce hydrogen / deuterium exchange under similar conditions.

(c) At present no evidence suggests that dinitrogen, co-ordinated to transition metals in relatively stable complexes, reacts significantly differently from free dinitrogen. The co-ordinated dinitrogen in these complexes cannot be reduced. Most of the observed reactions\(^{26}\) of these complexes either involve the loss of the co-ordinated dinitrogen as free \(N_2\), or in some cases, the formation of new dinitrogen complexes. Probably the most interesting reactions of these complexes are those in which co-ordinated dinitrogen can co-co-ordinate to a second metal ion to form a bridged species.

The present work is concerned with the chemistry of some of the stable dinitrogen complexes and these will now be reviewed in greater detail.

**Stable Metal Complexes of Dinitrogen**

Transition metal complexes of dinitrogen are chemically interesting as regards their reactions and properties. The literature up until approximately the end of 1969 has been reviewed by Fergusson and Love\(^{26}\). A copy of this review is included (end of thesis).
From the information at present available the requirements to prepare dinitrogen complexes appear to be:

1. The metal ions are to be in low oxidation states, especially those with the d$^6$ and d$^8$ electron configurations.

2. The other ligands associated with the complexes should not be strong $\pi^*$-acceptor ligands*. The other ligands present in the complexes are predominantly amines and phosphines together with ligands such as water, hydride, or halide.

3. The source of dinitrogen can be either free dinitrogen (the metal complex requires a labile site) or a nitrogen containing molecule, which readily forms dinitrogen on reaction with a transition metal ion. The most common nitrogen containing molecules used in reactions to produce co-ordinated dinitrogen are hydrazine and organic or inorganic azide. Other sources used are nitrous oxide & diazotization of co-ordinated ammonia or azide with nitrous acid. The unusual reaction in which ammonia is decomposed to dinitrogen in the presence of ruthenium (III) or (IV) and a reducing agent is also a source of dinitrogen.

* A number of impure dinitrogen complexes containing $\pi$ bonded ligands have been proposed recently but formulations such as azides, also seem consistent with the evidence reported for most of these products. (See discussion on new complexes below)
The presence of dinitrogen in metal complexes is demonstrated by use of the techniques listed below.

(i) Infrared spectra by identification\(^{26}\) of the \(\tilde{\gamma} (\text{NN})\) absorption around 2000 cm\(^{-1}\). If the \(^{15}\text{N}\dfrac{^{15}}{^{14}}\text{N}\) isotope is used a decrease in energy of the \(\tilde{\gamma} (\text{NN})\) absorption of 60-70 cm\(^{-1}\) occurs which is good evidence for the presence of dinitrogen. Precautions have to be taken in interpretation of infrared data because the absence of an infrared absorption is not definite proof as to the absence of dinitrogen, e.g. \([\text{Ru}_2(\text{NH}_3)^{10}(\text{N}_2)^4]^+\), and the presence of a band at 2000 cm\(^{-1}\) may be due to co-ordinated CO, NO\(^+\), CN\(^-\) or H\(^+\).

(ii) Decomposition and identification of the evolved gas, by for example Mass spectra, is a good method of indicating co-ordinated dinitrogen.

(iii) The method of preparation, analytical figures (if possible) including decomposition products; infrared spectra; and chemical properties also need to be considered for most complexes.

A brief survey will now be given of the work reported since the appearance of the review\(^{26}\) mentioned above.

(a) \textbf{New Dinitrogen Complexes}. A number of new complexes 27-39
have been reported and these complexes (together with some of their properties) are listed as an appendix to this thesis. The more significant results are discussed below.

Probably the most interesting new complexes are the bridged dinitrogen complexes prepared by Chatt's group\(^1\)\(^3\)\(^0\)\(^,\)\(^3\)\(^1\), from the reaction of \(\text{Re}(\text{N}_2)\text{Cl}(\text{PMe}_2\text{Ph})_4\) with electron acceptor molecules. Little work, except for infrared spectral data has yet been published but the bridged complexes do have extremely low frequencies (i.e down to 1630 cm\(^{-1}\) with \(\text{NbCl}_5\)) for the \(\nu(\text{NN})\) infrared absorption. This large decrease in the \(\nu(\text{NN})\) absorption energy, compared with free dinitrogen (a decrease of ca. 700 cm\(^{-1}\) or 419 kJ mole\(^{-1}\)\(^2\))\(^3\)\(^0\), leads to the hope that dinitrogen in these complexes may be reduced under mild conditions.

Chatt et al.\(^3\)\(^4\) and Bancroft et al.\(^3\)\(^8\) have both prepared series of related complexes. These are \(\text{M(N}_2\text{H}_2(\text{PMe}_2\text{Ph})_3\)\(^3\)\(^4\) and \(\text{[MH(N}_2\text{)}(\text{diphos})_2\text{]} \text{BPh}_4\)\(^3\)\(^8\) respectively (where \(\text{M = Fe, Ru, Os}\)).

In the first series\(^3\)\(^4\), the frequency of the \(\nu(\text{NN})\) absorption in the infrared increases in the order \(\text{Fe} < \text{Os} \ll \text{Ru}\) but the stability of the three complexes decreases in the order \(\text{Fe} > \text{Ru} > \text{Os}\). This work supports previous observations\(^2\)\(^6\) that the frequency of the \(\nu(\text{NN})\) absorption does not correlate closely with the stability of dinitrogen complexes. In the second series of complexes\(^3\)\(^8\), viz \(\text{[MH(N}_2\text{)}(\text{diphos})_2\text{]} \text{BPh}_4\), the stability of the complexes does
correlate with the frequency of the respective $\nu$(NN) absorptions. However, the order of increasing frequency of the $\nu$(NN) absorptions, Fe $\ll$ Os $\ll$ Ru, in these complexes differs from that of the $\nu$(CO) absorptions in the isoelectronic complexes $\{\text{M}^{}(\text{CO})_{2}((\text{diphos})_{2})\text{BPh}_{3}\}$ (The $\nu$(CO) frequency increases in the order Fe $\ll$ Ru $\ll$ Os.) Bancroft et al.\textsuperscript{36} attribute the different order of absorption energies to differences in coupling between the $\nu$(NN) or $\nu$(CO) vibration modes with the $\nu$(MH) vibration mode.

The dinitrogen complex $\{\text{Rh}_{2}(\text{N}_{2})(\text{CO}_{2})((\text{PPh}_{3})_{2}\}$\textsuperscript{35} and ion $\{$[Cr(CN)$_{5}$(N$_{2}$)]$^{4-}$\}$\textsuperscript{35}$ contain carbonyl or cyanide ligands respectively and they require further investigation. In each case the ligands, CO and CN, are of a very different type to those previously associated\textsuperscript{26} with stable dinitrogen complexes. The preparation of these two complexes involves the use of azide and none of the measured properties seem inconsistent with an azide product, and Feltham has shown\textsuperscript{27} that the distinguishing of azide and dinitrogen can be a problem.

Three rhenium carbonyl dinitrogen complexes $\{\text{ReCl}(\text{N}_{2})(\text{PR}_{3})_{2}(\text{CO}_{2})\}$\textsuperscript{29}, $\{\text{Re}(\text{CO})_{3}(\text{NH}_{3})(\text{N}_{2})(\text{PR}_{3})\}$\textsuperscript{37} and $\{\text{Re}(\text{CO})_{3}(\text{NH})(\text{N}_{2})(\text{PR}_{3})\}$\textsuperscript{37} have been prepared using hydrazine\textsuperscript{37} or dinitrogen\textsuperscript{29} as the source of dinitrogen. The infrared spectrum of the latter products, in which the $\nu$(NN) absorption is at 2220 cm$^{-1}$, seems inconsistent with azide products\textsuperscript{41}, while for
the first complex, the use of $^{15}\text{N}^{15}\text{N}$ confirms the existence of a dinitrogen complex. These two Re (I) carbonyl products in which the $\nu$(NN) vibration modes in the infrared are above 2100 cm$^{-1}$, show the predicted$^{26}$ destabilising influence of $\pi$ bonding ligands on the metal dinitrogen bond. Other Re (I) dinitrogen complexes$^{42}$ which do not contain carbon monoxide have the $\nu$(NN) absorption at approximately 1950 cm$^{-1}$ in their infrared spectra.

(b) Reformulation of Previously Prepared Dinitrogen Complexes

The complexes $\{\text{Ru(diars)}_2(N_2)\text{Cl}\}$, $\text{N}_2\text{H}_5\text{Cl}$, and the copper (II) - and silver (I) - osmium dinitrogen bridged complexes$^{46}$, have been reformulated. Feltham has shown that the former compound$^{43}$ is the azide $[\text{Ru(diars)}_2(N_3)]\text{Cl}^{27}$. However, the dinitrogen compound $[\text{Ru(diars)}_2(N_2)\text{Cl}]\text{PF}_6$ can be prepared from this azide, by a reaction involving NO$^+$. Kane-Maguire et al.$^{44}$ have used a similar reaction to prepare cis - $[\text{Ru(en)}_2(N_2)_2](\text{BPh}_4)_2$.

Chatt et al.$^{45}$ have proposed that the unstable osmium-silver- and osmium-copper-dinitrogen bridged complexes, reported by Das et al.$^{46}$ as containing the species Os - N = N - M, are probably nonbridged complexes of osmium in higher oxidation states, probably Os (IV). The intermediate Os (III) compound can be detected$^{45}$ under appropriate conditions. The infrared spectra of these osmium compounds show a progression in $\nu$(NN) absorption energy corresponding to decreasing metal $\pi$-electron donation into the
dinitrogen \( \pi^* \) orbitals. These \( \pi \) (NN) absorptions are at 2050 cm\(^{-1}\) in Os (II); 2130 cm\(^{-1}\) in Os (III) and 2225 cm\(^{-1}\) in Os (IV), (in each case as the tetraphenylborate salt).

Elson et al.\(^47\) have confirmed the possibility of oxidation of some ammine dinitrogen complexes. They showed that both

\[
[\text{Os(NH}_3\text{)}_5\text{(N}_2\text{)}]^{2+} \quad \text{and} \quad [\text{Ru}_2\text{(NH}_3\text{)}_{10}\text{(N}_2\text{)}]^{4+}
\]

will undergo cyclic, one electron, oxidation then reduction reactions in aqueous (25\(^\circ\)C) \( \text{K}_2\text{SO}_4 - \text{H}_2\text{SO}_4 \) solution. The rate constants for the decomposition of these oxidised complexes are \( 2 \times 10^{-2} \) sec\(^{-1}\) and \( 1 \times 10^{-1} \) sec\(^{-1}\) respectively\(^47\). The monomer \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]^{2+}\) could not be detected in an oxidised form as on oxidation this compound gives an immediate evolution of dinitrogen\(^47\).

(c) **New Preparative methods**

Only one further preparative method for dinitrogen complexes has been developed\(^40\). A mixture of the two ruthenium dinitrogen complex ions \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]^{2+} \quad \text{and} \quad [\text{Ru}_2\text{(NH}_3\text{)}_{10}\text{(N}_2\text{)}]^{4+}\), can be prepared by the acid decomposition of \([\text{Ru(NH}_3\text{)}_5\text{(N}_3\text{)}]^{2+}\). It is suggested\(^40\) that acid reacts with the azide starting material to first give a nitrene intermediate, which then further reacts to form the dinitrogen products.

(d) **Physical Properties. (i) Thermodynamic data.**

Elson et al.\(^48\) and others\(^49,50\) have published additional thermodynamic data (at 25\(^\circ\)C) on the reaction\(^76\) of \([\text{Ru(NH}_3\text{)}_5\text{(H}_2\text{O)}]^{2+}\)
Figure 3  Possible Modes of Co-ordination of Dinitrogen to the $\text{[Ru(NH}_3)_5\text{]}^{2+}$ Unit
with dinitrogen, and the subsequent reaction giving the dimeric ion \([\text{Ru}_2(\text{NH}_3)_10(\text{N}_2)^{14+}\)). There is agreement on the measured data on the first reaction producing \([\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}\) as product, but data on the second reaction cannot be compared because of variations in the ionic strength present.

The enthalpy difference between the two possible modes of co-ordination of molecular nitrogen to the ruthenium (II) pentaammines (Fig. 3) has been estimated to be approximately 92 kJ·mole\(^{-1}\) by considering the activation energy for the reaction \(\text{Ru}^\text{14N} \rightleftharpoons \text{Ru}^\text{15N} \rightleftharpoons \text{Ru}^\text{14N}\). The intermediate in this reaction has structure (B) in the figure opposite, but the above activation energy means that this intermediate is only slightly more stable, (29± 17 kJ·mole\(^{-1}\)), than the nonbonded system composed of free dinitrogen and \([\text{Ru}(\text{NH}_3)_5]\)^{2+}.

(ii) Spectral data - Gray et al. have assigned the intense absorption at 200 - 270 nm in the spectra of ruthenium and osmium dinitrogen complexes to a metal to ligand charge transfer transition. For the dimer, \([\text{Ru}_2(\text{NH}_3)_10(\text{N}_2)]^{4+}\), the transition is \(e_u \rightarrow e_g (\pi^* \text{N}_2)\) while for the monomers (\(\text{M}(\text{NH}_3)_5(\text{N}_2)\)) \(2^{4+}\) (\(\text{M} = \text{Ru, Os}\)) the transition is of a similar type (\(b_2\) or \(e\)) \(\rightarrow e(\pi^* \text{N}_2)\). Gray proposed that the total bonding electrons transferred into the dinitrogen \(\pi^*\) orbitals are similar in the two ruthenium complexes, but in the dimer these electrons come from two ruthenium atoms.
### TABLE 3

**Significant Bond Lengths in Structure**

**Determinations of Dinitrogen Complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Comments</th>
<th>NN distance (pm)</th>
<th>MN₂ distance (pm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>gas</td>
<td>109.8</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>CoH(N₂)(PPh₃)₃</td>
<td></td>
<td>111.2 (1.1)</td>
<td>180.7 (23)</td>
<td>54</td>
</tr>
<tr>
<td>[Ru₂(NH₃)₁₀(N₂)₁] (BF₄)₄</td>
<td></td>
<td>112.4 (15)</td>
<td>192.8 (6)</td>
<td>52</td>
</tr>
<tr>
<td>[Ru(N₃)(N₂)(en)₂] PF₆</td>
<td></td>
<td>110.6 (11)</td>
<td>189.4 (9)</td>
<td>55</td>
</tr>
<tr>
<td>[Os(NH₃)₅(N₂)] Cl₂</td>
<td></td>
<td>112 (2)</td>
<td>184 (1) present work</td>
<td></td>
</tr>
<tr>
<td>[Ru(NH₃)₅(N₂)] Cl₂ disordered</td>
<td></td>
<td>Total distance MNN=322 (6)</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>ReCl(N₂)(PMe₂Ph)₄ Cl₁N₂ disordered</td>
<td></td>
<td>&quot;</td>
<td>MNN=302 (2)</td>
<td>57</td>
</tr>
</tbody>
</table>

Numbers given in parenthesis are the estimated standard deviations in the least significant digits.
hence in the dimer, the ruthenium d-electrons are at a higher energy and consequently the energy of the Ruthenium $\rightarrow (\pi^* N_2)$ transition is lower.

Chatt et al.\textsuperscript{53} has compared the frequencies of the $\bar{v} (CO)$ and $\bar{v} (NN)$ absorptions in a number of isoelectronic carbonyl and dinitrogen complexes. It was shown that the ratio of $\frac{\bar{v} (NN)}{\bar{v} (CO)}$ is identical and equal to 1.088 for all isoelectronic pairs considered*, including the free gases. This is interpreted\textsuperscript{53} in terms of the similarity of the type of bonding of these two molecules to metal ions.

(e) \textbf{Structures of Dinitrogen Complexes.} At present the structures of six dinitrogen complexes have been determined by X-ray methods\textsuperscript{52, 54-57} (Table 3). In the four ordered structures the $\equiv N$ bond length ranges from 112.4 pm\textsuperscript{52} for $[\text{Ru}_2 (\text{NH}_3)_10(N_2) ] (\text{BF}_4)_4$ to 110.6 pm\textsuperscript{55} for $[\text{Ru} (\text{N}_3) (\text{N}_2) (\text{en})_2 ] \text{PF}_6$ (Table 3), compared with the bond length of free dinitrogen in the gaseous state of 109.8 pm\textsuperscript{58}. The metal dinitrogen bond lengths range from 180.7 pm\textsuperscript{54} for $\text{Co} (\text{N}_2) \text{H} (\text{PPh}_3)_3$ to 192.8 pm for $[\text{Ru}_2 (\text{NH}_3)_10(N_2) ] (\text{BF}_4)_4$.

In each case the $M \equiv N \equiv N$ group is linear to within a few degrees. The data on the two disordered structures\textsuperscript{56, 57}, is less complete but is in overall agreement with the results of the ordered structures.

The significant observations from these dinitrogen structures are the short metal to dinitrogen bonds, the linear metal-dinitrogen

\textsuperscript{*} $\bar{v} (XY)$, is the energy of the observed $(XY)$ absorption for complex (i) $(XY = \text{CO or NN})$. 
group and the little changed NN bond length in dinitrogen.
Similar observations apply to carbon monoxide complexes.
Probably the most significant observation is that the measured
metal-dinitrogen bonds lengths are almost identical to reported
metal-carbon bond lengths in carbon monoxide complexes.\textsuperscript{59}

Summary of the Present Work

The aim of the present work was to add to our understanding
of the chemistry of dinitrogen as a ligand.

**Part A** (a) When this present work was started it was thought
that dinitrogen in the complex \textsuperscript{60,61} ion \([\text{Ru(NH}_3\text{)}_5(N_2)]^{2+}\) could be
reduced to yield one mole of ammonia, while the other
nitrogen atom was unaccounted for. The dinitrogen in the few other
known complexes could not be reduced\textsuperscript{17}. The complex \textsuperscript{2,17}
\text{CoH} (N_2)(PR_3)_3
had been prepared from gaseous dinitrogen so that this compound
together with the ruthenium compound suggested a model route
for biological dinitrogen fixation. It was hoped to study why the
ruthenium dinitrogen complex was readily reduced.

One of the first things discovered independently and then in
collaboration with Chatt’s group at Sussex\textsuperscript{62,63} was the presence
of impurities in samples of \([\text{Ru(NH}_3\text{)}_5(N_2)]^{2+}\) prepared using
hydrazine hydrate - the original reported method. The
impurities contain hydrazine, probably as the complex ion
\([\text{Ru(NH}_3\text{)}_5(N_2H_4)]^{2+}\).
Mixture $[\text{Ru(NH}_3\text{)}_5(\text{N}_2\text{})\text{]}\text{Cl}_2$
and cis-$[\text{Ru(NH}_3\text{)}_4(\text{N}_2\text{)}_2\text{]}\text{Cl}_2$

$\text{N}_2\text{H}_4\text{H}_2\text{O}$

$\text{N}_2\text{H}_4\text{H}_2\text{O}$ at $\text{o}^{\circ}\text{C}$

Mixture $[\text{Ru(NH}_3\text{)}_5(\text{N}_2\text{})\text{]}\text{Cl}_2$
and cis-$[\text{Ru(NH}_3\text{)}_4\text{Cl}_2\text{]}\text{Cl}$

Hydrazine reduced to Ammonia

[NH$_3$]$_6$Cl$_2$

$\text{Zn/\text{NH}_3}$

boiling $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O/CO}_2$

$\text{H}_2\text{C}_2\text{O}_4/\text{HCl}$

$\text{N}_2\text{H}_4\text{H}_2\text{O}$

$\text{N}_2\text{H}_4\text{H}_2\text{O}$

$\text{N}_2\text{H}_4\text{H}_2\text{O}$

Bottomley's Red Product

Cool in Air.

Mixture $[\text{Ru(NH}_3\text{)}_5(\text{N}_2\text{)}\text{]}\text{Cl}_2$
and $[\text{Ru(NH}_3\text{)}_5(\text{N}_2\text{H}_4\text{)}\text{]}\text{Cl}_2$

FIGURE 4 Reactions of $[\text{Ru(NH}_3\text{)}_5\text{Cl}\text{]}\text{Cl}_2$ with Hydrazine Hydrate under various conditions
(This work and refs. 62-65)
Reduction of the above impure \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]\) \(\text{Cl}_2\) reduces the co-ordinated hydrazine to ammonia, but the dinitrogen present in \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]^{2+}\) is not reduced.

(b) This present work has demonstrated that the reaction of simple ruthenium compounds with hydrazine may give a variety of products. The actual product isolated depends on the conditions used as indicated in Figure 4. The complexity of the reactions, and variety of products produced makes it important to be able to confirm the presence of dinitrogen especially as ligands such as carbon monoxide, hydride, or azide, may occur in the products; (this work and refs. 27, 62-65).

Decomposition of the complexes followed by Mass spectral gas analysis will distinguish dinitrogen from hydrogen or carbon monoxide. Co-ordinated azide is more difficult to distinguish, but most dinitrogen complexes are prepared under conditions in which azides are unlikely. Detailed reaction chemistry and oxidation state measurements would be required in difficult cases.

During this work, the new compounds \([\text{Rh(H)}(\text{NH}_3\text{)}_5]\) \(\text{Br}_2\), \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]\) \(\text{ZnCl}_2\), and \([\text{Os(NH}_3\text{)}_5(\text{CO})]\) \(\text{Cl}_2\) were prepared. Evidence for \([\text{Ir(NH}_3\text{)}_4(\text{CO})\text{Cl}]\) \(\text{Cl}_2\), \([\text{Ru(NH}_3\text{)}_4(\text{N}_2\text{)}_2]\) \(\text{Br}_2\) (impure) and \(\text{Fe(dtc)}_2(\text{CO})_m\) (impure) were also obtained. The first compound \(\text{RhH(NH}_3\text{)}_5\) \(\text{Br}_2\) has since been reported by Wilkinson et al.\textsuperscript{66}. The carbonyl \(\text{[Ru(NH}_3\text{)}_5(\text{CO})]\) \(\text{Cl}_2\) has now been prepared by a new and more efficient route.
(c) The structure of $[\text{Os(NH}_3\text{)}_5\text{(N}_2\text{)}] \text{Cl}_2$ has been determined by a single crystal X-ray analysis. This structure is ordered, and the Os-$N_2$ bond length is 184.2 pm, the $N\equiv N$ bond length is 112 pm and the average Os-$\text{NH}_3$ bond length is 214 pm. The OsNN bond angle is 178° and the environment of the osmium is octahedral. The final $R$ factor was 3.9%, and the weighted $R$ factor was 4.4%.

(d) The solid solutions of $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}] \text{Cl}_2$ in $[\text{Ru(NH}_3\text{)}_5\text{Cl}] \text{Cl}_2$ and in $[\text{Ru(NH}_3\text{)}_5\text{(CO)}] \text{Cl}_2$ have been investigated. These mixtures form solid solutions in which the dinitrogen group is probably no longer disordered with the ammonia ligands as occurs in pure $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}] \text{Cl}_2$.

(e) The low frequency infrared spectra (400 - 40) cm$^{-1}$ of a number of metal ammines, prepared during this work, were recorded.

PART B

Towards the end of this work it was decided to investigate complexes of penta-valent rhenium containing the species Re-O. The short rhenium-oxygen bond confers a strong tetragonal distortion to octahedral rhenium (V) complexes and this gives rise to spin pairing. The complex $\text{Cs}_2\text{ReOCl}_5$ has been reported as paramagnetic$^{70-72}$. If this is so, it is of interest as an example of a system which may exhibit the magnetic cross-over phenomenon. It was shown that the
complex is in fact spin paired with a small positive molar susceptibility due to temperature independent paramagnetism. The reason for the high magnetism reported earlier is due to the products being contaminated with some paramagnetic $\text{Cs}_2\text{ReCl}_6$. 
CHAPTER 2

The Purity and Some Reactions of $[\text{Ru(NH}_3)_5(\text{N}_2)]^2+ \text{Cl}_2$

Introduction

Since the preparation of the first stable dinitrogen complexes, chemists have hoped that these would enable them to understand the ability of nitrogenase to fix molecular dinitrogen. Eventually this knowledge may lead to other economic industrial methods for the fixation of dinitrogen.

This exciting prospect seemed imminent when Allen and Senoff reported$^{60,61}$ that the cation $[\text{Ru(NH}_3)_5(\text{N}_2)]^2+$ could be reduced to yield six moles of ammonia for each mole of ruthenium. The other dinitrogen complexes known at this time, $\text{CoH(N}_2)(\text{PR}_3)_3$ and $\text{Ir(N}_2)\text{Cl(PR}_3)_2$, decomposed with evolution of dinitrogen gas on reduction$^{26}$.

It is now found in the present work that the purity of the dinitrogen complex is important in the apparent reduction. The results of this work will be discussed in this chapter.
Figure 5  Infrared Spectra of $[\text{Ru(NH}_3)_5(\text{N}_2\text{)}_2]\text{ZnCl}_4$

i) Prepared using $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$

ii) Prepared by $\text{HgCl}_2$ oxidation of product (i), (an identical product is obtained by using azide)
Reactions of \([\text{Ru(NH}_3\text{)}_5\text{N}_2\text{]}\) \(\text{Cl}_2\) were initially carried out on products obtained at room temperature by treating \([\text{Ru(NH}_3\text{)}_5\text{Cl}]\) \(\text{Cl}_2\) with hydrazine hydrate.

When this product is added to mercuric chloride solution, no gas is evolved but a conspicuous precipitate of grey mercurous chloride/mercury is formed, leaving a clear solution. The addition of excess mercuric chloride to the filtrate led to the formation of clear needle crystals. These crystals appeared isomorphous with \([\text{Ru(NH}_3\text{)}_6\text{]}\) \((\text{HgCl}_2\text{)}_3\), prepared\(^{73,74}\) by the addition of mercuric chloride to pure \([\text{Ru(NH}_3\text{)}_6\text{]}\) \(\text{Cl}_3\). However, the infrared spectrum of these needles contains a weak absorption at 2015 cm\(^{-1}\). The relative intensity of this absorption varied between different preparations, hence the clear needle crystals appear to be a mixture of products which include a dinitrogen complex.

In an attempt to separate the products a number of anions were added to precipitate the dinitrogen component. The anion \(\text{ZnCl}_4^{2-}\) gave a product (product 1) from the clear aqueous solution, which had an intense \(\nu(\text{NN})\) infrared absorption in the infrared. The infrared spectrum of this zinc tetrachloride salt is given in Figure 5.
### Table 4

Properties of the Two Products formed from
the Mercuric Chloride Oxidation of
\[
\text{[Ru(NH}_3\text{)}_5\text{ (N}_2\text{)] Cl}_2 \text{ (Hydrazine Prep.)}
\]

<table>
<thead>
<tr>
<th>Property</th>
<th>Product 1</th>
<th>Product 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu_{\text{eff}})^*</td>
<td>0.6 B.M.</td>
<td>2.3 B.M.</td>
</tr>
<tr>
<td>Infrared (\nu) (NN)</td>
<td>2115 cm(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>(\delta) (NH)</td>
<td>1302; 1285 cm(^{-1})</td>
<td>1340 cm(^{-1})</td>
</tr>
<tr>
<td>(\alpha) (NH)</td>
<td>775 cm(^{-1})</td>
<td>800 cm(^{-1})</td>
</tr>
<tr>
<td>Analysis +</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl; H; N/Ratio</td>
<td>4.0:16.5:7.0</td>
<td>4.8:20.0:6.0</td>
</tr>
<tr>
<td>Conductivity/Conc*</td>
<td>2.22 (\times) 10(^{-3})</td>
<td>1.93 (\times) 10(^{-3})</td>
</tr>
<tr>
<td>(in H(_2)O) Moles/1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar*</td>
<td>240</td>
<td>440</td>
</tr>
<tr>
<td>Cond.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction
with \(\text{N}_2\text{H}_4\text{H}_2\text{O}\) (cold)
No effect
Reduced to
\[
\text{[Ru(NH}_3\text{)}_6\text{]} \text{ Cl}_2
\]

\(^*\) The analytical figures given in the experimental section
at the end of this chapter.

\(^+\) Based on the molecular formulation
\[
\text{[Ru(NH}_3\text{)}_5\text{(N}_2\text{)] ZnCl}_4\text{ for Product 1 and [Ru(NH}_3\text{)}_6\text{]} \text{ ClZnCl}_4\text{ for Product 2.}
\]
Most of the remaining ruthenium could be recovered from the filtrate, from which the $\text{ZnCl}_4^{2-}$ salt of the dinitrogen product had been removed, by addition of methanol (product 2). The properties of the dinitrogen product and the methanol precipitated product are outlined in Table 4.

The latter product, product 2, has properties which are consistent with a compound of composition $\left[\text{Ru(NH}_3)_6\right] \text{Cl.ZnCl}_4$. A product with an identical X-ray powder photo, infrared spectrum and analysis to product 2, is obtained when the cation $\left[\text{Ru(NH}_3)_6\right]^{3+}$ is precipitated from an aqueous solution by use of zinc chloride and methanol.

Product 1, the dinitrogen complex precipitated as the $\text{ZnCl}_4^{2-}$ salt, was more difficult to explain. The X-ray powder photo of this product is identical to the powder photo of $\left[\text{Ru(NH}_3)_6\right] \text{ZnCl}_4$, hence the low magnetic moment of this compound is consistent with a monomeric ruthenium (II) complex. However, some properties of this new complex (Product 1) are significantly different from those of the tetrachlorozinc (II) salt of the starting material. The complex $\left[\text{Ru(NH}_3)_5\text{N}_2\right] \text{ZnCl}_4$, prepared by the hydrazine method is unstable in the air at room temperature and the pale yellow solid darkens to a black powder after a few days. The product obtained by the mercuric chloride treatment on the other hand, is stable for months under identical conditions.
The infrared spectra of the original dinitrogen complex and product 1 (Fig. 5) show differences in intensity and positions of various absorptions. In addition, two absorptions at 1100 cm$^{-1}$ and 940 cm$^{-1}$ also occur for the dinitrogen complex (hydrazine prep.). These additional absorptions do not have frequencies normally associated with ruthenium ammine or dinitrogen groups, and they seem best assigned to the presence of hydrazine co-ordinating as a monodentate ligand. Such a ligand has the vibration modes $^{77}$ \( \text{NH}_2 \) twist and \( \nu (\text{NN}) \) occurring at approximately 1170 cm$^{-1}$ and 930 cm$^{-1}$ respectively.

The complex \( [\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}] \text{ZnCl}_4 \) was then prepared using the azide method of Allen et al. $^{61}$. This compound had identical spectra (infrared and ultraviolet) and X-ray powder photo and air stability to those of product 1.

It was concluded that the dinitrogen product obtained from the reaction of hydrazine hydrate on \( [\text{Ru(NH}_3\text{)}_5\text{Cl}]^+ \text{Cl}_2 \) is a mixture containing \( [\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{H}_4\text{)}] \text{Cl}_2 \), \( [\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}] \text{Cl}_2 \), and possibly \( [\text{Ru(NH}_3\text{)}_6\text{]}^+ \text{Cl}_2 \). Mercuric chloride oxidizes this mixture to a new mixture containing the \( [\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]^2+ \) and \( [\text{Ru(NH}_3\text{)}_6\text{]}^3+ \) ions. These two ions can then be separated using \( \text{ZnCl}_4^{2-} \) as a precipitating agent. The mercuric chloride may oxidize the hydrazine impurity to \( [\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]^2+ \) or it could react to give insoluble white mercury (II) amides $^{78}$ together with \( [\text{Ru(NH}_3\text{)}_6\text{]}^3+ \).
Analytical figures for the starting material together with yields of the various products, tend to support this latter suggestion.

Results of Other Work on the Purity of

Hydrazine Prepared \([\text{Ru(NH}_3]_5(N_2)\]^{2+}\)

At about the time the above work was carried out, a number of other attempts to reduce \([\text{Ru(NH}_3]_5(N_2)\]^{2+}\) were reported. Borod'ka et al. reported\(^7^9\) that no \(^{15}\text{N}\text{H}_3\) was obtained on the reduction of \([\text{Ru}^{(14}\text{NH}_3]_5(15\text{N}^{15}\text{N})\]^{2+}\). Chatt's group at Sussex confirmed this result\(^8^0\). They found no \(^{15}\text{N}\) enrichment of the ammonia recovered from the decomposition of \([\text{Ru}^{(14}\text{NH}_3]_5(15\text{N}^{15}\text{N})\] (BF\(_4\))\(_2\) with hot concentrated sulphuric acid or alkali borohydride. They also found that solutions of supposedly pure \([\text{Ru(NH}_3]_5(N_2)\]^{2+}\), prepared using hydrazine hydrate, give a positive test for hydrazine. Not less than 6\% hydrazine was found to be present. Allen's\(^6^0\) original compound has a high hydrogen analysis which suggests that his preparations also have hydrazine present.

The present work and the work of others, reported above\(^6^2,6^3\), explains the apparent reduction of \([\text{Ru(NH}_3]_5(N_2)\] Cl\(_2\) to give
six moles of ammonia. The additional mole of ammonia comes from the hydrazine impurity and not the co-ordinated dinitrogen.

During other work described in this chapter (see below) it was found that approximately 5.7 moles of ammonia are obtained from the decomposition, of the hydrazine preparation of \( [\text{Ru(NH}_3\text{)}_5(\text{N}_2)]\text{Cl}_2 \), by strong alkali in the presence of Devarda's alloy. Pure ruthenium complexes such as \( [\text{Ru(NH}_3\text{)}_5(\text{N}_2)]\text{Cl}_2 \) (azide preparation), \( [\text{Ru(NH}_3\text{)}_5\text{Cl} ]\text{Cl}_2 \) and \( [\text{Ru(NH}_3\text{)}_5 ]\text{Cl}_2 \) give only the moles of ammonia predicted by their composition. This result supports the proposal that co-ordinated hydrazine is the source of the additional ammonia.

Since this work was published Allen et al.\(^{31}\) have confirmed that the co-ordinated dinitrogen in \( [\text{Ru(NH}_3\text{)}_5(\text{N}_2)]\text{Cl}_2 \) cannot be reduced with alkaline borohydride. However, these workers go on to say that even \( [\text{Ru(NH}_3\text{)}_6 ]\text{Cl}_2 \) gives greater than the predicted six moles of ammonia, when it is decomposed with alkaline borohydride, in the conditions used by them.

Attempts have been made to measure\(^{46,76}\) the reduction potentials of \( [\text{Os(NH}_3\text{)}_5(\text{N}_2)]^{2+} \) and \( [\text{Ru(NH}_3\text{)}_5(\text{N}_2)]^{2+} \), but without success, which is consistent with the chemical evidence that co-ordinated dinitrogen in "stable" complexes cannot be reduced to ammonia.
This work has shown that the preparation of $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]\text{Cl}_2$ by use of hydrazine hydrate is inferior to the method using azide, as suggested by Allen et al.\textsuperscript{61}.

The overall result is somewhat disappointing in that it has shown that dinitrogen, in the stable ruthenium dinitrogen complex $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]\text{Cl}_2$ cannot as yet be reduced in aqueous solution.

Reactions of $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]\text{Cl}_2$

During the work just described a number of other reactions of $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]^{2+}$ were attempted in order to elucidate what was happening. Also it was of interest to investigate the fate of the co-ordinated dinitrogen in chemical reactions especially as it was not removed from co-ordination by treatment with mercuric chloride. A number of the reactions, to be described, were first carried out on the Ruthenium dinitrogen complex before it was known to be impure, where these differ from reactions of the pure complex this is noted.

Recent papers by Lever & Powell\textsuperscript{73,74} outline a considerable amount of reaction chemistry of the complex ion $[\text{Ru(NH}_3\text{)}_6]^{2+}$. The chemistry described by them was a guide to the products formed in the reactions of the complex ion $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}]^{2+}$. 
In most cases interest lay in the loss or retention of dinitrogen and therefore infrared spectroscopy was an adequate means of identification for this purpose. Since the compounds are relatively simple molecularly, involving just a few ligands such as NH\textsubscript{3}, N\textsubscript{2}, halogen, the infrared spectra are simple and diagnostic for the presence of the ligands. In addition it is possible to distinguish the oxidation state of the ruthenium by changes in position of certain of the co-ordinated ammonia vibrational modes\textsuperscript{113}.

(a) Reaction with mercuric chloride - This work has been described in the previous section of this chapter. No reaction occurs whereas \([\text{Ru(NH}_3\text{)}_6\text{]}\text{Cl}_2\) is oxidised to \([\text{Ru(NH}_3\text{)}_6\text{]}^{3+}\) \textsuperscript{73,74}

(b) Reaction with Aqueous NaAuCl\textsubscript{4} - Both pure and hydrazine contaminated \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2\) react with NaAuCl\textsubscript{4} in solution to give a vigorous gas evolution with the formation of a yellow solution. Excess NaAuCl\textsubscript{4} produces further gas and a deep purple solution. The infrared spectra of the products obtained from both these solutions above, show no absorption attributable to the \(\nu\)(NN) stretching frequency. The product from the yellow solution contained ruthenium (III) ammines while the product from the purple solution did not contain co-ordinated ammonia.

This reaction is probably similar to that observed\textsuperscript{73,74} for the reaction of \([\text{Ru(NH}_3\text{)}_6\text{]}\text{Cl}_2\) and NaAuCl\textsubscript{4}, but in this case the
reaction stops with the formation of the insoluble complex,
\[
[\text{Ru}_2(\text{NH}_3)_8(\text{NH})]\text{Cl}_6\text{H}_2\text{O}.
\]

(c) **Reaction with \([\text{Co(NH}_3]_6\text{Cl}_3\)** - This cobalt (III) complex reacts similarly to \(\text{HgCl}_2\) solution. The hydrazine impurity \([\text{Ru(NH}_3]_5(\text{N}_2\text{H}_4)]^{2+}\) and \([\text{Ru(NH}_3]_6]^{2+}\), \(73,74\) are both oxidised to ruthenium (III) complexes, but \([\text{Ru(NH}_3]_5(\text{N}_2)]^{2+}\) does not react.

(d) **Reaction with chlorine and bromine waters** - The ruthenium in \([\text{Ru(NH}_3]_5(\text{N}_2)]\text{Cl}_2\) and \([\text{Ru(NH}_3]_6\text{Cl}_2\) is oxidised to ruthenium (III) with loss of dinitrogen from the first complex.

(e) **Reaction with dilute hydrochloric acid** - Reaction with dilute hydrochloric acid gives rise to \([\text{Ru(NH}_3]_5\text{Cl}]\text{Cl}_2\). This reaction is discussed in more detail in Chapter 5. The hexaammine \([\text{Ru(NH}_3]_6\text{Cl}_2\) is reported to react differently since coordinated ammonia is also lost, and the product is
\[
[\text{Ru(NH}_3]_3(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}.
\]

(f) **Reaction with nitrous acid** - The two ruthenium (II) complexes \([\text{Ru(NH}_3]_5(\text{N}_2)]\text{Cl}_2\) and \([\text{Ru(NH}_3]_6\text{Cl}_2\) react with nitrous acid to give the same nitrosyl product \([\text{Ru(NO)(NH}_3]_5]\text{Cl}_3\). These reactions were confirmed in the present work.

(g) **Reaction with aqueous sodium hydroxide** - Hot sodium hydroxide solution, in the presence of Davarda's alloy, decomposes pure \([\text{Ru(NH}_3]_5(\text{N}_2)]\text{Cl}_2\) to give five moles of ammonia, and
decomposes \([\text{Ru(NH}_3\text{)}_6] \text{Cl}_2\) to give six moles of ammonia. The impure \([\text{Ru(NH}_3\text{)}_5(N_2)] \text{Cl}_2\), containing \([\text{Ru(NH}_3\text{)}_5(N_2H_4)] \text{Cl}_2\), is decomposed under these conditions to give 5.7 moles of ammonia.

In the absence of Devarda’s alloy, the latter reaction only gives 5 moles of ammonia, whereas the complex \([\text{Ru(NH}_3\text{)}_6] \text{Cl}_2\) still gives six moles of ammonia.

(h) Reaction with Hot Water. \([\text{Ru(NH}_3\text{)}_5(N_2)] \text{Cl}_2\) is decomposed in hot water with gas evolution, and the solution becomes bright red. The presence of hydrazine impurities have no effect on this reaction. The complex \([\text{Ru(NH}_3\text{)}_6] \text{Cl}_2\) reacts in hot water to deposit one third of the ruthenium as metal, while the remaining complex is oxidised to ruthenium (III) ammines.

Discussion of Reactions

The reactions (a to h above) show that \([\text{Ru(NH}_3\text{)}_5(N_2)] \text{Cl}_2\) reacts similarly to \([\text{Ru(NH}_3\text{)}_6] \text{Cl}_2\) under many conditions, but with mild oxidising agents, such as \(\text{HgCl}_2\) and \([\text{Co(NH}_3\text{)}_6]^3+\), the dinitrogen complex is stable. Stronger oxidants, oxidise both species to ruthenium (III) complexes. \([\text{Ru(NH}_3\text{)}_6] \text{Cl}_2\) is oxidised\(^73,74\) to \([\text{Ru(NH}_3\text{)}_6]^3+\) while \([\text{Ru(NH}_3\text{)}_5(N_2)]^2+\) gives pentaammine products such as \([\text{Ru(NH}_3\text{)}_5 \text{Cl}] \text{Cl}_2\).

The hydrazine impurity in \([\text{Ru(NH}_3\text{)}_5(N_2)] \text{Cl}_2\) is often oxidised to similar products as obtained from the dinitrogen complex. It is possible that the hydrazine ligand is oxidised to dinitrogen before subsequent reaction occurs.
The different oxidation reactions, listed above, with
\[ [\text{Ru(NH}_3\text{)}_5(N_2)]\text{Cl}_2 \] suggest that in near neutral aqueous solution, the oxidation potential of \([\text{Ru(NH}_3\text{)}_5(N_2)]\text{Cl}_2\) is less than that for the half reaction \(\text{Hg}_2\text{Cl}_2 \rightarrow 2\text{Hg}^{2+} + 2\text{Cl}^- + 2\text{e}^- (-0.905 \text{ volts})^{12}\) but that it is greater than for the half reactions

\[ \text{Au} + 4\text{Cl}^- \rightarrow \text{AuCl}_4^- + 3\text{e}^- (-0.994 \text{ volts})^{12} \text{ and } 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- (-1.358 \text{ volts})^{12}. \]

Hence the oxidation potential for the oxidation of \([\text{Ru(NH}_3\text{)}_5(N_2)]^{2+}\) in neutral aqueous conditions is deduced to be around \((-0.95 \pm 0.05) \text{ volts}\).

This value is lower than that reported\(^{76}\) \((-0.72 \text{ volts})\) in \(\text{H}_2\text{SO}_4/\text{K}_2\text{SO}_4\) solvent at \(\text{pH} = 2.6\). These observations suggest that \([\text{Ru(NH}_3\text{)}_5(N_2)]^{2+}\) is more readily oxidised in acidic conditions, hence the observed oxidation of \([\text{Ru(NH}_3\text{)}_5(N_2)]\text{Cl}_2\) by 1-2 molar hydrochloric acid (Chapter 6).

**Experimental**

**Preparation of dinitrogen pentaaquamine ruthenium (II) chloride**

\[ [\text{Ru(NH}_3\text{)}_5(N_2)]\text{Cl}_2 \] using Hydrazine Hydrate-

This preparation is based on that published by Allen and Senoff\(^{60}\). \([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) (0.6g) was added to hydrazine hydrate (5 mls) and the solution stirred for 20 minutes at room temperature. The brown solution was filtered to remove excess \([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) and the yellow product was obtained by precipitation using solid \(\text{NH}_4\text{Cl}\). (Yield 0.2 g)
(Found N, 34.6%, Cl₂H₁₅N₇Ru requires N, 34.2%). Other salts such as the ZnCl₂ salt are prepared by dissolving this impure complex in water, then addition of the appropriate anion precipitates the required salt. These salts were not analysed as they were known at this stage to be impure. Purification \([\text{Ru(NH}_3)_5(N_2)]\text{Cl}_2\) (hydrazine preparation) with HgCl₂ - The product obtained above (0.1 gm) was treated with saturated aqueous mercuric chloride solution (1.1 mls). After the precipitated mercury compounds had been filtered off, ammonium chloride and zinc chloride were added to precipitate the pure dinitrogen complex \([\text{Ru(NH}_3)_5(N_2)]\text{ZnCl}_4\).

This compound was reprecipitated from water using \(\text{NH}_4\text{Cl}\) and \(\text{ZnCl}_2\). (Yield 0.02 gms). (Found Cl, 32.7% H, 3.8%; N (total), 22.4%; N (NH₃ only), 16.2%; Cl₄H₁₅N₇RuZn requires Cl, 33.6%; H, 3.6%; N (total), 23.2%; N (NH₃ only) 16.6%).

Preparation of hexaammine ruthenium (III) chloride, tetrachlorozinc (II) -

Method (a) Methanol was added to the filtrate from the preparation of pure \([\text{Ru(NH}_3)_5(N_2)]\text{ZnCl}_4\) given above. The product was obtained as white crystals after reprecipitation from \(\text{NH}_4\text{Cl/ZnCl}_2\) solution with methanol (Yield 0.07 gms). (Found Cl, 38.5%; H, 4.4%; N, 18.9%; Cl₅H₁₆N₆RuZn requires Cl, 39.4%; H, 4.1%; N, 18.8%).

Method (b) The complex \([\text{Ru(NH}_3)_6]\text{Cl}_3\) dissolved in water was treated with \(\text{NH}_4\text{Cl},\) and \(\text{ZnCl}_2\). The product was precipitated using methanol.
(Found N, 18.95%; $\text{Cl}_5\text{H}_{18}\text{N}_6\text{RuZn}$ requires N, 18.8%).

**Preparation of Pentaamminedinitrogen ruthenium (II)**

tetrachlorozinc (II) $[\text{Ru(NH}_3)_5(\text{N}_2)]\text{ZnCl}_4$  — See Experimental section for the method using azide.
CHAPTER 3

Reactions of Some Metal Complexes with Hydrazine Hydrate
and with Metallic Reducing Agents in Ammonical Solution

Introduction

First row transition metals complexes normally react with
hydrazine hydrate and simple hydrazinium salts to give hydrazine
complexes\(^7\). In contrast, ruthenium and a number of other second
and third row transition metal complexes react to give a number of
products which have often had quite unexpected compositions.
Amongst the earliest products reported are a red and a yellow
compound which resulted from the reaction of \(\text{K}_2\text{RuCl}_5\text{H}_2\text{O}\) with
hydrazine dihydrogen chloride. These compounds were proposed\(^8\)
as having hydrazine bridging between ruthenium atoms. Further
investigation\(^6\) of the yellow compound showed that it was
\[
\left[\text{Ru(NH}_3\text{)}_5\text{Cl}\right]\text{Cl}_2,
\]
and the red compound has more recently been
found\(^5\) to be the hydrazinium salt of either \(\left[\text{RuCl}_5\text{(H}_2\text{O)}\right]^{2-}\) or
\(\left[\text{RuCl}_5\text{(N}_2\text{H}_4\text{)}\right]^{2-}\), the nature of this sixth ligand is still in
question.

The most interesting reaction reported between a ruthenium
compound and hydrazine is the preparation of the first stable di-
nitrogen complex \(\left[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\right]\text{Cl}_2\) by Allen and Senoff\(^6\).
Irrespective of the fact that the compound has subsequently been
found to be impure this does not detract from the importance of the
discovery.
Bottomley has recently investigated the effects of pH on the products obtained from the reaction of hydrazine and \([\text{Ru}(\text{NH}_3)_5\text{Cl}]_2\). He found that in hot acidic conditions, \((\text{N}_2\text{H}_6\text{Cl}_2\text{ solution})\) the final product is \([\text{Ru}(\text{NH}_3)_5\text{Cl}]_2\), while the initial oxidation product detectable is \([\text{Ru}(\text{NH}_3)_6]^{3+}\). In neutral conditions \((\text{N}_2\text{H}_5\text{Cl}\text{ solution})\) a mixture of products are obtained containing

\([\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2\), \([\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2\) and the ion \([\text{Ru}(\text{NH}_3)_6]^{3+}\); while the dinitrogen product \([\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2\) is the major compound formed under alkaline conditions \((\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\text{ solution})\). Under the latter conditions a deep red intermediate is formed which Bottomley has proposed to be due to the ion

\([\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{H}_2)]^{2+}\). In alkaline hydrazine hydrate the Ru (III) compounds \([\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2\) and \(\text{RuCl}_3\cdot\text{H}_2\text{O}\) react similarly to \([\text{Ru}(\text{NH}_3)_6\text{Cl}_2]\), to form the dinitrogen product \([\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2\).

In the present work a number of reactions of various metal ions with hydrazine hydrate were carried out in order to search for dinitrogen complexes. Reactions, based on that involving the treatment of ruthenium trichloride with zinc in concentrated ammonia, were also tried with various metal ions as this original reaction had been reported to produce dinitrogen complexes.

The compounds \([\text{Ru}(\text{NH}_3)_5(\text{CO})\text{Cl}_2], [\text{Rh}(\text{NH}_3)_5\text{H}]\text{Br}_2\) and \([\text{Ir}(\text{NH}_3)_4(\text{CO})\text{Cl}]\text{Cl}_2\) have been isolated, (the latter two for the first time) from these reactions. Evidence for a bisdinitrogen
complex ion $\left[ \text{Ru(NH}_3\text{)}_4(\text{N}_2)\text{_2} \right]^{2+}$ and the new complex $\left[ \text{Os(NH}_3\text{)}_5(\text{CO})_2 \right] \text{Cl}_2$ has been obtained. The latter compound was also prepared pure by a different route. Evidence for a species $\text{Fe(dtc)}_2(\text{CO})_n$ has also been obtained.

Results and Discussion (a) Compounds.

The work will now be discussed in terms of the compounds prepared.

$\left[ \text{Ru(NH}_3\text{)}_5(\text{CO})_2 \right] \text{Cl}_2$.

The tervalent complex $\left[ \text{Ru(NH}_3\text{)}_5\text{Cl} \right] \text{Cl}_2$ gives a deep red solution when it is dissolved in hot (80°C) hydrazine hydrate, and a vigorous gas evolution occurs. The ruthenium containing complexes can be precipitated with either alcohol or ammonium chloride, after cooling. The product may be either a deep red or yellow, the colour depends on the time taken to cool the solution in contact with air. The red product is obtained after rapid cooling, while the yellow product is obtained if precipitation is delayed until the solution has stood for about one hour. The infrared spectra of both these products are identical and the same as the infrared spectrum of mixtures of $\left[ \text{Ru(NH}_3\text{)}_5(\text{N}_2) \right] \text{Cl}_2 / \left[ \text{Ru(NH}_3\text{)}_5(\text{N}_2\text{H}_4) \right] \text{Cl}_2$ (see Chapter 2) except for the addition of a sharp absorption at 1930 cm$^{-1}$. The component, giving rise to the 1930 cm$^{-1}$ absorption, could not be separated from the $\left[ \text{Ru(NH}_3\text{)}_5(\text{N}_2) \right]^{2+}$ known to be present.

A similar reaction occurs when divalent ruthenium (as $\left[ \text{Ru(NH}_3\text{)}_6 \right] \text{Cl}_2$) is heated in hydrazine hydrate, but relatively more of the new complex is obtained in the product. The relative intensity
FIGURE 6  Infrared Spectrum of $[\text{Ru(NH}_3)_5\text{(CO)}]\text{Cl}_2$ prepared using $\text{N}_2\text{H}_4, \text{H}_2\text{O}/\text{CO}_2$
Table 6  
Comparison of the Properties of $[\text{RhH(NH}_3\text{)}_5]\text{Br}_2$

<table>
<thead>
<tr>
<th>Properties from Present Work</th>
<th>Properties Reported by Wilkinson</th>
</tr>
</thead>
</table>

**Infrared Spectrum (cm$^{-1}$)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Present Work</th>
<th>Wilkinson</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(NH)</td>
<td>3285, 3190 (sh)</td>
<td>3276, 3186</td>
</tr>
<tr>
<td>$\nu$(Rh-H)</td>
<td>2013</td>
<td>2015</td>
</tr>
<tr>
<td>$\delta_a$(NH)</td>
<td>1610</td>
<td>1609</td>
</tr>
<tr>
<td>$\delta_a$(NH)</td>
<td>1275</td>
<td>1278</td>
</tr>
<tr>
<td>$\rho$(NH$_3$)</td>
<td>813</td>
<td>820</td>
</tr>
<tr>
<td>$\nu$(Rh-NH$_3$)</td>
<td>480, 448</td>
<td>483, 452</td>
</tr>
<tr>
<td>$\delta$(NH$_3$-Rh-NH$_3$)</td>
<td>265, 157 (broad)</td>
<td></td>
</tr>
</tbody>
</table>

- **Low freq. Lattice Modes**: 87
- **I.R. Other, probably $\delta$(Rh-H)**: 1185, 1170 (sh) 1171

**Ultraviolet, visible Spectrum (nm)**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>205</td>
<td></td>
</tr>
<tr>
<td></td>
<td>233 (sh)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>305 (w,sh)</td>
<td>307 (reflectance)</td>
</tr>
<tr>
<td></td>
<td>350 (w,sh)</td>
<td></td>
</tr>
</tbody>
</table>

**Reactions**  
Dilute acid - New Product, as Cl$^-$, $[\text{RhH(NH}_3\text{)}_4]^{\text{+}}$

- $\nu$(Rh-H) at 2138 cm$^{-1}$
- $\nu$(H$_2$O)$\text{SO}_4$ formed, $\nu$(Rh-H) at 2146 cm$^{-1}$

- **Halide ion**  
  - Mixed rhodium (III)  
  - Mixed ammine halide

- **in neutral solution**  
  - Products together with rhodium metal products.
of the 1930 cm\(^{-1}\) band in the infrared spectrum can also be increased by repeated reactions, on one ruthenium sample, using fresh samples of hydrazine hydrate. Analysis of a sample obtained from

\[\text{[Ru(NH}_3\text{)}_6\text{]}\text{Cl}_2\] showed that it contained 3.1% carbon, it appeared that the product was composed principally of \[\text{[Ru(NH}_3\text{)}_5(\text{N}_2\text{)}\text{]}\text{Cl}_2\] and \[\text{[Ru(NH}_3\text{)}_5(\text{CO})\text{]}\text{Cl}_2\]. The product can be obtained in the absence of organic solvents and carbon containing compounds, except for the traces of carbon dioxide dissolved in hydrazine hydrate.

Pure \[\text{[Ru(NH}_3\text{)}_5(\text{CO})\text{]}\text{Cl}_2\] was then found to be readily obtained if additional carbon dioxide was dissolved in the hydrazine hydrate, used in the reaction. Under these conditions no deep red solution is formed. This carbonyl product, the infrared spectrum of which is shown in Figure 6, has been prepared previously by the more laborious \(^67,68\) method of reacting carbon monoxide with

\[\text{[Ru(NH}_3\text{)}_5(\text{H}_2\text{O})\text{]}^{2+}\]. The properties described for this complex\(^67,68,65\) are identical to those of the carbonyl prepared during this present work.

\[\text{[RhH(NH}_3\text{)}_5\text{]}\text{Br}_2\] Rhodium trichloride and \[\text{[Rh(NH}_3\text{)}_5\text{Cl}\text{]}\text{Cl}_2\] react with zinc in ammonia to give the hydrido-complex ion \[\text{[Rh(NH}_3\text{)}_5\text{H}\text{]}^{2+}\]. The pure complex can be obtained by precipitation with sodium bromide. A number of properties of this bromide salt have been measured (Table 6). Wilkinson et al.\(^66\) have since reported the isolation of this compound and their results are similar to those obtained during this work. At the time this work was carried out, Wilkinson had only reported the N.M.R. spectrum of the hydride.
FIGURE 7  Infrared Spectrum of [Ir(NH$_3$)$_4$(CO)$_2$Cl]Cl$_2$

(insert shows addition band formed after dissolution in water)
species in solution.$^89$

The complex $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ reacts with hydrazine hydrate or hydrazinium carbonate to give a product with no absorptions near $2000 \text{ cm}^{-1}$ in its infrared spectrum. The above products appeared complex and the infrared spectra suggested that co-ordinated hydrazine was present. Further investigation did not seem warranted.

\[ \left[ \text{Ir(NH}_3\text{)}_4 (\text{CO}) \text{Cl}_2 \right] \cdot \text{Cl}_2 \] An insoluble form of $\text{IrCl}_3$ and the complex $\text{Ir(NH}_3\text{)}_3 \text{Cl}_3$, react with hydrazine hydrate and with zinc dust in concentrated ammonia to give similar products all of which have an infrared absorption at $2078 \text{ cm}^{-1}$. The product obtained from the zinc in ammonia reaction was the only one that could be purified further and was the only one to be more fully investigated.

After reaction with zinc in ammonia, the iridium product is isolated by freeze drying the filtrate from the reaction mixture. Further purification is accomplished by dissolution of the carbonyl in water and quickly removing an insoluble residue of mainly zinc hydroxide. The product is obtained by freeze drying the filtrate. It is necessary to work rapidly as the carbonyl decomposes significantly within five minutes in water, but it is stable when frozen in ice.

The product, which was never obtained completely pure because of its instability in water and insolubility in other solvents is postulated as a carbon monoxide derivative on the following evidence:

(1) The complex has an intense infrared absorption at $2078 \text{ cm}^{-1}$, (Fig.7).
(2) Decomposition of the compound with concentrated hydrochloric acid produced a gas of mass 28 together with a trace of hydrogen. The iridium product remaining in solution is trans-

\[ \text{Ir} (\text{NH}_3)_4 \text{Cl}_2 \] Cl which was identified by analysis and X-ray powder photography.

(3) Acidic ceric oxidation and thermal decomposition both give a gas of mass 28 which was identified as a mixture of dinitrogen and carbon monoxide. Some dinitrogen can be obtained from \[ \text{Ir} (\text{NH}_3)_5 \text{Cl} \] Cl\(_2\), by similar decompositions. Analysis of a sample of the complex showed carbon to be present, and the amount (2%) suggests approximately 60% purity, based on the formulation \[ \text{Ir} (\text{NH}_3)_4 (\text{CO})\text{Cl} \] Cl\(_2\).

(4) The compound is isomorphous with \[ \text{Ru} (\text{NH}_3)_5 \text{Cl} \] Cl\(_2\). This suggests a di positive cation with two chloride anions. (Faint lines corresponding to NH\(_4\)Cl are also present).

(5) The compound is diamagnetic. \( \chi_m \times 10^6 = -113 \) cgs.

Diamagnetic corrections for \[ \text{Ir} (\text{NH}_3)_4 (\text{CO})\text{Cl} \] Cl\(_2\) are \(-138 \times 10^{-6}\) cgs. (Inclusion of contributions from the probable impurities, NH\(_4\)Cl and \[ \text{Ir} (\text{NH}_3)_5 \text{Cl} \] Cl\(_2\), produces compensating errors in the calculation of the magnetic data above). The evidence is consistent with the proposal that the new product

\[ \text{Ir} (\text{NH}_3)_4 (\text{CO})\text{Cl} \] Cl\(_2\) has been formed.

In aqueous solution this compound is unstable and it partially converts, to give a new product having an additional infrared absorption
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CO) cm$^{-1}$</th>
<th>ref.</th>
<th>Compound</th>
<th>$\nu$(CO) cm$^{-1}$</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ru(NH$_3$)$_3$Cl$_2$(CO))</td>
<td>1896</td>
<td>68</td>
<td>[Ir(NH$_3$)$_4$Cl(CO)]Cl$_2$</td>
<td>2078</td>
<td>(This work)</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_4$H$_2$O(CO)]Cl$_2$</td>
<td>1921</td>
<td>68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$(CO)]Cl$_2$</td>
<td>1925</td>
<td>67, 68 K [Ir$_4$(CO)]</td>
<td>2051</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_2$[(RuCl$_4$(H$_2$O)(CO))]</td>
<td>1951</td>
<td>86 (a)</td>
<td>K$_2$(Ir$_5$(CO))N=Cl</td>
<td>2079</td>
<td>87</td>
</tr>
<tr>
<td>RuCl$_2$(CO)(Py)$_3$</td>
<td>1919</td>
<td>86(b)</td>
<td>=Br</td>
<td>2061</td>
<td>87</td>
</tr>
<tr>
<td>RuCl$<em>2$(CO)(C$</em>{18}$H$_{15}$P)$_3$</td>
<td>1950</td>
<td>86(c)</td>
<td>=1</td>
<td>2035</td>
<td>87</td>
</tr>
</tbody>
</table>

See also 86 (d) for additional monocarbonyls, but these have the $\nu$(CO) absorption in a similar range of energies to above.
at 2120 cm\(^{-1}\), (Figure 7). Dilute acid catalyses this reaction whereas strong ammonia solution stops or reverses the reaction. If a sample of product with both the 2120 cm\(^{-1}\) and 2078 cm\(^{-1}\) absorptions in the infrared spectrum is dissolved in 0.880 ammonia, then freeze dried, the resulting product has only the 2078 cm\(^{-1}\) absorption. The effect of 0.880 ammonia can be explained two ways.

(i) The addition of ammonia reverses the initial reaction, this would require that the initial reaction involves replacement of some or all the co-ordinated ammine groups with solvent water.

(ii) The addition of ammonia stabilises the component of the mixture having a 2078 cm\(^{-1}\) absorption in the infrared spectrum; the other component, with the 2120 cm\(^{-1}\) absorption, still decomposes, but with no replenishment through reaction of the "2078 cm\(^{-1}\) component". A sample having only the 2120 cm\(^{-1}\) absorption in its infrared spectrum could not be isolated, hence the two explanations (i, ii) above could not be tested to distinguish which is correct.

No evidence obtained completely confirms the absence of dinitrogen product, but on the basis of comparisons between other known dinitrogen and carbonyl compounds it seems that iridium ammine, dinitrogen compounds may be too unstable to isolate. Monocarbonyl non-hydrido-complexes of metals such as ruthenium (II) (table 7) have the \(\nu\)(CO) absorptions in the infrared at similar frequencies\(^{67,68,86}\). Iridium (III) monocarbonyls (table 7)\(^{87}\) have \(\nu\)(CO) absorptions at approximately 2060 cm\(^{-1}\) which adds
supporting evidence to the proposal that the compound prepared during this work is an iridium (III) carbonyl. Presumably the iridium must first be reduced, probably to Ir(I), before any stable dinitrogen complexes are likely to be isolated.

The compound Ir(NH$_3$)$_5$, proposed by Watt$^{88}$ to be the product of the reaction of [Ir(NH$_3$)$_5$Cl]Cl$_2$ with sodium in liquid ammonia, was prepared to see if it was a dinitrogen complex but the infrared spectrum of this product showed no absorptions near 2000 cm$^{-1}$, ruling out a mononuclear dinitrogen complex. No investigations to check for a dimer were made.

cis [Ru(NH$_3$)$_4$(N$_2$)$_2$]Br$_2$. The complex [Ru(NH$_3$)$_5$Cl]Cl$_2$ reacts with cold (< 0°C) hydrazine hydrate to form a brown solution. No further visible change occurs in this solution after standing at < 0°C for one to two hours.

The ruthenium containing species in this solution can be isolated as a brown solid by precipitation with sodium bromide. The infrared spectrum of the solid, after precipitation shows absorptions characteristic of hydrazine together with a absorption at 2105 cm$^{-1}$, attributable to the $\tilde{\nu}$(NN) stretch in monodinitrogen, ruthenium (II) complexes.

If the [Ru(NH$_3$)$_5$Cl]Cl$_2$ / hydrazine hydrate solution is left at < 0°C for longer than one hour before the brown ruthenium containing product is precipitated, then the infrared spectrum of this solid shows
After one hour
(no change after one week)

After one year

FIGURE 8 Infrared Spectra of the Product of the Reaction of $\left[\text{Ru(NH}_3)_4\right]\text{Cl}_2 \text{Cl}$ with Hydrazine Hydrate at $\leqslant 0^\circ\text{C}$.
two additional absorptions at 2230 cm\(^{-1}\) and 2180 cm\(^{-1}\) (Figure 8). The two additional absorptions are at similar frequencies to the two \(\sqrt{NN}\) absorptions of the bisdinitrogen complex cis \([\text{Ru(en)}_2(N_2)_2]\) \((\text{BPh}_4)_2\) prepared by Kane-Maguire et al.\(^{44}\).

This new product can be obtained more readily by the reaction of cold hydrazine hydrate on \textit{cis} \([\text{Ru(NH}_3)_4\text{Cl}_2]\) Cl. In this reaction only a five to ten minute reaction time is required before the product can be precipitated as the bromide. The product has an identical infrared spectrum to that obtained previously except the 2230 cm\(^{-1}\) and 2180 cm\(^{-1}\) absorptions are both relatively more intense. The more rapid reaction and the greater proportion of new product present when \textit{cis} \([\text{Ru(NH}_3)_4\text{Cl}_2]\) Cl is used as the source of ruthenium, suggests that this product is \textit{cis} \([\text{Ru(NH}_3)_4(N_2)_2]\) \(\text{Br}_2\), as does the infrared spectrum.

Greater yields of the bisdinitrogen product were obtained by mild oxidation, with cold bromine water, of the brown product precipitated from the reaction mixture of \textit{cis} \([\text{Ru(NH}_3)_4\text{Cl}_2]\) Cl and cold hydrazine hydrate. Presumably this reaction involves the oxidation, of the co-ordinated hydrazine in this product, to co-ordinated dinitrogen.

All these preparations containing \textit{cis} \([\text{Ru(NH}_3)_4(N_2)_2]\) \(\text{Br}_2\) are much too impure to allow any sensible analytical results to be obtained. Further purification was not possible because of the
instability of the complex in solution. Hence the existence of this bisdinitrogen complex can only be proposed on the basis of its infrared spectrum, preparative method and comparison with 
\[
\text{cis} - \left[ \text{Ru(en)}_2 (N_2)_2 \right] \text{Br}_2
\]
\[44\]. Possibly the most interesting thing about the two ruthenium bisdinitrogen complexes
\[
\text{cis} - \left[ \text{Ru(NH}_3)_4 (N_2)_2 \right] \text{Br}_2 \quad \text{and} \quad \text{cis} - \left[ \text{Ru(en)}_2 (N_2)_2 \right] (BPh_4)_2
\]
is that they differ significantly in their reported stabilities in the solid state. Co-ordinated ammonia or ethylenediamine could be expected to behave as very similar ligands, in complexes but the stability of dinitrogen as a ligand has previously been noted\[93\] to be very sensitive to minor changes in the metal complex to which it is bonded. Impurities can also have large effects on the stability of dinitrogen complexes and on the frequency of the \( \nu(NN) \) infrared absorption (ref. 26 and Chapter 5). An additional reason for the observed stability of the bisdinitrogen complex \[
\text{cis} - \left[ \text{Ru(NH}_3)_4 (N_2)_2 \right] \text{Br}_2
\]
relative to \[
\text{cis} - \left[ \text{Ru(en)}_2 (N_2)_2 \right] (BPh_4)_2
\]
could be that hydrazine impurities in samples of the former complex, continually decompose, to produce more of the bisdinitrogen complex. During this present work an attempt was made to prepare \[
\text{cis} - \left[ \text{Ru(en)}_2 (N_2)_2 \right] \text{Br}_2
\]
using the low temperature hydrazine hydrate reaction on \[
\text{cis} - \left[ \text{Ru(en)}_2 \text{Cl}_2 \right] \text{Cl}
\]
but without success. This observation suggests additional factors may be involved other than the hydrazine impurities.

\[
\left[ \text{Os(NH}_3)_5 \text{(CO)} \right] \text{Cl}_2
\]

Traces of the carbonyl \[
\left[ \text{Os(NH}_3)_5 \text{(CO)} \right] \text{Cl}_2
\]
can be prepared by a reaction similar to that used to prepare the ruthenium carbonyl.
<table>
<thead>
<tr>
<th>Infrared Spectrum</th>
<th>Assignment</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu(NH) )</td>
<td></td>
<td>3320, 3260 (sh)</td>
</tr>
<tr>
<td>( \nu(CO) )</td>
<td></td>
<td>1898, 1848 (sh)</td>
</tr>
<tr>
<td>( \delta(NH) )</td>
<td></td>
<td>1633</td>
</tr>
<tr>
<td>( \delta_2(NH) )</td>
<td></td>
<td>1315, 1300 (sh), 1298</td>
</tr>
<tr>
<td>( \alpha(NH_3) )</td>
<td></td>
<td>808</td>
</tr>
<tr>
<td>( \nu(Os-CO), \delta(OsCO) )</td>
<td></td>
<td>604</td>
</tr>
</tbody>
</table>

**Ultraviolet-visible Spectrum**

No absorptions at energies below 210 nm but has an absorption above this energy (i.e., similar to the ruthenium complex).

**Stability**

Stable in hot concentrated hydrochloric acid, and in the same solvent in the presence of dissolved iodine.
Os(III) or Os(IV) salt as Cl$^-$

$\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$
Boil with CO$_2$

↓

Mixture of $[\text{Os(NH}_3)_5(\text{N}_2)]\text{Cl}_2$ and $[\text{Os(NH}_3)_5(\text{CO})]\text{Cl}_2$

↑

$\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$
Boil with CO$_2$

↓

I$_2$ oxidation in HCl

↓

Mixture of $[\text{Os(NH}_3)_5(\text{CO})]\text{Cl}_2$ and $[\text{Os(NH}_3)_5\text{Cl}]\text{Cl}_2$

FIGURE 9  Cycle for the Purification of $[\text{Os(NH}_3)_5(\text{CO})]\text{Cl}_2$
When a mixture of hydrazine hydrate and hydrazinium carbonate is heated with either \([\text{Os(NH}_3\text{)}_5\text{Cl} ]\text{Cl}_2\) or \((\text{NH}_4\text{)}_2(\text{OsCl}_6)\), the product has a weak infrared absorption at 1887 cm\(^{-1}\), corresponding to the frequency of the \(\tilde{\nu}(\text{CO})\) absorption in pure \([\text{Os(NH}_3\text{)}_5(\text{CO})]\text{Cl}_2\), (see below) together with a strong absorption at 2008 cm\(^{-1}\) corresponding to the dinitrogen complex \([\text{Os(NH}_3\text{)}_5(\text{N}_2)]\text{Cl}_2\). The yield of carbonyl could not be increased by any changes of conditions (e.g. by using Zn dust in ammonia).

The carbonyl is stable to concentrated hydrochloric acid and iodine oxidation, hence it may be partially purified by the reaction cycle shown in Figure 9. Mechanical losses prevent this method being used for small scale preparations of the pure carbonyl, but on a larger scale it would probably be feasible to separate the carbonyl after only one or two cycles.

However, a much better method to prepare the pure osmium carbonyl complex is to use a method analogous to that reported\(^{67,68}\) previously to prepare \([\text{Ru(NH}_3\text{)}_5(\text{CO})]\text{Cl}_2\). The complex \([\text{Os(NH}_3\text{)}_5\text{Cl} ]\text{Cl}_2\) was reduced with Zinc amalgam, then carbon monoxide was bubbled through for sixty hours. The properties of this osmium carbonyl are shown in Table 8 and Figure 10.

During the preparation it was observed that dinitrogen was competing with carbon monoxide for co-ordination to the osmium (II). Incomplete exclusion of air from the reaction mixture gives a product whose infrared spectrum shows a distinct \(\tilde{\nu}(\text{NN})\) absorption at 2005 cm\(^{-1}\).
Infrared Spectrum of $\{\text{Os(NH}_3)_5\text{(CO)}\} \text{Cl}_2$
as well as the absorption at 1885 cm\(^{-1}\) due to the \(\nu(CO)\) absorption of the carbonyl component. Reactions carried out in air with relatively low partial pressures of carbon monoxide (about 40 mm) give products which have little detectable carbonyl but have strong \(\nu(\text{NN})\) absorptions in their infrared spectra. Even at higher carbon monoxide concentrations, a little dinitrogen product was detected. This qualitative evidence suggests that the reduced species, obtained from 

\[\text{[Os(NH}_3)_5\text{Cl]} \text{Cl}_2,\]

reacts with dinitrogen at a comparable rate to its reaction with carbon monoxide, especially as the latter gas is approximately 1.5 times as soluble in water (at 0°C 3.5 cm\(^3\) per 100 mls compared with 2.33 cm\(^3\) per 100 mls for dinitrogen)\(^{12}\). Previously it has been observed for ruthenium (II), that the rate constants for addition of CO\(^{97}\) or \(N_2^{48}\) to \([\text{Ru(NH}_3)_5(\text{H}_2\text{O})]\)^{2+}, are similar.

In this case it appears\(^{48}\) that the rate determining step is the initial dissociation of the \([\text{M(NH}_3)_5(\text{H}_2\text{O})]\)^{2+} into a five co-ordinate species which reacts rapidly with dinitrogen, carbon monoxide or other substrates.

\[\text{Fe(dtc)}_2(\text{CO})_n\] - The complex trisdiethylidithiocarbamate iron (III), \(\text{Fe(dtc)}_3\), reacts with hydrazine hydrate solution to give a product with an infrared absorption at 2070 cm\(^{-1}\). Originally it was hoped that this new complex would be a dinitrogen complex, which could be a model system for the iron, sulphur, dinitrogen complex
Infrared Spectra of samples of Fe(dtc)$_2$CO$_{(n)}$

FIGURE 11

i) — Product from evaporation of reaction mixture.

ii) — Product after reaction of above with HgCl$_2$ solution.
proposed to exist in nitrogenase. The complex Fe\((\text{dtc})_3\) readily loses at least one dithiocarbamato ligand to give a variety of products, such as the halides Fe\((\text{dtc})_2X\) (\(X=\text{Cl}, \text{Br}, 1\))\(^{90}\) and the nitrosyl Fe\((\text{dtc})_2(\text{NO})\)\(^{91}\), while the carbonyl cis Fe\((\text{dtc})_2(\text{CO})_2\)\(^{92}\) has been prepared although not by carbon monoxide displacement of dithiocarbamate.

Solutions of Fe\((\text{dtc})_3\) or Fe\((\text{dtc})_2\text{Cl}\) both react similarly in ethanol with hydrazine hydrate to give a product with an infrared absorption at 2070 cm\(^{-1}\). In both products Fe\((\text{dtc})_3\) and hydrazine hydrate can be detected (infra red spectra) and use of Fe\((\text{dtc})_2\text{Cl}\) appeared to offer no advantage. The Fe\((\text{dtc})_3\) can be removed by dissolving the product in water while the excess hydrazine hydrate is removed by oxidation with mercuric chloride solution. The yield of product, the infrared spectrum of which is shown in Figure 11, is extremely low. The two products in this figure are considered to contain an identical complex with an infrared absorption at 2070 cm\(^{-1}\). The differences between the spectra are thought to be due to variations in the impurities present. (Product(1) is known to have hydrazine hydrate present.

The evidence below suggests that the product with the 2070 cm\(^{-1}\) infrared absorption contains co-ordinated carbon monoxide rather than the hoped for dinitrogen.

(a) Acid ceric oxidation and thermal decomposition both give a
<table>
<thead>
<tr>
<th>Property</th>
<th>cis-Fe(dtc)$_2$(CO)$_2$</th>
<th>New Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared</td>
<td>2090, 2040 cm$^{-1}$</td>
<td>2078 cm$^{-1}$</td>
</tr>
<tr>
<td>(v(CO))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Both compounds have numerous other absorptions due to the dithiocarbamate ligands.

Stability  
Heat  
CO lost in both cases after short periods of warming.

Colour  
Both products are pale cream.
gas composed of a mixture of carbon monoxide and dinitrogen. The infrared spectra of the sample decomposed above showed some hydrazine present, hence the evolved dinitrogen. The carbon monoxide suggests the presence of a carbonyl complex in the mixture.

(b) The compound cis-Fe(dtc)$_2$(CO)$_2$ is known$^9$ and this compound has properties which are similar but not identical to those of the product above. A comparison of the properties of these two compounds is shown in Table 9.

The most probable composition for this new compound appears to be one of the following two:

(i) trans Fe(dtc)$_2$(CO)$_2$ - one ν(CO) infrared absorption.

(ii) Fe(dtc)$_2$(CO) Fe(dtc)$_2$(NO) - analogous to the nitrosyl.

The lack of thermal stability of this new compound, together with the reported observation$^9$ that cis - (Fe(dtc)$_2$(CO)$_2$ can only be prepared pure at temperature less than 0°C, makes it unlikely that the new carbonyl can be prepared pure by the above hydrazine method. The most pure product, described above, was prepared at temperatures of about 40°C. Lower temperatures result in slower reactions and less pure products, while no carbonyl is produced when the reaction mixture is cooled on an ice bath. At this stage it was decided that further investigation of this reaction of Fe(dtc)$_3$ in
TABLE 10

Products from the Reaction of some Metal Complexes with Hydrazine Hydrate and with Metal Reductants in Concentrated Ammonia

<table>
<thead>
<tr>
<th>Metal Complex</th>
<th>Temperature</th>
<th>Hydrazine Hydrate</th>
<th>Metal in Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0°C</td>
<td>25°C</td>
<td>60°C</td>
</tr>
<tr>
<td>[Os(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;Cl]&lt;sub&gt;2&lt;/sub&gt; and (NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;OsCl&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Mixture of [Os(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]Cl&lt;sub&gt;2&lt;/sub&gt; and [Os(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Similar to 0°C</td>
<td>Mixture of [Os(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; and [Os(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]Cl&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;Cl]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Analagous mixture to reaction but with no [Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Similar to above</td>
<td>Mixture of [Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; and [Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>RhCl&lt;sub&gt;3&lt;/sub&gt;·nH&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Rhodium hydrazine products</td>
<td></td>
<td>[Rh(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;H]&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>IrCl&lt;sub&gt;3&lt;/sub&gt; and Ir(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;Cl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Mixture of [Ir(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;(CO)Cl]&lt;sub&gt;2&lt;/sub&gt; and hydrazine containing products</td>
<td></td>
<td>(Ir(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;(CO)Cl]&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>Fe(dicarboxylate)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Fe(dicarboxylate)&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;n&lt;/sub&gt; at 40°C reaction</td>
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hydrazine hydrate would be unlikely to give improved results, and certainly no dinitrogen complex.

(b) Reactions

The actual products obtained under various reaction conditions are summarised in Table 10. The compounds $[\text{RhH(NH}_3)_5 \text{Br}_2$, $\text{cis} \ [\text{Ru(NH}_3)_4 (N_2)_2 \text{Br}_2$, $\text{Fe(dtc)}_2 (\text{CO})_n$, $[\text{Os(NH}_3)_5 (\text{CO})] \text{Cl}_2$ and $[\text{Ir(NH}_3)_4 (\text{CO}) \text{Cl}] \text{Cl}_2$ are new species which have not been reported at the time they were detected. $[\text{RhH(NH}_3)_5 \text{Br}_2$ has since been reported$^{66}$. This present work has also shown that $[\text{Ru(NH}_3)_5 (\text{CO})] \text{Cl}_2$ can be produced by a new reaction and the osmium dinitrogen complexes $[\text{Os(NH}_3)_5 (N_2)_2 \text{Cl}_2$ and $\text{cis} \ [\text{Os(NH}_3)_4 (N_2)_2 \text{Cl}_2$ have been detected as products from the reduction of Os (III) and Os (IV) complexes with both hydrazine hydrate and reducing metals in ammonia. Of these reactions, probably the most unexpected is the preparation of carbonyl complexes from the reduction of carbon dioxide to carbon monoxide in the presence of metal ions. The preparation of the iridium complex, using hydrazine hydrate and zinc in ammonia, suggests that the significant environment is a suitable metal complex in a strongly reducing ammoniacal solution containing some soluble carbonate.

Two mechanisms appear possible for the preparation of the carbonyl products.

(i) Reduction of carbon dioxide to carbon monoxide in solution, which then co-ordinates to the metal ion.
Co-ordination of the dissolved carbon dioxide to suitable metal ions, then reduction of this group to give co-ordinated carbon monoxide.

The preparation of pure \([\text{Ru(NH}_3)_5\text{ (CO)}]\text{Cl}_2\) using hydrazine hydrate/carbon dioxide suggests, but does not prove, that free carbon monoxide is not involved. Ruthenium metal complexes cause vigorous catalytic decomposition of hot hydrazine hydrate solution to dinitrogen and dihydrogen. The proposed mechanism of carbon monoxide and dinitrogen addition to ruthenium (II) would suggest that this dinitrogen should compete with any free carbon monoxide for co-ordination to the ruthenium ion, but no dinitrogen product is obtained. Also the iron complex, \(\text{Fe(dtc)}_2\text{(CO)}_n\) cannot be prepared using carbon monoxide gas and \(\text{Fe(dtc)}_3\) solution. In this reaction, an iron carbonyl complex (probably \(\text{Fe(CO)}_4\), from infrared spectra), is formed and it certainly is not the same product as obtained using hydrazine hydrate. These observations make it unlikely that any free carbon monoxide is involved in the reactions.

The preparation of the dinitrogen complexes from the reaction of ruthenium and osmium complexes with reducing metals in ammonia is interesting as this reaction involves the oxidation of ammonia nitrogen in the presence of strong reducing agents. Chatt and Fergusson have suggested a ruthenium hydride, as an intermediate in the preparation of the ruthenium dinitrogen complex by
FIGURE 12  Infrared Spectrum of the Product from the Reaction
of $\text{[Os(NH}_3)_5\text{Cl]}\text{Cl}_2$ with Mg/Hg in 880 Ammonia Solution.
the reduction of RuCl$_3$ with zinc in concentrated ammonia, but the reaction with osmium, (as [Os(NH$_3$)$_5$Cl]$^2_2$), under similar conditions, to form the bisdinitrogen complex cis [Os(NH$_3$)$_4$(N$_2$)$_2$]Cl$_2$ does not seem to be able to be explained by any hydride intermediate. The unit, [Os(NH$_3$)$_5$], seems to be stable in neutral and slightly acidic conditions, with both the +3 and +2 oxidation states (Osmium (III) as [Os(NH$_3$)$_5$Cl]$^{2+}$ is quite stable, even to strong acid while osmium (II) as [Os(NH$_3$)$_5$X]$^{n+}$ (X probably = H$_2$O) is stable enough for it to take part in a relatively slow reaction with carbon monoxide or dinitrogen). It seems unreasonable to suppose that the [Os(NH$_3$)$_5$] group will be less stable in concentrated ammonia, but it is still possible under these conditions to prepare a bisdinitrogen complex in a reaction of less than ten minutes. It seems that the co-ordinated ammonia, nitrogen atoms must supply at least one of the nitrogen atoms in the resulting co-ordinated dinitrogen groups.

The initial step of the reaction must involve some change to the co-ordinated ammonia so as to enable it to dimerise with another ammonia to form a NN bonded group which can be degraded into co-ordinated dinitrogen. A possible reaction route could involve intermediates, similar to the nitrene [Ru(NH$_3$)$_5$(NH)]$^{3+}$, said to form during the acid degradation of [Ru(NH$_3$)$_5$(N$_3$)]$^{2+}$ to give [Ru(NH$_3$)$_5$(N$_2$)]$^{2+}$ and [Ru$_2$(NH$_3$)$_{10}$(N$_2$)]$^{4+}$.

* See Figure 12. This product is impure but the frequencies of the 2120 and 2175 cm$^{-1}$ absorptions are identical to those of authentic cis [Os(NH$_3$)$_4$(N$_2$)$_2$] (BPh$_4$)$_2$
Co-ordinating Properties of the Ammines of Osmium, Ruthenium, Iridium and Rhodium.

The various reactions of the ammines of Os, Ru, Ir and Rh are shown in Table 10. The osmium and ruthenium ammines react with hydrazine hydrate and zinc dust in ammonia to give similar products such as the mono- and bis-dinitrogen complexes. In hydrazine hydrate, monocarbonyl products may also be obtained. Iridium reacts to give the carbonyl product from both reactions while rhodium reacts to give hydrido- (zinc/ammonia) or other bonded products (e.g. with hydrazine).

In all these metal complexes above, the metal ion in the product has the $d^6$ configuration, but ruthenium and osmium are in oxidation state (II) while iridium and rhodium are in oxidation state (III) the latter of which is less favourable for the bonding of $\pi$ acceptor ligands. These oxidation state effects will partly explain, the preference of rhodium for a $\sigma$ bonded hydrido- ligand, and the relative weakness of the iridium to carbon bond in

$$[\text{Ir(NH}_3)_4 (CO) \text{Cl}] \text{Cl}_2$$

compared with osmium and ruthenium to carbon bonds in the complexes $$[\text{Ru(NH}_3)_5 (CO)] \text{Cl}_2,$$ and $$[\text{Os(NH}_3)_5 (CO)] \text{Cl}_2,$$ (e.g. decomposition of the iridium complex in concentrated hydrochloric acid but not the other two carbonyls).

The reduction of oxidation state seems to result in the metal preferring co-ordination to dinitrogen instead of carbon monoxide.
This suggests that the change in $\pi$ donor ability of the metal is more important for the bonding of dinitrogen, than for the bonding of carbon monoxide. The two 3rd row metals also favour acceptor ligands compared with the corresponding 2nd row metal (e.g. stable bisdinitrogen complexes with osmium but not with ruthenium).

**Experimental**

**Preparation of carbonylpentaammineruthenium (II) chloride**

$[\text{Ru(NH}_3\text{)}_5\text{(CO)}] \text{Cl}_2$

Freshly prepared $[\text{Ru(NH}_3\text{)}_6\text{Cl}_2\text{]}^*$ (0.5 g) was refluxed for 15 minutes in a solution of hydrazine hydrate / hydrazinium carbonate (prepared by saturating one ml. of $N_2H_4 \cdot H_2O$ with $CO_2$ gas, before addition of remaining 5 mls. $N_2H_4 \cdot H_2O$). This solution was then cooled on ice and the product precipitated (if required) by addition of ammonium chloride. (Yield 0.4 gms).

(Found C, 4.29; H, 5.4; $\text{CCl}_2\text{H}_15\text{N}_5\text{ORu}$ requires C, 4.21; H, 5.25).

*Any Ru (III) present will give same dinitrogen component in the product. If the sample is of doubtful purity then it can be reduced by being dissolved in the minimum 1.0 molar $NH_3$ solution. After reduction with zinc dust and filtering, this solution can be used directly in the above preparation.*
Preparation of carbonylpentaammineosmium (II) dichloride

\[ [\text{Os(NH}_3\text{)}_5\text{(CO)}] \text{Cl}_2 \cdot \]

\[ [\text{Os(NH}_3\text{)}_5\text{Cl}] \text{Cl}_2 \text{ (0.2 gm)} \text{ was dissolved in 0.1 molar sulphuric acid (30 mls). Hg/Zn amalgam was then added and carbon monoxide gas (prepared from formic acid/phosphoric acid)} \]

was bubbled through for sixty hours. The resultant solution was then evaporated to about 15 mls, then ammonium chloride was added to precipitate the product as colourless leaflets. (Yield 0.1 gms). (Found C, 3.3; H, 2.7; \text{CCl}_2\text{H}_5\text{N}_5\text{OOs requires C, 3.2; H, 4.0}).

Preparation of carbonyltetraamminechloroiridium (III) chloride

\[ [\text{Ir(NH}_3\text{)}_4\text{(CO)}\text{Cl}] \text{Cl}_2 \cdot \]

\[ \text{Ir(NH}_3\text{)}_3\text{Cl}_3 \text{ (0.1 gm)} \text{ (or other suitable starting material such as } \text{(NH}_4\text{)}_2\text{IrCl}_6 \text{ or an insoluble form of } \text{IrCl}_3 \text{) was added to } \text{860 ammonia (10 mls)} \text{ together with zinc dust. This yellow solution was stirred for about 30 hours with ammonia gas slowly bubbling through. At the end of the reaction the solution had become almost colourless. The product was isolated by freeze drying the filtrate. This white product was dissolved in distilled water and after rapid filtering, the aqueous solution was frozen, and again freeze dried. (yield 0.05 gms). (Found, C, 2.0; H, 4.7%; CCl}_3\text{N}_5\text{Ir}_4\text{O requires C, 3.1; H, 3.1}). \text{ Infrared spectra suggest that the purity of the} \]
above complex varies with scale of reaction. Smaller scale reactions give the most pure product.

Preparation of triamminetrichloroiridium (III) Ir(NH₃)₃Cl₃.

Chloroiridic acid (0.5 gm) was dissolved in the minimum water, then added to hot 880 ammonia. Gas was evolved and the solution was evaporated to dryness and the ammonia treatment repeated. The crude product was dissolved in water, conc. hydrochloric acid was added (about 1:4 of water). The solution was then left to stand and the product precipitated out. (Yield 0.3 g).

(Found N, 12.5, Cl₃H₃IrN₃ requires N, 12.1).

Preparation of trans-tetraamminedichloroiridium (II) chloride.

trans-[Ir(NH₃)₄Cl₂]Cl

[Ir(NH₃)₄(CO)Cl]Cl₂ was heated in concentrated hydrochloric acid on a steam bath (about 10 ml. / 0.1 gm of iridium complex). After 1 hour, the solution was cooled and the crystals of the product were filtered off. These were isomorphous with trans-[Co(NH₃)₄Cl₂]Cl.

(Found N, 14.9; Cl₃H₁₂IrN₄ requires N, 15.1).

Preparation of pentaamminehydridorhodium (III) bromide

[Rh(H)₂(NH₃)₅]³⁺Br₂

RhCl₃·nH₂O (0.5 gm) was added to 880 ammonia containing an excess of zinc dust (1.2 gms). (The two solids cannot be in
contact without ammonia present). The solution was stirred for 15 minutes, then filtered and the product precipitated with sodium bromide (Yield 0.5 gm).

(Found, H, 4.7; N, 19.2; Br2H16N5Rh requires H, 4.6; N, 20.0).

Preparation of cis-bis[ethylenediaminedichlororuthenium chloride
cis \( [\text{Ru (en)}_2\text{Cl}_2] \text{Cl}. \) This complex was prepared from \( [\text{Ru (en)}_2\text{(ox)}] [\text{Ru(ox)}_2\text{(en)}] \) in HCl by the literature method 100.

Preparation of tris(diethylidithiocarbamato iron (III) Fe(dtc)3

\( \text{Fe(NO}_3)_3\cdot\text{6H}_2\text{O} \) (7 gms) and Na(dtc) (11 gm) were each dissolved in separate portions of ethanol. The Na(dtc) portion was added to the iron containing solution, to give fine red crystals of the product. This product was identical to that obtained and analysed by Dr K. Emerson 83.

Preparation of \( [\text{Ru(NH}_3)_4\text{(oxalate)}]_2\text{S}_2\text{O}_6 \)

\( [\text{Ru(NH}_3)_5\text{Cl}]\text{Cl}_2 \) (1 gm) was dissolved in water (80 mls) with oxalic acid (0.5 gm) and \( \text{Na}_2\text{S}_2\text{O}_6 \) (1 gm) by heating the solution almost to boiling. The solution was kept at this temperature for 4 hrs, then warmed at about 60°C for a further 24 hrs while yellow powdery crystals of the insoluble product were formed. (Yield 0.4 gm).

(Found N, 15.9%. \( \text{C}_4\text{H}_2\text{N}_8\text{O}_{14}\text{Ru}_2\text{S}_2 \) requires N, 16.5%.) Gleu142
reports that this reaction is almost quantitative but the above yield is only about 60%.

Preparation of cis \([\text{Ru(NH}_3\text{)}_4\text{Cl}_2]\text{Cl} \, 3/2 \text{H}_2\text{O}\).

\([\text{Ru(NH}_3\text{)}_4\text{(oxalate)}]_2\text{S}_2\text{O}_6\) (0.2 gm) was dissolved in boiling concentrated \(\text{HCl}\) (15 mls). The solution was filtered and cooled. Ethanol (30 mls) was added to precipitate the pale yellow orange needle crystals of the product. (Yield 0.15 gm). The product was recrystallised from \(\text{HCl} / \text{Ethanol}\) but both the crude and recrystallised samples appear to be identical and recrystallisation yields are low.

(Found N, 18.7%. \(\text{Cl}_3\text{H}_15\text{N}_4\text{O}_3 / 2\text{Ru}\) require N, 18.5%.

Preparation of the iron carbonyldiethyldithiocarbamate Complex \(\text{Fe(dtc)}_2(\text{CO})_n\).

\(\text{Fe(dtc)}\) (0.5 gm) was dissolved in the minimum volume of \(\text{THF}\) (about 20 mls). An ethanol solution of 0.2 Molar hydrazine hydrate (35 mls) was added and oxygen bubbled through the mixture for 3 minutes. The product was then rapidly evaporated in a stream of air to give the product as a black to red oil. Solution of this oil in water left a black residue of \(\text{Fe(dtc)}_3\) - the pale yellow oil, containing the product, was obtained on freeze drying this solution.

Other Compounds - The preparation of the other compounds used in this chapter are given in Part C. These are the complexes

\([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2;\; [\text{Ru(NH}_3\text{)}_6\text{]}\text{Cl}_2;\; [\text{Os(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2;\)
Many of the products prepared during the present work were detected by infrared spectra. The spectrum of the product was compared with those of known complexes. Correspondence of absorptions were used to suggest likely products. Where possible these were purified, but often the reactions gave mixtures of very similar products which are difficult (usually impossible) to separate owing to their instability in solution.
CHAPTER 4

The Structure of the Complex Dinitrogenpentaammine

Osmium (II) Chloride. \([\text{Os}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2\)

Introduction and Summary

The crystal and molecular structures of the dinitrogen complex, dinitrogen pentaammine osmium (II) chloride \([\text{Os}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2\), have been determined from three-dimensional X-ray data collected by counter technique. The central metal atom is in an ordered, distorted octahedral environment of six nitrogen atoms, five from ammonia ligands and one dinitrogen ligand. The osmium-ammonia (N) bonds range from 212 to 215 pm and the osmium-dinitrogen bond is 184.2 pm while the dinitrogen NN bond is 112 pm. The OsNN angle is 179°.

Crystal data: Orthorhombic; space group Pnma; \(a = 1357.5\), \(b = 1046.5\), \(c = 687.3\) pm, \(z = 4\); \(D_{\text{obs}} = 2.56 + 0.03\), \(P_{\text{cal}} = 2.54 \text{ gm cm}^{-3}\). The structure was refined using 706 reflections for which \(F^2 > \sigma (F^2)\). The conventional R factor is 3.9%.

Earlier structure analyses of dinitrogen complexes have been affected by problems of disorder\(^{56,57}\), complexity\(^{54}\), and instability\(^{55}\). In the ordered structures, metal-dinitrogen bond lengths have been found to be short as is characteristic of multiple bonding, while the dinitrogen \(N \equiv N\) bond has been found to be little changed from its length in gaseous dinitrogen\(^{55}\) (Table 3). The metal -N \equiv N bond
angles have all been observed to be close to 180°.

The compound \([\text{Os(NH}_3\text{)}_5\text{(N}_2\text{)}]\text{Cl}_2\) was chosen for the present study because of its molecular simplicity and its X-ray powder photographs indicated that it was probably isomorphous with \([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) whose structure has been reported\(^6\). In this latter structure, the central ruthenium ion is at the centre of an ordered octahedral arrangement of one chlorine and five ammonia ligands, with three of the ammonia groups, the ruthenium and coordinated chlorine atoms lying on crystallographic mirror planes. This ruthenium structure was solved using 550 reflections, whose intensities were estimated by eye from Weissenberg films. The structure was analysed as an ordered structure but the R-factor was rather high at 16.7%. The reason for this high R-factor was unknown. Disorder was suggested\(^6\) as being a possible reason.

Chemically, the osmium dinitrogen complex is interesting because of the stability of the Os-N\(_2\) entity, and the relatively low energy of the \(\nu(N \equiv N)\) absorption together with the high energy of the \(\nu(Os-N\_2)\) absorption in its infrared spectrum.

**Collection and Reduction of Data**

The dinitrogen complex \([\text{Os(NH}_3\text{)}_5\text{(N}_2\text{)}]\text{Cl}_2\) is prepared as a pale yellow microcrystalline solid by the prolonged boiling of
\[ \text{Os(\text{NH}_3)_5 \text{Cl}} \text{Cl}_2 \text{ or } \text{(NH}_4 \text{)_2 OsCl}_6 \text{ in hydrazine hydrate.} \]

Recrystallisation of this complex proved difficult. Allen and Stevens\textsuperscript{101} report that the complex is stable in aqueous solution and in concentrated hydrochloric acid, hence recrystallisation was attempted from both water and dilute hydrochloric acid. In water, the complex was found to decompose to give brown sludges after several days at room temperature, although at lower temperatures (approximately 5°C) this did not occur. In dilute hydrochloric acid (0.1M) slow decomposition to pale yellow \[ \text{Os(\text{NH}_3)_5 \text{Cl}} \text{Cl} \text{ occurs.} \]

A crystal fragment, suitable for X-ray intensity work, was finally obtained by slow cooling, from about 60°C, of a saturated hydrazine hydrate solution of \[ \text{Os(\text{NH}_3)_5 (N}_2 \text{)} \text{Cl}_2 \text{. } \]

Microscopic and photographic examination of the approximately octahedral crystals indicated that very few were suitable for X-ray intensity work.

Preliminary precession photographs revealed orthorhombic symmetry and all recorded spectra satisfied the conditions \( h = 2n; \) \( okl, k + 1 = 2n. \) These conditions are consistent with the space groups \text{Pnma} (centrosymmetric) or \text{Pa n2} (non-centrosymmetric). This analysis has confirmed the centrosymmetric space group as the correct one.

The crystal was mounted rigidly but in a random orientation
for data collection using a Hilger and Watts, four circle automatic diffractometer. All diffractometer experiments were carried out using zirconium filtered Mo Kα radiation, for which the mean Kα wave length was taken as 71.07 pm. A take-off angle of 3° was used and the circular receiving aperture was positioned 23 cm from the crystal.

The setting angles of twelve reflections, accurately centred in a 1.5 mm diameter circular receiving aperture, were used for a least-squares refinement of the cell parameters and crystal orientation matrix. The cell parameters, with standard deviations, for the orthorhombic space group Pnma, were found to be a = 1357.5 (4), b = 1046.5 (2), c = 687.3 (2) pm, (T = 25°). The density of the bulk sample was obtained using a calibrated density gradient tube (bromoform / 1, 2-dibromomethane) and found to lie in the range (2.56 ± 0.03) g cm⁻³. For four molecules in the unit cell the calculated density is 2.54 g cm⁻³. The mosaicity of the crystal was examined by means of open-counter ω scans. The width, at half peak height for a typical strong, low angle reflection, was 0.20°.

The intensity data were then collected, using a circular receiving aperture of 5 mm. diameter, and the θ-2θ scan technique. A symmetric scan range of 1.60° in 2θ, centred on the calculated peak position was composed of 80 steps of 0.75 seconds duration. Stationary crystal, stationary counter background counts of 15 seconds
were taken at each end of the scan range. Attenuation was not required as the intensity of the diffracted beam did not exceed 5000 counts/second for any reflection.

The intensities of 2370 reflections, belonging to the three forms \{hk\}, \{hkl\}, and \{hkl\} were collected in the range $0 < \theta \leq 25^\circ$. For the second and third forms, collection was limited to those 768 reflections for which $I > \sigma(I)$ in the first form. The data were corrected for absorption and the equivalent reflections averaged. During the data collection, the intensities of three standard reflections were recorded at regular intervals. The crystal showed no signs of decomposition since the intensities of these standards only showed those deviations from the mean predicted by counting statistics.

The linear absorption coefficient for the compound $[\text{Os(NH}_3)_5(\text{N}_2)]\text{Cl}_2$ using Mo Kα radiation is 143.8 cm$^{-1}$. The triangular wedge shape of the crystal was characterised by bounding planes $(-201)$, $(-11-2)$, $(120)$, $(-2-1-1)$ and $(2-21)$ and appropriate dimensional measurements. Transmission coefficients calculated using Gaussian integration, ranged from 0.5306 for the $(-4-30)$ reflection to 0.2185 for the $(-3-1-1)$ reflection. For many equivalent reflections, the intensity of the $(h \, k \, l)$ reflection was significantly different from the intensity of the other two equivalent reflections, before absorption corrections were applied, but agreed well after absorption correction.
After averaging, the 2370 recorded reflections yielded a data set of 912 reflections of which \( I > 3\sigma(I) \) for 578 reflections, \( 3\sigma(I) > I > 2\sigma(I) \) for 66 reflections, \( 2\sigma(I) > I > \sigma(I) \) for 62 reflections and \( I < \sigma(I) \) for the remaining 206 reflections.

Solution and Refinement of the Structure

All full-matrix least-squares refinements were carried out on \( F \), the function minimized being \( \sum w( | F_O | - | F_C | )^2 \) where the weight \( w \) is taken as \( 1/F_O^2 \) and \( | F_O | \) and \( | F_C | \) are the amplitude of the observed and calculated structure factors. In all calculations of \( F_C \), the atomic scattering factors for osmium were taken from Cromer and Waber, those for hydrogen from Stewart et al., and other atoms from usual tabulations. The effect of anomalous dispersion from the osmium and chlorine atoms were included in the calculation of \( F_C \), the values of \( \Delta f' \) and \( \Delta f'' \) used were those of Cromer.

Initial positional parameters for all nonhydrogen atoms, except those in the dinitrogen ligand, were those given by Prout and Powell for the corresponding atoms in \([\text{Ru(NH}_3)_5\text{Cl}]\text{Cl}_2\). Using isotropic temperature factors, and one form data uncorrected for absorption, the refinement converged to give agreement factors of \( R_1 = 10.1\% \); \( R_2 = 12.8\% \), where \( R_1 = \sum | F_O | - | F_C | / \sum | F_O | \) and the weighted R-factor \( R_2 = (\sum w( | F_O | - | F_C | )^2 / \sum ( | F_O | )^2 )^{1/2} \). A difference fourier synthesis revealed four peaks of intensity.
approximately $6 \times 10^{-6}$ e.p.m. $^{-3}$. Two of these were close to the osmium atom and the other two clearly revealed a co-ordinated dinitrogen ligand. This structure, with anisotropic temperature factors assigned to the osmium and chlorine atoms, refined to give agreement factors of $R_1 = 7.7\%$; $R_2 = 7.6\%$. After correction for absorption and averaging equivalent forms, the refinement converged to give agreement factors of $R_1 = 4.0\%$; $R_2 = 4.5\%$.

Another difference synthesis was calculated and this revealed no peaks of height greater than $1.5 \times 10^{-6}$ e.p.m. $^{-3}$. The high electron density was near the ammonia, nitrogen atoms. Hydrogen positions for the "in plane" ammonia groups were calculated for each of the two orientations possible if these groups are ordered. The temperature factors of the hydrogen atoms in the calculated positions were then refined and best agreement was found when the hydrogen atoms were near high peaks in the difference maps. These calculations were taken to indicate definite orientations for the $\text{NH}_3$ groups lying in the crystallographic mirror plane. Final refinement with these hydrogen atoms in their calculated positions, and with anisotropic thermal parameters applied, to osmium and chlorine atoms, resulted in values of $3.9\%$ and $4.4\%$ for $R_1$ and $R_2$ respectively. The largest co-ordinate shift in this refinement was 0.01 of its estimated standard deviation. (Refinement with all non-hydrogen atoms anisotropic, showed no significant improvement in the agreement factors which reduced to $R_1 = 3.8\%$, $R_2 = 4.3\%$). There is no evidence of significant secondary extinction effects.
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<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{11}$ or $B_{22}$</th>
<th>$B_{33}$</th>
<th>$B_{12}$</th>
<th>$B_{13}$</th>
<th>$B_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>0.10523(5)</td>
<td>0.250000</td>
<td>0.18327(9)</td>
<td>0.00310(4)</td>
<td>0.00387(6)</td>
<td>0.00998(14)</td>
<td>0.00000</td>
<td>-0.00015(8)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1409(2)</td>
<td>0.004(3)</td>
<td>0.6833(4)</td>
<td>0.0038(1)</td>
<td>0.0063(3)</td>
<td>0.0143(6)</td>
<td>0.0003(2)</td>
<td>-0.0001(3)</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.0043(1)</td>
<td>0.2500</td>
<td>0.0047(2)</td>
<td>2.4(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>-0.0556(11)</td>
<td>0.2500</td>
<td>-0.108(2)</td>
<td>3.6(3)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>N(3)</td>
<td>0.0073(10)</td>
<td>0.2500</td>
<td>0.425(2)</td>
<td>3.3(3)</td>
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<td></td>
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</tr>
<tr>
<td>N(4)</td>
<td>0.2221(11)</td>
<td>0.2500</td>
<td>0.395(2)</td>
<td>3.1(3)</td>
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<tr>
<td>N(5)</td>
<td>0.2121(10)</td>
<td>0.2500</td>
<td>-0.041(2)</td>
<td>3.5(3)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>N(6)</td>
<td>0.1087(7)</td>
<td>0.0451(10)</td>
<td>0.1889(13)</td>
<td>3.1(2)</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

* For atoms refined anisotropically, the form of the thermal ellipsoid is $- (B_{11} x^2 + B_{22} y^2 + B_{33} z^2 + 2B_{12} x y + 2B_{13} x z + 2B_{23} y z)$. Numbers given in parentheses in this table and in others in this chapter are estimated standard deviations in the least significant digits.
### Idealised Positional Parameters for In-plane Ammonia Hydrogen Atoms

<table>
<thead>
<tr>
<th>Ammonia Group</th>
<th>Hydrogen</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (3)</td>
<td>H(1)</td>
<td>0.050885</td>
<td>0.250000</td>
<td>0.565453</td>
</tr>
<tr>
<td></td>
<td>H(2)</td>
<td>-0.041027</td>
<td>0.338177</td>
<td>0.420124</td>
</tr>
<tr>
<td>N (4)</td>
<td>H(1)</td>
<td>0.296034</td>
<td>0.250000</td>
<td>0.318475</td>
</tr>
<tr>
<td></td>
<td>H(2)</td>
<td>0.216472</td>
<td>0.338181</td>
<td>0.489886</td>
</tr>
<tr>
<td>N (5)</td>
<td>H(1)</td>
<td>0.289362</td>
<td>0.250000</td>
<td>0.025827</td>
</tr>
<tr>
<td></td>
<td>H(2)</td>
<td>0.204049</td>
<td>0.338181</td>
<td>-0.134435</td>
</tr>
<tr>
<td>#</td>
<td>OBS</td>
<td>CALC</td>
<td>#</td>
<td>OBS</td>
</tr>
<tr>
<td>---</td>
<td>-----</td>
<td>------</td>
<td>---</td>
<td>-----</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>72</td>
<td>2</td>
<td>4</td>
</tr>
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<td>5</td>
<td>6</td>
<td>52</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>20</td>
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</tr>
<tr>
<td>25</td>
<td>6</td>
<td>52</td>
<td>50</td>
<td>6</td>
</tr>
<tr>
<td>50</td>
<td>6</td>
<td>52</td>
<td>50</td>
<td>6</td>
</tr>
</tbody>
</table>

**TABLE 13** Observed and Calculated Structure Factors.
Average values of the minimised function obtained after the final cycle of refinement, showed little dependence on $F_0$ or on $\lambda^{-1}\sin \theta$ which indicates that the relative weighting system is reasonable.

The error in an observation of unit weight was $0.613$. A final difference map still shows peaks of up to $1.4 \times 10^{-6}$ e.pm$^{-3}$ near the hydrogen atom positions, but in the remainder of the map, peaks do not rise above $1.0 \times 10^{-6}$ e.pm$^{-3}$.

Final positional and thermal parameters are shown in Table 11 along with estimated standard deviations obtained from the final cycle of the least squares refinement. The idealised positional parameters ($\langle N-H \rangle = 113$ pm, Os-N-H = $109^\circ 58'$) for the hydrogen atoms are listed in Table 12. The final values of $|F_o|$ and $|F_c|$ (in electrons) are given (Table 13) for the 706 reflections used in the final refinement. For the 206 reflections omitted from the refinement, for which $F_o^2 < \sigma(F_c^2)$, none had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. These data are not included in Table 13.

The successful solution of this osmium structure as an ordered dinitrogen structure in which all the atoms, other than dinitrogen, are within experimental error of the reported positions of the corresponding atoms in the $[\text{Ru(NH}_3)_5\text{Cl}]\text{Cl}_2$ structure, suggests that the ruthenium structure is as reported$^{64}$, and that no disorder is present.
<table>
<thead>
<tr>
<th>Atom</th>
<th>Minimum</th>
<th>Intermediate</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>14.7 (1)</td>
<td>15.4 (1)</td>
<td>17.0 (1)</td>
</tr>
<tr>
<td>Cl</td>
<td>18.1 (4)</td>
<td>18.5 (4)</td>
<td>19.4 (4)</td>
</tr>
</tbody>
</table>
FIGURE 13  Unit Cell Contents for $\text{Os(NH}_3\text{)}_5\text{(N}_2\text{)}_3\text{Cl}_2$
TABLE 14  
Selected Bond Lengths and Angles  
in the Complex \([\text{Os(NH}_3\text{)}_5\text{(N}_2\text{)}]^{2+}\)Cl\(_2\)  

<table>
<thead>
<tr>
<th>Bond lengths between -</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os-N(1)</td>
</tr>
<tr>
<td>Os-N(3)</td>
</tr>
<tr>
<td>Os-N(4)</td>
</tr>
<tr>
<td>Os-N(5)</td>
</tr>
<tr>
<td>Os-N(6)</td>
</tr>
</tbody>
</table>

| Bond Angles in the Cation \([\text{Os(NH}_3\text{)}_5\text{(N}_2\text{)}]^{2+}\)  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)N(1)Os</td>
<td>178.3 (1.3)°</td>
<td>N(3)OsN(4)</td>
<td>86.1 (0.6)°</td>
</tr>
<tr>
<td></td>
<td>N(3)OsN(5)</td>
<td>175.3 (0.6)°</td>
<td></td>
</tr>
<tr>
<td>N(1)OsN(3)</td>
<td>93.3 (0.6)°</td>
<td>N(3)OsN(6) N(^1)(6)</td>
<td>90.0 (0.2)°</td>
</tr>
<tr>
<td>N(1)OsN(4)</td>
<td>179.4 (0.5)°</td>
<td>N(4)OsN(5)</td>
<td>89.2 (0.6)°</td>
</tr>
<tr>
<td>N(1)OsN(5)</td>
<td>91.4 (0.6)°</td>
<td>N(4)OsN(6) N(^1)(6)</td>
<td>88.4 (0.3)°</td>
</tr>
<tr>
<td>N(1)OsN(6) N(^1)(6)</td>
<td>91.6 (0.3)°</td>
<td>N(5)OsN(6) N(^1)(6)</td>
<td>89.9 (0.2)°</td>
</tr>
<tr>
<td></td>
<td>N(6)OsN(^1)(6)</td>
<td>176.7 (0.5)°</td>
<td></td>
</tr>
</tbody>
</table>

(N(6) and N\(^1\)(6) are the two N(6) nitrogen atoms related by the mirror plane through the cation.)

Distances from the chloride anion  
to various ammine nitrogen atoms (less than 360 pm)

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl - N(3)</td>
<td>339 (1) pm</td>
<td>Cl-N(6)</td>
<td>343 (1) pm</td>
</tr>
<tr>
<td>Cl - N(4)</td>
<td>346 (1) pm</td>
<td>Cl-N(6)</td>
<td>346 (1) pm</td>
</tr>
<tr>
<td>Cl - N(4)</td>
<td>353 (1) pm</td>
<td>Cl-N(6)</td>
<td>354 (1) pm</td>
</tr>
<tr>
<td>Cl - N(5)</td>
<td>337 (1) pm</td>
<td>Cl-N(6)</td>
<td>353 (1) pm</td>
</tr>
</tbody>
</table>

(In each case where more than one N\(_1\) is given, these additional N\(_1\) belong to a number of neighbouring cations).
Description of Structure

The structure consists of discrete \([\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}\) units situated so that the osmium atom, three ammonia groups and the two atoms of the dinitrogen group, lie on a crystallographic mirror plane. The remaining two co-ordinated ammonia groups are situated on each side of this plane, almost directly above and below the osmium atom. The four ammonia ligands cis to the dinitrogen group, are bent slightly away (approximately 2°) from it and towards the trans ammonia ligand, but the displacement is too small to be statistically significant.

The closest non-bonded contacts of the chloride anion are given in Table 14. These distances suggest that significant hydrogen bonding to some ammonia groups occurs. A view of the unit cell is given in Figure 13 and the co-ordination of the cation is depicted in Figure 14. This figure also shows the numbering system used for the cation, nitrogen atoms. A selection of interatomic bond lengths and angles are presented in Table 14 together with their estimated standard deviations. The route-mean-square amplitudes of vibration along the principle axes of thermal motion are given in Table 15 for the osmium and chloride atoms. The directions of the principal axes can be discerned, at least approximately, from the figures.
FIGURE 14  Diagram of the Cation \( \text{Os(NH}_3)_5\text{(N}_2\text{)} \)^{2+}  

Bond lengths in pm \( \times 10^{-2} \)
Discussion

For the structure, \( \text{[Os(NH}_3)_5(N_2)\]Cl}_2 \), the important bond lengths and bond angles, are those involving the dinitrogen group. The dinitrogen (NN) bond at 112 (2) pm and the Os-N≡N angle at 178 (1)° are both similar to the corresponding distances obtained in other ordered dinitrogen complexes. The most interesting feature is the short Os-N\(_2\) bond length of 184 pm. These observations will now be considered in more detail.

All cation bond angles are normal and will not be discussed further.

(a) The dinitrogen (NN) bond length - The dinitrogen (N≡N) bond length at 112 (2) pm is only slightly longer than that observed for free gaseous dinitrogen (109.8 pm)\(^{136}\), and it is similar to that observed in other relevant structures (Table 3). These range from 110.6 pm for Co(H(N\(_2\)) (PPh\(_3\))\(_3\)\(^{54}\) to 112.4 pm for the dimeric complex \([\text{Ru}_2(\text{NH}_3)_{10}(N_2)](\text{BF}_4)_4\)\(^{52}\).

The slight increase in the dinitrogen (NN) bond length on complex formation is not surprising, in addition the infrared spectra of these complexes suggest that the N≡N bond is considerably weakened, for example the (NN) absorption energy is lowered by 320 cm\(^{-1}\), from the value for free dinitrogen, in the complex \([\text{Os(NH}_3)_5(N_2)]\text{Cl}_2\). The information in Figure 15 shows that the N-N bond length, in multiple bonded nitrogen containing molecules, is not very sensitive to changes in the force constants of
FIGURE 15 Variations of Force Constants with Bond Length for NN Bonded Systems
the N - N bond$^{125}$.

Force constants of bonds are related to the ease of distorting bonds from their mean positions and they are closely related to bond strengths. Approximate calculations (from the infrared stretching frequency) of the force constant for the NN bond in

\[ \text{[Os(NH}_3)_5(N_2)]Cl_2 \] (assuming an isolated bond) suggests that this bond has a force constant of approximately $1.7 \times 10^5$ dynes.m$^{-1}$. This suggests that the bond would thus be of similar strength to the NN bond in $N_2O$ and is weaker than the NN bond in free dinitrogen (force constant $= 2.22 \times 10^5$ dynes.m$^{-1}$).

From Figure 15 it would appear the calculated force constant corresponds to a bond length of 113 pm which is identical, within experimental error, to the value of 112 (2) pm measured in this structure determination.

(b) The osmium-dinitrogen bond length - The short metal-dinitrogen bond length of 184 (1) pm is probably the most interesting feature of the present structure. The short bond is indicative of multiple bonding, a feature of dinitrogen complexes that has been previously commented on$^{54}$. The Os - $N_2$ bond length is similar to the metal-carbon bond length in carbonyls$^{59}$, and the metal-nitrogen bond length in nitrosyls$^{134}$. The structure of a mono-carbonyl complex has not yet been determined, but the structure of the ruthenium (II) complex $[\text{Ru(NH}_3)_5(\text{NO})]Cl_3H_2O$ has been
reported. In this structure the Ru-NO bond length$^{134}$ of $180 (2)$ pm is similar to that observed for the osmium-dinitrogen bond length. The similarity in the (Os-$N_2$, Ru-NO) bond lengths suggests that the bonds are of comparable strength$^{134}$. In contrast, interpretation of Mössbauer spectra$^{33,53}$ has led to the conclusion that dinitrogen is less strongly bonded than carbon monoxide to metal ions, a result not in agreement with the X-ray structural work. However, these results do not refer to the osmium complex.

The osmium-dinitrogen bond length of $184$ pm may also be compared with bond lengths of other osmium nitrogen bonds. The bond length is less than for the single bond distance of $215$ pm observed for Os-$NH_3$ bond but it is longer than the Os= N triple bond of $161$ pm$^{135}$ observed in $K_2 OsNC_5$. Ruthenium and rhenium $M= N$ double bonds$^{55}$ are about $170$ pm, hence it would appear that the Os-$N_2$ bond is probably intermediate in character between a single, and a double bond.

(c) **The osmium ammonia bond lengths.** The trans $N (4)$ ammonia-osmium bond length of $215$ pm is slightly greater than every cis osmium - ammonia bond length in the mirror plane. The difference of $3$ pm is hardly significant especially as the Os - $N (6)$ bonds are $215$ pm in length. These results are in contrast to the complex $[Ru(NH_3)_5(NO)] Cl_3 H_2 O$ where the Ru - $NH_3$ bond trans to the nitric oxide is $10$ pm longer than the rest of the Ru - $NH_3$
bonds. The difference is also reflected in the greater lability of the trans ammonia ligand in the nitrosyl complex.

One may conclude that the bonding between transition metals and the three isoelectronic ligands \((N_2), (NO^+),\) and \((CO)\) is similar and that the bonding involves both \(\sigma\) and \(\pi\) components, to give an overall metal-ligand bond order of between one and two. The results also suggest that the dinitrogen NN bond is probably destabilised in the dinitrogen complexes. However, additional destabilisation still appears to be necessary before chemical reactions of the \(N_2\) ligand, and in particular reduction, will occur.
CHAPTER 5

Studies on Solid Solutions Formed Between

\[
\text{[Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2 \text{ and [Ru(NH}_3\text{)}_5\text{Cl]}\text{Cl}_2
\]

Introduction

In preliminary investigations, Mr D.E. Johnstone found that dilute hydrochloric acid reacts with the impure hydrazine preparation of \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2\) to give a mixture of compounds, including what appeared to be a new dinitrogen compound, in which the \(\tilde{v} (\text{NN})\) vibration frequency in the infrared was lowered by 48 cm\(^{-1}\) to 2057 cm\(^{-1}\). The new dinitrogen complex amounted to about 12% of the total product, the remainder being \([\text{Ru(NH}_3\text{)}_5\text{Cl]}\text{Cl}_2\). Johnstone obtained some evidence that suggested that this new dinitrogen product was \([\text{Ru(NH}_3\text{)}_4\text{(H}_2\text{O)}\text{(N}_2\text{)}\text{]}\text{Cl}_2\).

Results

The reaction described above was confirmed in the present work. Pure \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2\) reacts with dilute hydrochloric acid to again give a new product, but the energy of the \(\tilde{v} (\text{NN})\) infrared absorption, now at 2085 cm\(^{-1}\) was not lowered by as much as reported by Johnstone. In this reaction, slightly stronger acid was also required. The X-ray powder photograph of the reaction
product only showed the diffraction lines of $[\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2$, although dinitrogen analysis of the reaction product showed that it now contained about 70% of a dinitrogen complex.

In an attempt to characterise the dinitrogen component, of the above mixture, various anions were tried in order to separate the reaction products. Sodium perchlorate precipitated the dinitrogen component, from solutions of the reaction product above, as the complex $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{(ClO}_4\text{)}_2$. Hence it appeared that dilute hydrochloric acid reacts with pure $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2$ to give some $[\text{Ru(NH}_3\text{)}_5\text{Cl}\text{]}\text{Cl}_2$. This $[\text{Ru(NH}_3\text{)}_5\text{Cl}\text{]}\text{Cl}_2$ and unreacted $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2$ then crystallise out as a solid solution.

Various solid solutions of $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2$ and $[\text{Ru(NH}_3\text{)}_5\text{Cl}\text{]}\text{Cl}_2$ were then prepared by crystallisation of solutions containing known amounts of these two compounds. Products, with the appropriate ratio of the two components, have identical infrared spectra and powder photographs to the products formed by the action of hydrochloric acid on $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2$ described above and by Johnstone $^{107}$. In contrast physical mixtures, formed from pure $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}\text{]}\text{Cl}_2$ and $[\text{Ru(NH}_3\text{)}_5\text{Cl}\text{]}\text{Cl}_2$, have properties (e.g. infrared absorptions and X-ray powder diffraction lines, Figure 20), in which the components can be recognised.

Further investigation of the solid solutions, above, showed
<table>
<thead>
<tr>
<th>Solid Solution or Compound</th>
<th>Symmetry</th>
<th>( a ) (pm)</th>
<th>( b ) (pm)</th>
<th>( c ) (pm)</th>
<th>( \langle NN \rangle ) cm(^{-1} )</th>
<th>( \langle Ru-N_2 \rangle ) cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure ([Ru(NH_3)_5Cl]_2)</td>
<td>Pnma</td>
<td>1346.5 (4)</td>
<td>1054.2 (5)</td>
<td>680.2 (3)</td>
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<td></td>
</tr>
<tr>
<td>25% ([Ru(NH_3)_5(N_2)]_2)</td>
<td>Pnma</td>
<td>1348.5 (3)</td>
<td>1053.7 (3)</td>
<td>681.1 (2)</td>
<td>2065</td>
<td>NO.</td>
</tr>
<tr>
<td>in ([Ru(NH_3)_5Cl]_2)</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>56% ([Ru(NH_3)_5(N_2)]_2)</td>
<td>Pnma</td>
<td>1356 (1)</td>
<td>1052.0 (8)</td>
<td>683.5 (8)</td>
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<td>508</td>
</tr>
<tr>
<td>in ([Ru(NH_3)_5Cl]_2)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>pure ([Os(NH_3)_5(N_2)]_2)</td>
<td>Pnma</td>
<td>1357.5 (4)</td>
<td>1046.5 (2)</td>
<td>687.3 (2)</td>
<td>2005</td>
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<tr>
<td>90% ([Ru(NH_3)_5(N_2)]_2)</td>
<td>Cmcm</td>
<td>1033.7 (7)</td>
<td>926.0 (8)</td>
<td>1046 (1)</td>
<td>2105</td>
<td>498</td>
</tr>
<tr>
<td>in ([Ru(NH_3)_5Cl]_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% ([Ru(NH_3)_5(N_2)]_2)</td>
<td>Cmcm</td>
<td>1034.9 (3)</td>
<td>936.6 (7)</td>
<td>1037.3 (8)</td>
<td>2093</td>
<td>501</td>
</tr>
<tr>
<td>in ([Ru(NH_3)_5(CO)]_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>10% ([Ru(NH_3)_5(N_2)]_2)</td>
<td>Cmcm</td>
<td>1033.1 (4)</td>
<td>927.1 (4)</td>
<td>1044 (1)</td>
<td>2093</td>
<td>501</td>
</tr>
<tr>
<td>in ([Ru(NH_3)_5(CO)]_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure ([Ru(NH_3)_5(N_2)]_2Cl_2)</td>
<td>Fm(3m) (or other cubic)</td>
<td>1014.1 (1)</td>
<td></td>
<td></td>
<td>2108</td>
<td>498</td>
</tr>
</tbody>
</table>
that at least three different phases are formed, depending on the mole fraction of \([\text{Ru(NH}_3\text{)}_5\text{N}_2\text{]}\text{Cl}_2\) present (Table 16).

1. If the mole fraction of dinitrogen component is less than 0.7, then the solid solution crystallises in the orthorhombic space group \(\text{Pnma, isomorphic to \([\text{Ru(NH}_3\text{)}_5\text{Cl}\text{]}\text{Cl}_2\]}\).

2. If the mole fraction of dinitrogen component is about 0.9, then the solid solution crystallises in orthorhombic space group \(\text{Cmcm, isomorphic to } [\text{Ru(NH}_3\text{)}_5\text{(CO)}\text{]}\text{Cl}_2\).

3. Pure \([\text{Ru(NH}_3\text{)}_5\text{N}_2\text{]}\text{Cl}_2\) (i.e. mole fraction of 1.0) has previously been reported to crystallise in one of the indistinguishable cubic space groups (\(\text{Fm3m, F432 or F}\bar{4}3\text{m}\)).

In the solid solutions the frequency of the \(\tilde{\nu}(\text{NN})\) infrared absorption only varies significantly with change of composition, for the first phase with \(\text{Pnma symmetry}. \) In the second and third phases, the energy of the \(\tilde{\nu}(\text{NN})\) vibration is at \(2100 \pm 6 \text{ cm}^{-1}\), for the compositions studied.

The effect of change in composition, on the unit cell dimensions of the solid solutions, was then investigated in an attempt to discover the origin of the large changes in the energy of the \(\tilde{\nu}(\text{NN})\) absorption. The results obtained suggest that steric factors are important.
Discussion

Evidence for the formation of solid solutions

(i) Pure \( \left[ \text{Ru}(\text{NH}_3)_5(\text{N}_2) \right] (\text{ClO}_4)_2 \) can be recovered from an aqueous solution of the solid solutions by precipitation with perchlorate ions.

(Found Cl, 7.1%; \( \text{N(NH}_3) \), 16.5%; \( \text{N(N}_2) \), 6.9%)

\( \text{Cl}_2\text{H}_{15}\text{N}_5\text{O}_8\text{Ru} \) requires Cl, 7.1%; \( \text{N(NH}_3) \), 16.9%; \( \text{N(N}_2) \), 6.7%)

(ii) Infrared spectra of aqueous solutions formed from these solid solutions, including the product produced in hydrochloric acid, all have the \( \nu (\text{NN}) \) absorption at 2112 cm\(^{-1}\) in the infrared as does pure \( \left[ \text{Ru}(\text{NH}_3)_5(\text{N}_2) \right] \text{Cl}_2 \) in aqueous solution.

(iii) The solids, isolated from solutions containing the two complexes \( \left[ \text{Ru}(\text{NH}_3)_5(\text{N}_2) \right] \text{Cl}_2 \) and \( \left[ \text{Ru}(\text{NH}_3)_5\text{Cl} \right] \text{Cl}_2 \), have different physical properties (infrared spectra, X-ray powder photographs) to mixtures, of similar composition, formed between the two pure solid components (i.e., a mixed phase is present).

(iv) Crystallisation of mixed solutions of \( \left[ \text{Ru}(\text{NH}_3)_5(\text{N}_2) \right] \text{Cl}_2 \) and \( \left[ \text{Ru}(\text{NH}_3)_5\text{Cl} \right] \text{Cl}_2 \), give products which are identical to those obtained by hydrochloric acid treatment of pure \( \left[ \text{Ru}(\text{NH}_3)_5(\text{N}_2) \right] \text{Cl}_2 \).

In the case of the evidence given in (iv), it should be noted that some hydrochloric acid is always present to stabilise the \( \left[ \text{Ru}(\text{NH}_3)_5\text{Cl} \right]^{2+} \) ion in solution, however the amount is not sufficient to produce any observable reaction with the dinitrogen
complex alone. Also other acids, such as 0.5 molar perchloric acid, have no effect on the properties of the dinitrogen component isolated from these solvents.

The evidence (i), (ii) and (iv) above shows that no chemical change has occurred in the unreacted \([Ru(NH_3)_5(N_2)]^{2+}\) unit after addition of hydrochloric acid, and the evidence (i) to (iv) suggests that the observed infrared spectral changes (Table 16) are due to the presence of \([Ru(NH_3)_5Cl]Cl_2\), modifying the crystal structure of \([Ru(NH_3)_5(N_2)]Cl_2\) to Pnma or Cmcn symmetry by formation of solid solutions.

The solid solutions of Pnma symmetry will now be considered in more detail.

(a) Solid Solutions of Pnma Symmetry

From Table 16 it can be seen that as the mole fraction of \([Ru(NH_3)_5(N_2)]Cl_2\) is decreased, then the a and c unit cell dimensions decrease together with the frequency of the \(\nu(NN)\) absorption while the frequency of the \(\nu(Ru-N_2)\) absorption increases. However, the b unit cell dimension increases slightly in length. The overall change is an increase in unit cell volume with rising concentration of dinitrogen complex. The change in the infrared \(\nu(NN)\) and \(\nu(Ru-N_2)\) frequencies suggests that the ruthenium-dinitrogen bond is strengthened in solid solutions especially at low \([Ru(NH_3)_5(N_2)]Cl_2\) concentrations. This increased bond strength
must be explained by changes in the solid state interionic interactions. The Re-Cl bond strength, on the other hand, appears to be less dependent on the composition of the solid solutions, as the energy of the (Ru-Cl) vibration remains at 307 cm⁻¹ for all compositions studied.

The structure of pure Ru(NH₃)₅Cl₂Cl₂ has been reported and the structure of the isomorphous dinitrogen complex Os(NH₃)₅(N₂)Cl₂ has been determined during the present work. Within experimental error, the co-ordinated ammonia groups, the central metal ions, and the ionic chlorides in both these structures, have identical fractional co-ordinates. It seems reasonable to suppose that the atoms in the complex Ru(NH₃)₅(N₂)Cl₂ in the solid solutions which have the Pnma symmetry will be at similar positions to those of the osmium dinitrogen complex. Therefore, in the solid solutions, the dinitrogen and co-ordinated chlorine will be in the position taken up by the dinitrogen in the osmium complex. But the position will be disordered with respect to the chloro- and dinitrogen ligands.

The unit cell diagram (Figure 15) shows that the dinitrogen ligand in Os(NH₃)₅(N₂)Cl₂ is orientated towards the N₅ ammonia ligand of a neighbouring cation. Hence, in the solid solutions, the dinitrogen and co-ordinated chlorine will also be orientated towards N₅ ammonia ligand.

Therefore, it may be expected that as the amount of
**TABLE 17** Interaction Distances for the Co-ordinated Chloride and Dinitrogen Groups in the Solid Solutions of Pnma Symmetry

<table>
<thead>
<tr>
<th>Compound or solid solution</th>
<th>Non bonding distance</th>
<th>Van der Waals' radii</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2)</td>
<td>-Cl⋯N(5) 451pm</td>
<td>380pm</td>
</tr>
<tr>
<td>([\text{Ru(NH}_3\text{)}_5\text{N}_2\text{]}\text{Cl}_2)</td>
<td>N⋯N(5) 385pm</td>
<td>380pm</td>
</tr>
<tr>
<td>in almost pure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Ru(NH}_3\text{)}_5\text{N}_2\text{]}\text{Cl}_2)</td>
<td>N⋯N(5) 390pm</td>
<td>380pm</td>
</tr>
<tr>
<td>in pure form</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Os(NH}_3\text{)}_5\text{N}_2\text{]}\text{Cl}_2)</td>
<td>N⋯N(5) 395pm</td>
<td>380pm</td>
</tr>
</tbody>
</table>

The Van der Waals' distances are estimated assuming the radius of the ammonia ligand \(N(5)\) is identical to methane, and the \(N⋯N(5)\) distance is estimated as being approximately 5pm less for the ruthenium dinitrogen complex than for the osmium dinitrogen complex in an identical matrix, as the \(\text{Ru-N}_2\) bond in other dinitrogen complexes is at least 5pm longer than the \(\text{Os-N}_2\) bond.
[Ru(NH$_3$)$_5$(N$_2$)$_2$]Cl$_2$ increases in the solid solution, then the greater spatial requirement of the dinitrogen ligand, which lies in the xz plane of the unit cell at y = 0.25 and 0.75, will give rise to an increase in the length of the a and c axes, as observed.

Calculations show that in the osmium dinitrogen complex the terminal atom of the dinitrogen ligand is only 395 pm from the N(5) ammonia nitrogen. This distance is comparable to the sum of the Van der Waals' radii of the atoms concerned (380 pm). (In these calculations, the Van der Waals' radius of the ammonia ligand is assumed to be identical to methane, and the previously reported 72, 109 N radius is used).

The ruthenium (II) - dinitrogen bond$^{56}$ is longer than the osmium (II) - dinitrogen, and since the a and c unit cell axes are similar or shorter for the former complex, in solid solutions, then the dinitrogen ligand will be in a more restricted environment especially in those solid solutions consisting of small amounts of [Ru(NH$_3$)$_5$(N$_2$)$_2$]Cl$_2$ in [Ru(NH$_3$)$_5$Cl]Cl$_2$. (Table 17). The restriction could force the dinitrogen group closer to the ruthenium, hence strengthening the Ru-N$_2$ bond and in consequence weakening the N≡N bond, thus decreasing the observed frequency of the $\nu$(NN) vibration mode. The estimated change (based on changes in the unit cell dimensions) in the distance of the terminal dinitrogen atom from N(5) over the range of solid solutions is only 5 pm while the
$
u$(NN) frequency changes by $47 \text{ cm}^{-1}$, which indicates the sensitivity of infrared measurements to small structural changes (c.f. also P. 67.)

The proposal of Chatt et al. which relates the observed variations, of the $
u$(NN) vibration energy within the osmium and ruthenium dinitrogen complexes, with anion, to ammonia-anion interactions, cannot be used to explain the changes in frequency of the $
u$(NN) absorption observed for the solid solutions. Their proposal was based on the observation that in the related series of complexes, $[\text{M(NH}_3\text{)}_5\text{(N}_2\text{)}_2] X_2$ (M = Ru, Os) and $[\text{Ru(NH}_3\text{)}_5(\text{N} \equiv \text{C-R})] X_2$ ($X =$ uncharged anion), the $
u$(NN) or $
u$(C≡N) frequencies increase with increasing anion size. The triple bond, in the last series of complexes, is sterically sheltered, therefore anion interactions are said to occur through the ammonia ligands. The more highly charged (smaller) anions, repel bonding electrons from nearby ammonia groups towards the central metal ion, thus making the metal ion a better $\pi$ donor. The effect will produce a weakening of the triple bond of the co-ordinated ligands.

The solid solutions with Pnma crystal symmetry, have layers of cations $[\text{Ru(NH}_3\text{)}_5(\text{N}_2\text{)}_2]^{2+}$ or $[\text{Ru(NH}_3\text{)}_5\text{Cl}]^{2+}$, separated by layers of chloride anions. These layers lie along the $b$ axis, and the reduction in length of this axis with increasing amount of dinitrogen complex in the solid solution would suggest stronger cation-anion interactions. However, these increased interactions
give the opposite trend in the $\tilde{\nu}(NN)$ absorption energy to those expected on the basis of Chatt’s proposal \(^{80}\).

Whereas there seems little doubt, from a study of cation interactions, that the explanation \(^{80}\) given by Chatt is reasonable in explaining the changes in energy of the $\tilde{\nu}(NN)$ absorption for a series of complexes \([\text{Ru(NH}_3]_5(N_2)]^X_2\) \((X = \text{monocharged anion})\) it is not dominant in the solid solutions.

(b) Solid Solutions of Cmcm Symmetry

As the percentage of \([\text{Ru(NH}_3]_5(N_2)]^2Cl_2\) becomes high in the solid solution with \([\text{Ru(NH}_3]_5Cl]^2Cl_2\) a change of orthorhombic space group occurs. This gives rise to a significantly larger unit cell (see Table 16) and presumably gives more room for the dinitrogen ligand than it would achieve in the Pnma space group.

The solid solutions of \([\text{Ru(NH}_3]_5(N_2)]^2Cl_2\) in \([\text{Ru(NH}_3]_5(CO)]^2Cl_2\) were prepared to confirm that the structure of the second phase formed between \([\text{Ru(NH}_3]_5(N_2)]^2Cl_2\) and \([\text{Ru(NH}_3]_5Cl]^2Cl_2\) has Cmcm crystal symmetry. In the carbonyl, dinitrogen solid solutions, the exchange of dinitrogen for carbon monoxide has some effect on the unit cell dimensions, but the frequency of the $\tilde{\nu}(NN)$ infrared absorption which occurs at 2093 cm\(^{-1}\) is little changed (Table 16). This lack of change presumably reflects the similar spatial requirements of the dinitrogen and carbon monomide ligands.
Experimental

Preparation of Mixed Solid Solutions

(a) Solid Solutions of $\left[\text{Ru(NH}_3\right)_5\left(N_2\right)\left]Cl_2 \right.$ with $\left[\text{Ru(NH}_3\right)_5Cl\left]Cl_2 \right.$

Measured amounts of the two pure salts, $\left[\text{Ru(NH}_3\right)_5\left(N_2\right)\left]Cl_2 \right.$ and $\left[\text{Ru(NH}_3\right)_5Cl\left]Cl_2$ were dissolved in 0.05 molar hydrochloric acid to form a near saturated solution at room temperature. This solution is then evaporated over conc. sulphuric acid, sodium hydroxide desiccants using partially reduced pressure. The crystallised product is separated after the volume has been reduced by about one fifth. Further crops of crystals from this solution show little change in properties and composition. The composition of the solid solutions were determined by measurement of the intensity of the 221nm absorption ($\varepsilon = 15000$) in the ultraviolet, which is characteristic of $\left[\text{Ru(NH}_3\right)_5\left(N_2\right)\left]Cl_2 \right.$, and also from measurement of evolved dinitrogen after treatment of the solid solutions with ceric ions$^{111}$.

(b) Solid Solutions of $\left[\text{Ru(NH}_3\right)_5\left(N_2\right)\left]Cl_2 \right.$ with $\left[\text{Ru(NH}_3\right)_5\left(CO\right)\left]Cl_2 \right.$

These were prepared similarly to those above but with

$\left[\text{Ru(NH}_3\right)_5\left(CO\right)\left]Cl_2$ in place of $\left[\text{Ru(NH}_3\right)_5Cl\left]Cl_2$ and in neutral solution. The composition of the solid solutions in this case was determined from carbon analysis.

Reaction of $\left[\text{Ru(NH}_3\right)_5\left(N_2\right)\left]Cl_2 \right.$ with dilute HCl:-

$\left[\text{Ru(NH}_3\right)_5\left(N_2\right)\left]Cl_2$ was dissolved in 1 molar hydrochloric acid
and the resultant solution evaporated in the air or over conc.
H$_2$SO$_4$/NaOH desiccants until the product crystallised out. The
volume decreased by about 30%. Dinitrogen content was determined
by ceric ion decomposition and measurement of dinitrogen evolved.

**Instrumentation.** Powder diffraction data was recorded on a
Phillips PW1010/30 automatic recording goniometer using CuK$_\alpha$
radiation. The goniometer was calibrated using NaCl, the unit cell
size of which was taken as 563.907 pm. Unit cell sizes were
calculated from the measured diffraction pattern using least squares
procedures. This programme assigned the diffraction lines on a
best fit to the pattern predicted from initial cell parameters. In
the space groups Pnma and Cmcm more than one possible assignment
of some lines is possible, but where possible the assignments of
diffraction lines, in different samples belonging to the same space
group, were chosen to be similar.
CHAPTER 6

Infrared Studies

Introduction

A number of transition metal, ammine complexes were prepared during the present work, and the infrared spectra of these complexes have been recorded in the range 4000-40 cm\(^{-1}\).

Svatos et al.\(^{113}\) have shown that the frequency of the vibrations \(\delta_s(\text{NH}_3)\) and \(\rho_\nu(\text{NH}_3)\) are sensitive to the charge on the central metal atom. As the effective charge increases, as it does with an increase in oxidation state, or on substitution by more electron withdrawing ligands, then the frequency of both the vibrations above increase. The \(\nu(M-\text{NH}_3)\) absorption frequency is also sensitive to metal charge, but it is weak and often not observed. The infrared spectra of the complexes \([\text{Ru(NH}_3)_5(\text{N}_2)\text{]}\text{Cl}_2\) and \([\text{Ru(NH}_3)_5(\text{CO})\text{]}\text{Cl}_2\) suggest\(^{61}\) that the donation of \(\pi\) electrons from the ruthenium (II) ion, into the dinitrogen or carbon monoxide \(\pi^*\) orbitals, is sufficient to give the infrared spectra of the complexes the appearance of being typical of tervalent ruthenium.

Less work has been carried out on the low frequency infrared spectra of ammine complexes. The spectra of a number of metal hexammines have been recorded\(^{114}\) down to 80 cm\(^{-1}\) and the spectra of some ruthenium\(^{68}\) and iridium\(^{115}\) ammines are reported down to 200 cm\(^{-1}\).
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$(NH$_3$-M-NH$_3$) cm$^{-1}$</th>
<th>$\nu$(M-X) cm$^{-1}$</th>
<th>Lattice Mode cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>275.0</td>
<td>290 (w.sh)</td>
<td>132-117 (broad)</td>
</tr>
<tr>
<td>[Ir(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>275.0</td>
<td>307.0 (sh)</td>
<td>130 (sh), 115</td>
</tr>
<tr>
<td>[Ir(NH$_3$)$_5$Cl]Br$_2$</td>
<td>270.0</td>
<td>310.0</td>
<td>105.0, 82.5 (sh)</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>255.0</td>
<td>305.0</td>
<td>135-112 (broad)</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$Br]Cl$_2$</td>
<td>260.0</td>
<td>210.0</td>
<td>132.5, 112.5</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$Cl]Br$_2$</td>
<td>252.5</td>
<td>307.5</td>
<td>110.0; 90.0 (sh)</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$Br]Br$_2$</td>
<td>255.0</td>
<td>206.0</td>
<td>100.0; 80.0 (sh)</td>
</tr>
<tr>
<td>[Os(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>247.0</td>
<td>302.5</td>
<td>125.0 (sh) 112.5</td>
</tr>
</tbody>
</table>

w = weak
sh = shoulder
Results and Discussion

The low frequency infrared spectra of the metal (III) pentaamminehalide complexes \( \left\{ M(NH_3)_5X \right\} Y_2; \) \( M = \) metal ion, \( X, Y = \) halide ion) will be considered first, then the low frequency infrared spectra of a number of miscellaneous ammine complexes, and finally, the infrared spectra recorded above 400 cm\(^{-1}\) will be briefly discussed.

(a) Pentaammine halide Metal (III) Complexes

In the frequency range 400-40 cm\(^{-1}\), these complexes have three infrared active absorptions, (Table 19), two of which arise from vibrations within the cation, (viz \( \delta (NH_3-M-NH_3) \) (metal-ammonia bend), and \( \nu (M-X) \) (metal-halide stretch), while the third absorption is the lattice mode arising from vibrations within the ionic lattice. It is well known that the frequencies of the two vibrations, \( \nu (M-X) \) and the lattice mode, depend on the mass of the co-ordinated halide and ionic halide ions respectively, and the frequencies of the \( \delta (NH_3-M-NH_3) \) and \( \nu (M-X) \) modes depend on the mass of the central metal ion. Changes in the frequency of the lattice mode also affects the energy of the \( \nu (M-Cl) \) and \( \delta (NH_3-M-NH_3) \) vibrations, but these effects are much smaller than the influence of mass. Both the influence of mass and coupling of vibrations will now be described in more detail.

(i) Mass effects: Three different mass effects were observed during this present work —
the influence of the mass of the anion on the lattice mode;
(b) the effect of the mass of the co-ordinated halide on the
\( \tilde{\nu}(\text{Ru-X}) \) mode; and
(c) the effect of the mass of the central metal on the \( \tilde{\nu}(\text{M-X}) \)
and \( S(\text{NH}_3\text{-M-NH}_3) \) modes.

For the three pairs of complexes \( [\text{Ru(NH}_3)_5\text{Cl}_2] Y_2; \)
\([\text{Ru(NH}_3)_5\text{Br}_2] Y_2 \) and \([\text{Ir(NH}_3)_5\text{Cl}_2] Y_2 \) \( (Y = \text{Cl}, \text{Br}) \) (Table 19),
the average frequency of the lattice mode, for each complex,
decreases from 120 cm\(^{-1}\) to 95 cm\(^{-1}\) on exchange of the ionic
chloride for ionic bromide. This change is accounted for by the
relative masses of the anions, and hence the interionic force
constants are similar in the above series of complexes. In the two
pairs of ruthenium complexes \([\text{Ru(NH}_3)_5\text{X}_2] \text{Cl}_2 \) and \([\text{Ru(NH}_3)_5\text{X}_2] \text{Br}_2 \)
\( (X = \text{Cl}, \text{Br}) \) (Table 19), change in the frequencies of the \( \tilde{\nu}(\text{Ru-X}) \)
vibration modes is accounted for by the change in the mass of the
co-ordinated halogen. The \( \tilde{\nu}(\text{Ru-Cl}) \) modes both occur at 306 cm\(^{-1}\)
and the two \( \tilde{\nu}(\text{Ru-Br}) \) modes occur at 208 cm\(^{-1}\).

In contrast, neither of the two vibration modes, \( \tilde{\nu}(\text{M-Cl}) \)
and \( S(\text{NH}_3\text{-M-NH}_3) \) \( (M = \text{Ru}, \text{Rh}, \text{Os}, \text{Ir}) \), of the cations vary signif-
ificantly in frequency with changes in the mass of the central metal
ion. The frequency of the \( \tilde{\nu}(\text{M-Cl}) \) mode does decrease in the order
\( \text{Ir} > \text{Ru} > \text{Os} > \text{Rh} \) but the change is only from 308 cm\(^{-1}\) to 290 cm\(^{-1}\).
Allowing for the mass, the complexes containing the heavier metal
ions, osmium and (especially) iridium, have the larger force constants
for the metal-chlorine bond.
A similar observation can be made for the bending force constants of the metal-ammonia bonds within the cation.

(ii) **Effects of coupling between vibration modes**

The effects of coupling between vibration modes within these pentaammine halide complexes, are small (less than 10 cm\(^{-1}\)) but they are real and are reproducible between spectra of different samples of the same compound. For the series of complexes studied, coupling was only detected between the lattice mode and lower energy vibration modes of the cation.

The three pairs of complexes studied \([\text{Ru(NH}_3\text{)}_5\text{Cl}]_2\), \([\text{Ru(NH}_3\text{)}_5\text{Br}]_2\), and \([\text{Ir(NH}_3\text{)}_5\text{Cl}]_2\) \((Y = \text{Cl, Br})\), are iso-
morphous and any solid state effects could be considered to be similar. In these three pairs of complexes, exchange of ionic chloride for ionic bromide results in a decrease in the frequency of the \(\delta(\text{NH}_3 - \text{M-NH}_3)\) vibration modes, and a decrease in the frequency of the \(\gamma(\text{Ru-Br})\) vibration mode. In contrast, the frequency of both the \(\gamma(\text{Ru-Cl})\) and \(\gamma(\text{Ir-Cl})\) vibration modes increase.

The decrease in the frequency of the \(\delta(\text{NH}_3 - \text{M-NH}_3)\) and \(\gamma(\text{Ru-Br})\) vibration modes can be explained by coupling between these modes and the lattice mode. The decrease in the frequency of the lattice vibration mode results in a decrease in the frequency of the coupled cation vibration modes.
### Infrared Spectra of Miscellaneous Ammines

<table>
<thead>
<tr>
<th>Compound</th>
<th>(NH&lt;sub&gt;3&lt;/sub&gt;MNH&lt;sub&gt;3&lt;/sub&gt;) cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Lattice Mode cm&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;]Br&lt;sub&gt;3&lt;/sub&gt;</td>
<td>252.5</td>
<td>110.0, 100.0</td>
</tr>
<tr>
<td>[Co(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;]Br&lt;sub&gt;3&lt;/sub&gt;</td>
<td>325.0</td>
<td>120</td>
</tr>
<tr>
<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;]Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>257.5; 250 (sh)</td>
<td>112.5</td>
</tr>
<tr>
<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;]Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>250</td>
<td>85.0</td>
</tr>
<tr>
<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;]I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>247.5</td>
<td>77.5</td>
</tr>
<tr>
<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)]Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>260</td>
<td>115.0; 107.0</td>
</tr>
<tr>
<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)]Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>250</td>
<td>105.0 (sh); 90.0</td>
</tr>
<tr>
<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)]I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>247.5</td>
<td>92.5; 77.5</td>
</tr>
<tr>
<td>[Ru(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;(CO)]Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>262.5</td>
<td>125.0; 120</td>
</tr>
<tr>
<td>[Os(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;(N&lt;sub&gt;2&lt;/sub&gt;)]Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>260 (sh) 247.5</td>
<td>135.5; 95.0 (broad peak)</td>
</tr>
</tbody>
</table>

sh = shoulder
On the other hand, the $\nu (M-Cl)$ vibration mode is at a much greater frequency separation from the lattice mode. Hence coupling of the lattice mode with the $\nu (M-Cl)$ vibration is relatively unimportant and a second effect becomes dominant. This effect can be explained by a mechanism based on the proposal made by Chatt et al.\textsuperscript{80} (see Ch.5) to account for the anion effects on the $\nu (NN)$ stretching mode, in the ammine-dinitrogen and substituted nitrile complexes of osmium and ruthenium. Increased polarization of the ammine groups by the anions reduces the effective charge on the central metal ion, which becomes a better $\pi$ electron donor, but a weaker $\sigma$ electron acceptor. The latter effect may cause a reduction in the metal-chlorine bond strength, and hence the observed change in $\nu (M-Cl)$ frequency with change of anion.

(b) **Miscellaneous Ammine Complexes**: The remaining low frequency infrared spectra recorded, are shown in Table 20.

For the first two complexes, $[\text{Ru(NH}_3)_6\text{]}\text{Br}_3$ and $[\text{Co(NH}_3)_6\text{]}\text{Br}_3$, the frequencies of the lattice modes suggest that interionic vibrational force constants are similar, and the energy difference between the respective $S (\text{NH}_3-M-\text{NH}_3)$ modes, recorded in the spectra of these complexes, is accounted for by the different masses of the central metal ions.

The three ruthenium (II) hexaammine complexes provide an interesting comparison with the three pentaammine dinitrogen complexes. These six complexes are isomorphous\textsuperscript{56} and belong to one of the
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$(N-H)</th>
<th>$\nu$(N=N)</th>
<th>$\delta$ (NH)</th>
<th>$\delta$ (NH)</th>
<th>$\gamma$(NH$_3$)</th>
<th>$\nu$(M-N$_2$)</th>
<th>$\nu$(M-NH$_3$)</th>
<th>$\delta$(MNN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>3310-3170</td>
<td>1615</td>
<td>1295</td>
<td>801</td>
<td>450w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$(N$_2$)]Cl$_2$</td>
<td>3310/3195</td>
<td>2105</td>
<td>1635</td>
<td>1274</td>
<td>805</td>
<td>510</td>
<td>430w</td>
<td></td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$(N$_2$)]ZnCl$_4$</td>
<td>3320/3260/3220</td>
<td>2117</td>
<td>1625</td>
<td>1302/1287</td>
<td>775</td>
<td>501</td>
<td>467/447/425</td>
<td></td>
</tr>
<tr>
<td><a href="ClO$_4$">Ru(NH$_3$)$_5$(N$_2$)</a>$_2$</td>
<td>3360/3300</td>
<td>2150</td>
<td>1625</td>
<td>1292</td>
<td>772</td>
<td>485</td>
<td>402</td>
<td></td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$(CO)]Cl$_2$</td>
<td>3280/3170</td>
<td>1919</td>
<td>1633</td>
<td>1282</td>
<td>797</td>
<td>561</td>
<td>602</td>
<td></td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_6$]ZnCl$_4$</td>
<td>3320/3260</td>
<td>1622</td>
<td>1248</td>
<td>745</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_6$]Br$_3$</td>
<td>3250-3050</td>
<td>1615</td>
<td>1314</td>
<td>778</td>
<td>460w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>3250/3150</td>
<td>1750-1550</td>
<td>1316/1280</td>
<td>830</td>
<td>475/465w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os(NH$_3$)$_5$(N$_2$)]Cl$_2$</td>
<td>3300/3200</td>
<td>2025/2010</td>
<td>1640</td>
<td>1304</td>
<td>835</td>
<td>536</td>
<td>460</td>
<td>561</td>
</tr>
<tr>
<td>[Os(NH$_3$)$_5$(CO)]Cl$_2$</td>
<td>3310</td>
<td>1898</td>
<td>1632</td>
<td>1315/1300/1290</td>
<td>808</td>
<td>605</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(NH$_3$)$_4$(CO)]Cl$_2$</td>
<td>3300/3180</td>
<td>2070</td>
<td>1590</td>
<td>1295</td>
<td>853</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>3300/3200</td>
<td>1595</td>
<td>1301</td>
<td>878</td>
<td>498/488</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Rh(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>3280/3170</td>
<td>1555</td>
<td>1295/1260</td>
<td>853</td>
<td>490/480</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
indistinguishable cubic space groups F\textsubscript{3m\bar{3}}, F\textsubscript{432}, or F\textsubscript{\bar{4}3m}.

In the dinitrogen complexes, the five ammonia and the dinitrogen ligands are randomly disordered in the bulk crystal so that on the average the cation has \textit{O\textsubscript{h}} symmetry and the chloride ions have point group symmetry \textit{T\textsubscript{d}}. In contrast to X-ray measurements, which are concerned with the averaged bulk crystal, infrared measurements are concerned with each unique vibration mode of the crystal. Because of the disorder, the dinitrogen complexes will have cations and anions in a number of different environments and site symmetries. The infrared spectra of these complexes will therefore have a lattice mode (or modes) corresponding to each unique environment. The results suggest that these differences are quite significant, and that they cause the observed lattice mode to be split into two absorption maxima separated by about 20 cm\textsuperscript{-1}.

(c) \textbf{Spectra Recorded Above 400 cm\textsuperscript{-1}} The absorption maxima for the spectra recorded above 400 cm\textsuperscript{-1} are shown in Table 21. The assignments of these absorptions, also shown, are those normally accepted\textsuperscript{41} for absorptions in ammine complexes.

The only spectrum in which any significant disagreement with the literature occurs, is for the spectrum of \([\text{Os(NH\textsubscript{3})\textsubscript{5}(N\textsubscript{2})}]\text{Cl}_2\). This compound is reported\textsuperscript{101} to have an absorption maximum at 546 cm\textsuperscript{-1} which was assigned to the vibration mode \(\tilde{\nu}(\text{Os-N\textsubscript{2}})\). During the present work, two absorptions at 561 cm\textsuperscript{-1} and 536 cm\textsuperscript{-1} were observed in the infrared spectrum of \([\text{Os(NH\textsubscript{3})\textsubscript{5}(N\textsubscript{2})}]\text{Cl}_2\). The spectrum
FIGURE 16  Infrared Spectrum of $\text{[Os(NH}_3\text{)}_5\text{N}_2\text{]}\text{Cl}_2$, (insert shows $\nu$(NN) absorption on expanded scale.)
(Figure 16) is almost identical to that observed for the complex \([\text{Ru}(\text{NH}_3)_5(\text{CO})_2]\) Cl$_2$ (Figure 6), and by comparison$^{68}$, the two absorptions in the \([\text{Os}(\text{NH}_3)_5(\text{N}_2)]\) Cl$_2$ complex are assigned to the vibration modes:

- 561 cm$^{-1}$, $S$ (OsNN).
- 536 cm$^{-1}$, $\delta$ (Os-N$_2$).

**Experimental**

**Preparation of Chloropentaammineruthenium (III) dibromide**

\([\text{Ru}(\text{NH}_3)_5\text{Cl}]\) Cl$_2$ was dissolved in 0.01 Molar HCl to form a saturated solution of \(~ 40^\circ\text{C}\). Excess salt was filtered off and excess solid sodium bromide was added rapidly to the stirred solution. The bromide salt is rapidly precipitated under these conditions with no exchange of the co-ordinated chloride for bromide. (low frequency infrared spectrum and analysis).

(Found N, 17.9%; Br$_2$ClH$_{15}$N$_5$Ru requires N, 16.2%).

**Preparation of Bromopentaammineruthenium (III) dibromide.**

\([\text{Ru}(\text{NH}_3)_6\text{Cl}]\) Cl$_2$ was oxidised with bromine water to give the \([\text{Ru}(\text{NH}_3)_6]^{3+}\) ion in solution. The solution was made 1:1 with HBr (some \([\text{Ru}(\text{NH}_3)_6]^{3+}\) Br$_3$ precipitated) and it was heated for 3 hours (details similar to those used to prepare \([\text{Ru}(\text{NH}_3)_5\text{Cl}]\) Cl$_2$ Part C).

The salt was recrystallised from dilute HBr.

(Found N, 16.1%; Br$_3$H$_{15}$N$_5$Ru requires N, 16.4%).
FIGURE 17  Infrared Spectrum of \( \text{[Ru(NH}_3\text{)}_5\text{Br}]\text{Cl}_2 \) showing trace of \( \text{[Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2 \) (absorption at 300 cm\(^{-1}\))
Preparation of Bromopentaammineruthenium (III) dichloride

This preparation was similar to that used for $[\text{Ru(NH}_3\text{)}_5\text{Cl} ] \text{Br}_2$

$[\text{Ru(NH}_3\text{)}_5\text{Br} ] \text{Br}_2$ was dissolved in dilute hydrobromic acid, then the product was rapidly precipitated with ammonium chloride. In this case the infrared spectrum indicated a trace of $[\text{Ru(NH}_3\text{)}_5\text{Cl} ] \text{Cl}_2$ also present (Figure 17).

(Found N, 20.6%; BrCl$_2$H$_{15}$N$_5$Ru requires N, 20.7%).

Preparation of Chloropentaammineiridium (III) dibromide

This preparation was similar to that for $[\text{Ru(NH}_3\text{)}_5\text{Cl} ] \text{Br}_2$

$[\text{Ir(NH}_3\text{)}_5\text{Cl} ] \text{Cl}_2$ was dissolved in warm water (the co-ordinated chloride is non labile), and the product precipitated with sodium bromide.

(Found N, 14.9%; Br$_2$ClH$_{15}$IrN$_5$ requires N, 14.8%).

Preparation of salts of $[\text{Ru(NH}_3\text{)}_6 ]^{2+}$ and $[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)} ]^{2+}$.

The salts bromide and iodide were prepared by dissolving the chloride salts of the above two cations, in water, then precipitating the products with the appropriate anion.

Analysis

$[\text{Ru(NH}_3\text{)}_6 ] \text{Br}_2$ (N, 22.8%; Br$_2$H$_{18}$N$_6$Ru requires N, 23.1%)

$[\text{Ru(NH}_3\text{)}_6 ] \text{I}_2$ (N, 18.5%; H$_{18}$I$_2$N$_6$Ru requires N, 18.4%)

$[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)} ] \text{Br}_2$ (N, (NH$_3$) 18.4%; Br$_2$H$_{15}$N$_7$Ru requires N, (NH$_3$) 18.7%)

$[\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)} ] \text{I}_2$ (N, (NH$_3$) 15.2%; H$_{15}$I$_2$N$_7$Ru requires N, (NH$_3$) 15.1%).
Preparation of other complexes whose spectra were measured are described in Part C.
CHAPTER 7

Survey of Findings of the Present Study

The present study has highlighted three aspects of the coordination chemistry of dinitrogen which will be briefly discussed below.

(i) **Ease of Formation of Dinitrogen Complexes**

In the present study, the reactions of metal complexes with hydrazine hydrate and with metal reductants in ammonia, has shown that dinitrogen complexes of divalent ruthenium and osmium are formed in preference to carbon monoxide or hydrido-complexes, even when the latter ligands are potentially present in the reaction systems. On the other hand, the metal ions rhodium (III) and iridium (III) bond to the hydrido- and carbon monoxide ligands respectively, under the same conditions. Since divalent ruthenium and osmium are better π-donors than tervalent rhodium and iridium, the results of the reactions above suggest the importance of π-bonding for the coordination of dinitrogen.

(ii) **Similarity of Dinitrogen to Isoelectronic Species (NO⁻ and CO)**

Both the infrared spectra of dinitrogen complexes, and the crystal structure determination of \([\text{Os(NH}_3)_5(N_2)]\) \(\text{Cl}_2\) have emphasised the similarity between the bonding of dinitrogen and the bonding of isoelectronic species, such as CO and NO⁻, to transition metal ions. Reported metal to NO⁻ bond lengths are similar to the
metal to dinitrogen bond length found for $[\text{Os(NH}_3]^+_2\text{N}_2]_2\text{Cl}_2$
in the present study. Infrared spectral evidence indicates that
metal–carbon force constants in monocarbonyl complexes are similar
to the metal–nitrogen force constants in isoelectronic dinitrogen
and nitrosyl complexes. Finally, the formation of complexes with
these isoelectronic ligands, produce similar changes in the strengths
of the triple bonds, $\text{N} \equiv \text{N}$, $\text{C} \equiv \text{O}$ and $(\text{N} \equiv \text{O})^+$. All these lines
of evidence strongly suggest that the metal $-\text{N}_2$, $-\text{CO}$, and $-\text{NO}^+$,
bonds are similar and multiple in character.

(iii) **Modification of the Dinitrogen (NN) Bond.**

Infrared evidence suggests that the dinitrogen (NN) bond is
significantly weakened on complex formation. On the other hand,
the structural data from the X-ray structures reported so far, do not
show marked changes in the dinitrogen (NN) bond length. However,
bond lengths, for bonds of high multiplicity are not sensitive to
changes in bond strengths.

The present work has also demonstrated in a number of ways,
that the dinitrogen (NN) bond, in the complexes studied, has not yet
been modified sufficiently to allow easy reduction of the dinitrogen
species. The results obtained do suggest that some modification
of the bond has occurred and solid solution studies indicate that
further modification is possible. It is very likely that by obtaining
complexes with significantly stronger metal–dinitrogen bonds, or
complexes with dinitrogen acting as a bridging ligand, that it will
be possible to reduce co-ordinated dinitrogen under mild conditions.
PART B

The Rhenium (V) Anion \([\text{ReOCl}_5]^{2-}\)
Rhenium Atomic Orbitals

Molecular Orbitals of ReO$_5^{2-}$ Ion

Oxygen and Chlorine Atomic Orbitals

\[ \text{FIGURE 18 Energy Level Diagram of the ReO}_5^{2-} \text{ Ion from Gray and Hare} \]
The Rhenium(V) Complex Anion \((\text{ReOCl}_3)^{2-}\)

**Introduction**

Oxo- and nitrido- complexes of a number of transition metals, including rhenium, have been reported in the literature. Of these, possibly the most interesting are those in which the central metal ion has a \(d^2\) electronic configuration, as for pentavalent rhenium. These complexes are mostly described as diamagnetic\(^{68}\). The diamagnetism results\(^{117}\) from a strong tetragonal distortion within the complex anions, due to the short \(\text{Re} - \text{O}\) bond. The distortion splits the \(t_{2g}\) orbitals in octahedral symmetry to give a low lying \(b_2\) \((dxy)\) orbital (Figure 18) in which the two \(d\)-electrons are spin paired\(^{116}\).

A few salts of the species \(\text{ReOX}_5^{2-}\) \((X=\text{Cl}, \text{Br}, \text{I})\) are however, described\(^{70-72}\) as paramagnetic with magnetic moments in the region of 1.0 - 2.9 B.M. The spin only moment for spin-free rhenium (V) is 2.83 B.M. but in complexes, this moment may be considerably reduced by spin-orbit coupling\(^{117}\). It was decided to investigate these paramagnetic rhenium(V) complexes as it appeared that in the right environment it may be possible to obtain complexes in which the rhenium would exhibit cross-over between high and low spin \(d^2\) configurations. The investigation of such complexes may shed some light on the nature of the bonding of "small ligands", in this case oxygen.

(a) **Review of Rhenium(V) Mono-oxo and Nitrido-Complexes.**

The chemistry of rhenium, including the oxo-complexes of rhenium(V) has been reviewed by Fergusson\(^{69}\) up until 1966. The rhenium(V)
<table>
<thead>
<tr>
<th>Complex</th>
<th>Magnetic Moment (B.M.)*</th>
<th>Visible Spectrum* (nm)</th>
<th>Low Frequency I.R.* (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2(ReOCl_5)$</td>
<td>0.48 (121)</td>
<td>(12M. HCl) 1050, 750, 700, 475, 400 (71)</td>
<td>308, 236, 220, 180, 172, 164, 80 (123)</td>
</tr>
<tr>
<td>$Rb_2(ReOCl_5)$</td>
<td>1.4 (119)*</td>
<td>(12M. HCl) 1050, 750, 700, 475, 400 (71)</td>
<td>318, 310, 227, 214 (71)</td>
</tr>
<tr>
<td>$Cs_2(ReOCl_5)$</td>
<td>2.85 (70)</td>
<td>(12M. HCl) 1050, 750, 700, 475, 400 (71)</td>
<td>318, 310, 227, 214 (71)</td>
</tr>
<tr>
<td>(quin.H.H.)₂(ReOBr₃)</td>
<td>1.0-2.0 (71)</td>
<td>(3M. HCl) 675, 475, 405 (71)</td>
<td>318, 310, 227, 214 (71)</td>
</tr>
<tr>
<td>$Rb_2(ReOBr_5)$</td>
<td>1.4 (119)*</td>
<td>(reflect.) 920, 885, 485 (118)</td>
<td></td>
</tr>
<tr>
<td>$Cs_2(ReOBr_5)$</td>
<td>1.5 (119)*</td>
<td>(reflect.) 920, 885, 485 (118)</td>
<td></td>
</tr>
<tr>
<td>(quin.H.H.)₂(ReOBr₃)</td>
<td>0.3 (121, 138)</td>
<td>(acetone) 800, 532, 450, 380 (138)</td>
<td>222, 215, 194, 145, 116, 112, 89 (123)</td>
</tr>
<tr>
<td>(quin.H.H)₂(ReOCl₃)</td>
<td>diamag. (121, 138)</td>
<td>(acetone) 780, 540, 460, 365 (138)</td>
<td></td>
</tr>
<tr>
<td>(Ph₄As)(ReOCl₄)</td>
<td></td>
<td>(acetonitrile) 1190, 835, 480, 420, 360, 262 (139)</td>
<td></td>
</tr>
<tr>
<td>(Ph₄As)(ReOBr₄)</td>
<td>0.2 (139)</td>
<td>(acetone) 1135, 1020, 835, 528, 444, 399, 270, 262 (139)</td>
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</tr>
<tr>
<td>(Ph₃HP)(ReOCl₄PPh₃)</td>
<td></td>
<td>yellow 314, 296 (71)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>green 342, 325, 309, 286 (71)</td>
<td></td>
</tr>
</tbody>
</table>

*References are given in parenthesis

A number of other complexes have also been reported\textsuperscript{120}. These complexes are diamagnetic, and $\tilde{v}(ReO)$ is in the range 1000-900 cm\textsuperscript{-1}. Some crystal structures have been reported\textsuperscript{140} and these all show short rhenium-oxo- or rhenium-nitrido-bonds.
mono-oxo-complexes belong to one of the following groups:
$\text{ReOX}_3L_2$, $\text{ReO(OR)}X_2L_2$, $\text{ReOX}_4^-$, $\text{ReOX}_4L^-$, and $\text{ReOX}_5^{2-}$, ($X =$ halide; $L =$ monodentate ligand, such as phosphine, amine, etc.; $\text{OR} =$ alkoxide). Dioxo-, nitrido- and imido-complexes are also known, and are similar to the mono-oxo-complexes.

All these complexes above are diamagnetic except for some salts of $\text{ReOX}_5^{2-}$, ($X =$ Cl, Br), and amine complexes, of type $\text{ReOX}_3L_2$, prepared$^{72}$ from alkyl and aryl ammonium salts of these pentahalides.

The magnetic data for the complex $\text{Cs}_2\text{ReOCl}_5$ has been reported frequently in the literature, but results from different workers, $^{70,71,118-9}$ show wide variations (table 22). Groves and Wilkinson$^{71}$ have suggested this variation may be due to differences in the crystal structures of samples prepared by different methods. These authors$^{71}$ proposed the rhenium is in the spin-free configuration and that antiferromagnetic interactions were the reason for the low magnetic moment. The variation between different preparations was due to varying degrees of antiferromagnetic behaviour.

A pronounced infrared spectral property of the mono-oxo-complexes of $\text{Re(V)}$, is the sharp band around $900 - 1000 \text{ cm}^{-1}$ attributable to the $\nu(\text{ReO})$ vibration mode$^{69}$. In the case of the paramagnetic alkali metal salts of $\text{ReOCl}_5^{2-}$, this absorption is at $952 \text{ cm}^{-1}$, $^{118}$ which is a similar energy to that observed for this vibration in diamagnetic rhenium (V) mono-oxo complexes$^{69}$. 
Since 1966, a number of other Re(V) oxo-complexes have been isolated\textsuperscript{120}, and properties of some of these are shown in table 22.

(b) \textbf{Summary of Results of Present Work:}

Contrary to earlier findings\textsuperscript{70,71}, the work carried out in the present study has shown that pure Cs\textsubscript{2}ReOCl\textsubscript{5} and Rb\textsubscript{2}ReOCl\textsubscript{5} have low magnetic moments of 0.43 B.M. and 0.5 B.M. respectively at room temperature. For the caesium salt, this moment has been shown to be due to temperature independent paramagnetism (T.I.P.).

The measured magnetic susceptibilities of the two compounds above, are similar to those reported by Jezowska-Trzebiatowska et al\textsuperscript{121} for the compound K\textsubscript{2}ReOCl\textsubscript{5}. The reason for the high paramagnetic susceptibilities of previous preparations of Cs\textsubscript{2}ReOCl\textsubscript{5}, has been shown to be due to contamination with varying amounts of Cs\textsubscript{2}ReCl\textsubscript{6}.

\textbf{Results}

(a) \textbf{Preparation}

(1) \textbf{Method of Preparation} - The ReOCl\textsubscript{5}\textsuperscript{2-} ion can be prepared in solution by a number of methods,\textsuperscript{71,118-9,121} and most of these give products having magnetic moments of about 1.5 B.M.

At the start of this work, an attempt was made to prepare both K\textsubscript{2}ReOCl\textsubscript{5} and Cs\textsubscript{2}ReOCl\textsubscript{5} by reduction of perrhenic acid in concentrated hydrochloric acid with iodide\textsuperscript{119}. This reaction can also be used to prepare the ReCl\textsubscript{6}\textsuperscript{2-} anion and in this attempt addition of caesium chloride solution caused precipitation of the tetravalent complex Cs\textsubscript{2}ReCl\textsubscript{6}. In the case of the preparation of the potassium
salt, addition of the cation did not produce a precipitate, and the hot solution was evaporated in the air, but the product so obtained was mainly potassium perrenenate. In both cases, a little of the salts of ReOCl$_5^{2-}$ were detected in the products. From these observations it appeared that the intermediate Re(V) oxidation state might be obtained by reacting the calculated amounts of K$_2$ReCl$_6$ and KReO$_4$, in concentrated hydrochloric acid, under dinitrogen.

This reaction was attempted by heating K$_2$ReCl$_6$ and KReO$_4$ in a 2:1 mole ratio in hydrochloric acid. After two hours, the infrared spectrum of the caesium product (measured 1000–800 cm$^{-1}$), showed the presence of some Re(V), as ReOCl$_5^{2-}$, together with ReO$_4^-$. After 48 hours heating, the precipitated product was predominantly ReOCl$_5^{2-}$, but a little ReO$_4^-$ could still be detected in the infrared spectrum and the ultra-violet spectrum had an absorption at 284 nm which showed some ReCl$_6^{2-}$ still present. The magnetic moment of the product obtained after 48 hrs, as the caesium salt, was 1.7 B.M. Additional heating produced no apparent change in the composition of the precipitated product.

A further reaction using a 1:1 ratio of KReO$_4$ to K$_2$ReCl$_6$ (50% excess KReO$_4$) was also heated for 48 hrs, but ReCl$_6^{2-}$ was still present, even under these conditions. The magnetic moment of this product, as the caesium salt, was 1.4 B.M.

The various reactions described above suggest that in hot hydrochloric acid solution, the equilibrium $\text{ReO}_4^- + 2\text{ReCl}_6^{2-} + 2\text{H}^+ + 3\text{Cl}^- + \text{HCl}^\equiv \text{3ReOCl}_5^{2-} + \text{H}_2\text{O}$ exists.

Returning to the preparation of the ReOCl$_5^{2-}$ salts by
<table>
<thead>
<tr>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) ReCl$_5$ dissolved in conc. hot hydrochloric acid, Cs$^+$ precipitated.</td>
</tr>
<tr>
<td>(ii) [ReO$_2$(en)$_2$]Cl dissolved in conc. hydrochloric acid. - Cs$^+$ precipitated</td>
</tr>
<tr>
<td>(iii) (Et$_4$N)$_2$ReOCl$_5$ dissolved in hydrochloric acid - Cs$^+$ precipitated. The starting material is prepared in acetone/hydrochloric acid.</td>
</tr>
<tr>
<td>(iv) ReOCl$_4$ in HCl Cs$^+$ precipitated</td>
</tr>
<tr>
<td>(v) HReO$_4$ reduced with HI in HCl. Evaporated to 1/3 vol. then precipitated with Cs$^+$</td>
</tr>
</tbody>
</table>

$\mu_{eff}^*$

<table>
<thead>
<tr>
<th>Method</th>
<th>$\mu_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>2.85 (70)</td>
</tr>
<tr>
<td>(ii)</td>
<td>2.0 (71)</td>
</tr>
<tr>
<td>(iii)</td>
<td>1.7 (71)</td>
</tr>
<tr>
<td>(iv)</td>
<td>1.4 (71)</td>
</tr>
<tr>
<td>(v)</td>
<td>0.8 (118)</td>
</tr>
</tbody>
</table>

*References are in parenthesis*
reduction of perrhenate with iodide, it appeared that the two conditions to avoid were:

(i) high concentrations or an excess of reductant and,
(ii) high temperatures.

Both these problems were overcome by slow addition, with stirring, of two equivalents of reductant, (as a dilute 0.006M. solution of HI in HCl) to a concentrated hydrochloric acid solution of potassium perrhenate cooled to approximately -10°C with ice/salt. The product was obtained as the rubidium or caesium salt by precipitation with the appropriate cation. The magnetic moments of the products were in the region of 0.5 B.M.

(ii) Discussion of Preparation - In previously reported 70-72, 118-9, preparations of salts of ReOC15^-2 (cations Rb^+, Cs^+, (amine H^+)), the smallest paramagnetic susceptibilities have been obtained on products prepared at temperatures close to room temperature, while preparations that have involved higher temperature (i.e. boiling HCl) have given products with magnetic moments as high as 2.85 B.M. 70 Groves and Wilkinson 71 have investigated the three preparations of Cs2ReOCl5 outlined in table 23 and postulate varying antiferromagnetic interactions, but the present work has demonstrated that Cs2ReCl6 impurities probably contributed to the paramagnetism recorded. The preparation 72 of other rhenium(V) oxo-pentahalides (Rb2ReOCl5, Rb2ReOBr5, and (amine H)2ReOC15) has also been carried out at high temperatures. Rhenium(IV) impurities are the probable reason for the high magnetic moments reported.
<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Molar Susceptibility (Χ) x10^6</th>
<th>Diamagnetic Corrections x10^6</th>
<th>μ_{eff}(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>103</td>
<td>-215</td>
<td>-224</td>
<td>0.09</td>
</tr>
<tr>
<td>120</td>
<td>-223</td>
<td>-224</td>
<td>0</td>
</tr>
<tr>
<td>143</td>
<td>-181</td>
<td>-224</td>
<td>0.22</td>
</tr>
<tr>
<td>163</td>
<td>-199</td>
<td>-224</td>
<td>0.18</td>
</tr>
<tr>
<td>183</td>
<td>-178</td>
<td>-224</td>
<td>0.26</td>
</tr>
<tr>
<td>203</td>
<td>-170</td>
<td>-224</td>
<td>0.30</td>
</tr>
<tr>
<td>223</td>
<td>-135</td>
<td>-224</td>
<td>0.40</td>
</tr>
<tr>
<td>243</td>
<td>-117</td>
<td>-224</td>
<td>0.46</td>
</tr>
<tr>
<td>263</td>
<td>-157</td>
<td>-224</td>
<td>0.38</td>
</tr>
<tr>
<td>283</td>
<td>-149</td>
<td>-224</td>
<td>0.41</td>
</tr>
</tbody>
</table>
The three compounds $K_2\text{ReOCl}_5$, $(\text{quin R})_2\text{ReOBr}_2$, and $(\text{quin R})_2\text{ReCl}_5$, prepared by Jezowska-Trzebiatowska and coworkers\cite{121}, are the only Re(V) oxopentahalide complexes with magnetic moments below 0.3 B.M. that have been reported prior to the present work. The reported\cite{121} molar susceptibilities of $-100 \times 10^{-6}$, $-288 \times 10^{-6}$, and $-724 \times 10^{-6}$ cgs correspond to magnetic moments of 0.48 B.M., 0.3 B.M. for the first two compounds respectively, while the latter value corresponds to a diamagnetic complex. These complexes were prepared by slow addition of sulphur dioxide (as reducing agent) to cooled hydrohalic acid solutions of permanganic acid.

(b) **Physical Measurements**

The magnetic and infrared and visible spectral properties of $Cs_2\text{ReOCl}_5$ and to a lesser extent $Rb_2\text{ReOCl}_5$, have been recorded.

**Magnetic Properties** - At room temperature $Cs_2\text{ReOCl}_5$ has a magnetic moment of 0.43 B.M. and $Rb_2\text{ReOCl}_5$ has a moment of 0.52 B.M.

The molar susceptibility of $Cs_2\text{ReOCl}_5$ was recorded over the temperature range 103°K to 293°K. (Table 24) and the results show that within this temperature range, the molar susceptibility is constant at approximately $-155 \times 10^{-6}$ cgs. The calculated diamagnetic corrections are $-224 \times 10^{-6}$ cgs, hence the room temperature magnetic moment is 0.43 B.M. The significant observation about the molar susceptibility is that it is essentially constant within the measured temperature range, hence it appears likely that it can be attributed to temperature independent
### Magnetic Data on Some Rhenium (V) oxo-Complexes, (at room temp. 23°C)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar Susceptibility $(\chi) \times 10^6$</th>
<th>Diamagnetic Correction $\mu_{\text{eff}}$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cs}_2\text{ReOCl}_5$</td>
<td>$-149$</td>
<td>$-224$</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{ReOCl}_5$</td>
<td>$-60$</td>
<td>$-200$</td>
</tr>
<tr>
<td>$(\text{Ph}_3\text{HP})\text{ReOCl}_4\text{PPh}_3$</td>
<td>$-447$</td>
<td>$-503$</td>
</tr>
<tr>
<td>$\text{ReOCl}_3{\text{PPh}_3}_2$</td>
<td>$-210$</td>
<td>$-421$</td>
</tr>
<tr>
<td>$\text{ReNCl}_2{\text{PPh}_3}_2$</td>
<td>$-397$</td>
<td>$-435$</td>
</tr>
<tr>
<td>$\text{ReO(OEt)}_2\text{Cl}_2{\text{PPh}_3}_2$</td>
<td>$-281$</td>
<td>$-430$</td>
</tr>
<tr>
<td>$\text{ReO(OEt)}_2\text{Br}_2{\text{PPh}_3}_2$</td>
<td>$-401$</td>
<td>$-453$</td>
</tr>
</tbody>
</table>

Note: Diamagnetic correction and $\mu_{\text{eff}}$ values are given in units of $10^6$.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Low-frequency Infrared Spectra of $\text{Cs}_2\text{ReOCl}_5$, $\text{Rb}_2\text{ReOCl}_5$ and $\text{Cs}_2\text{ReCl}_6$, $\text{Rb}_2\text{ReCl}_6$ and $\text{K}_2\text{ReCl}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(in cm$^{-1}$)</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{ReOCl}_5$</td>
<td>$312.5$; $240.0$ (sh); $225.0$; $185.0$; $162.5$; $135.0$; $80.0$ (sh); $62.5$</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{ReOCl}_5$</td>
<td>$317.5$; $240.0$ (sh); $225.0$; $187.5$, $165.0$; $132.5$; $80.0$</td>
</tr>
<tr>
<td>$\text{CsReO}_4$</td>
<td>$337.5$; $320.0$</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{ReCl}_6$</td>
<td>$310.0$; $172.5$</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{ReCl}_6$</td>
<td>$317.0$; $170.0$</td>
</tr>
<tr>
<td>$\text{K}_2\text{ReCl}_6$</td>
<td>$320.0$; $170.0$; $82.5$</td>
</tr>
</tbody>
</table>
FIGURE 19  Low-frequency Infrared Spectra of

\[ \text{Transmittance} \]

\[ \text{Wavenumber (cm}^{-1} \text{)} \]

\[ \begin{align*}
\cdots & \text{Cs}_2\text{ReOCl}_5 \\
\cdots & \text{Cs}_2\text{ReCl}_6
\end{align*} \]
The magnetic susceptibilities at room temperature were measured for a few oxo-complexes of Re(V) (table 25). These complexes had previously been reported to be diamagnetic, but without giving experimental figures. During this present work, the central metal ions of these complexes were shown to have small positive magnetic susceptibilities, similar in size to those observed for \( \text{Rb}_2\text{ReOCl}_5 \) and \( \text{Cs}_2\text{ReOCl}_5 \).

(ii) Infrared Spectrum - Above 400 cm\(^{-1}\), there is only one infrared active mode, at 951 cm\(^{-1}\), for the alkali metal salts of ReOCl\(_2^2^-\). This absorption is assigned to the vibration \( \nu(\text{ReO}) \) in the anion ReOCl\(_2^2^-\), and the value observed during the present work agrees with the previously reported value of 952 cm\(^{-1}\). Small amounts of ReCl\(_6^2^-\) impurity have no observable affect on this absorption.

The infrared spectrum, between 40 and 400 cm\(^{-1}\), has a number of sharp absorptions due to the anion ReOCl\(_2^2^-\). (Table 26, Fig. 19). The frequencies of these absorptions agree with previous reported values, except that an absorption reported at 172.5 cm\(^{-1}\), was not observed during the present work for pure \( \text{Cs}_2\text{ReOCl}_5 \). This additional absorption coincides in energy to the bending vibration \( \delta(\text{ClReCl}) \) in \( \text{Cs}_2\text{ReCl}_6 \).

The intense absorption at 225 cm\(^{-1}\) for the ReOCl\(_2^2^-\) anion has been attributed to a \( \psi_s(\text{ReO}) \) rocking mode or a \( \delta(\text{OReCl}) \) bending mode. Another possible assignment, ignored by others, is that it corresponds to the \( \nu(\text{ReCl}) \) stretching mode for the chlorine.
to the oxygen, the other $\nu(\text{ReCl})$ stretching vibrations occurring at the normal position of $300 - 320 \text{ cm}^{-1}$. Structural work on related compounds\textsuperscript{69} indicates the ligands trans to the oxo- ligand are attached by longer bonds than expected. Hence a significant decrease in the frequency of the stretching vibration mode of the trans ligand is expected.

(c) Ultraviolet - Visible Spectrum

The ultraviolet spectrum of a solution of $\text{ReOCl}_5^{2-}$ prepared in cold concentrated hydrochloric acid, has an absorption maximum at 220 nm, which agrees with the reported spectrum\textsuperscript{124}.

The visible, solid state reflectance spectrum of $\text{Cs}_2\text{ReOCl}_5$, has absorptions at $\approx 480$ (sh), 900 and 1320 nm, which agree with those reported\textsuperscript{118} previously (485 nm and 885, 920 nm). Previously reported\textsuperscript{72} solution spectra (Table 22) of the $\text{ReOCl}_5^{2-}$ ion in the visible region appear rather complex, but many of the reported absorption maxima correspond to absorptions of the $\text{ReCl}_6^{2-}$ ion. During this work, it was observed that the reflectance spectrum of $\text{K}_2\text{ReCl}_6$ has absorption maxima at 650, 700 (sh), 1080 and 1290 nm.

(d) E.S.R. Spectrum

An attempt was made to record the esr spectra of pure $\text{Cs}_2\text{ReOCl}_5$, impure $\text{Cs}_2\text{ReOCl}_5$ ($\mu_{\text{eff}} = 1.4 \text{ B.M.}$) and $\text{Cs}_2\text{ReCl}_6$, but these spectra could not be detected, even at liquid nitrogen temperature, hence the esr spectra reported by Groves and Wilkinson\textsuperscript{72} could not be confirmed.
(e) **Stability**

Both $\text{Rb}_2\text{ReOCl}_5$ and $\text{Cs}_2\text{ReOCl}_5$ are readily hydrolysed and on addition of water, these complexes immediately blacken to give $\text{ReO}_2$. The solid caesium salt is stable in air, but the rubidium salt darkens within a few days, presumably through reaction with water vapour.

The initial interest, in the complexes of the oxo-species $\text{ReOCl}_5^{2-}$, because of the reported paramagnetism, was now removed. It would appear that, while the $d^2$ configuration in a distorted octahedral field is a situation where both high and low spin compounds could be formed, all species of type $\text{ReOX}_5^{2-}$ and $\text{ReOX}_3Y_2$ ($X =$ halogen $Y =$ donor ligand) at present known are low spin and diamagnetic.

**Experimental**

**Preparation of Caesium pentachlorooxorhenium (V) - $\text{Cs}_2\text{ReOCl}_5$.**

$\text{KReO}_4$ (1gm) was added to concentrated hydrochloric acid (25 mls) and the mixture cooled in an ice/salt bath. A calculated amount of 0.6 molar HI (about 10 mls) in concentrated hydrochloric acid, diluted with this acid to 200 mls, was added dropwise (over 3 hrs) to the cooled, stirred suspension. The solution was stirred a further 30 minutes, filtered, and the remaining iodine washed out with cold chloroform.

The product was precipitated from the pale green solution, by addition of 2 gms CsCl dissolved in the minimum concentrated
hydrochloric acid. This product is fine and difficult to filter and is best collected by means of a centrifuge (Yield 1.8 gm).

(Found Cl, 27.2%; Cl₆Cs₂ORe requires Cl, 27.4%).

Preparation of rubidium pentachlorooxorhenium(V) $\text{Rb}_2\text{ReOCl}_5$

The preparation was identical to that of the caesium salt above, except RbCl was added in place of CsCl. The yellow product crystallises in larger particles and is more easily filtered.

(Found Cl, 32.0% Cl₆Rb₂ORe requires Cl, 32.2%).

Preparation of potassium hexachloro-
orhenium(IV) $\text{K}_2\text{ReCl}_6$

$\text{KReO}_4$ (0.5gm) and KCl (0.15 gm) were heated together on a steam bath in concentrated hydrochloric acid (15 mls), containing hypophosphorous acid (4 mls). The solution goes dark brown, then dark green, and pales as green crystals of the product are formed. The product was recrystallised from concentrated hydrochloric acid (Yield 0.5 gm).

(Found Cl, 44.0%; Cl₆K₂Re requires Cl, 44.5%).

Preparation of potassium perrhenate $\text{KReO}_4$

Rhenium metal was dissolved in excess hydrogen peroxide (130 vol., about 25 mls/gm of Re). After the initial vigorous reaction had stopped, the solution was evaporated to give a thick oil of $\text{HReO}_4$. This was again evaporated after addition of 1 - 2 mls of water.

The insoluble potassium salt was prepared by dissolution of this oil in water and addition of potassium chloride.
Standardisation of hydroiodic acid solution (HI in HCl)

The solution, approximately 0.6 molar, was prepared by diluting 25 mls of AR HI to 250 mls. with concentrated hydrochloric acid.

Total free I$_2$ present (about 1% of the I$^-$ present) was determined with standard thiosulphate solution, and this value was used to correct the total iodide (plus free iodine) as determined by the Andrews titration.
PART C

Experimental
Experimental

Preparation of Pentaamminechlororhodium (III) Chloride.
\[(\text{Rh(NH}_3)_5\text{Cl})\text{Cl}_2\] \(127\).

Rh\text{Cl}_3\cdot n\text{H}_2\text{O} (0.25 gm) was added to excess 0.880 ammonia and the solution boiled, filtered, and evaporated to dryness. The residue was dissolved in hot water and the pale yellow product precipitated by addition of concentrated hydrochloric acid. (Yield 0.2 gms.) (Found N, 23.0%; Cl\text{3H}_15\text{N}_5\text{Rh requires N, 23.6%).}

Preparation of Pentaamminechloroiridium (III) Chloride.
\[(\text{Ir(NH}_3)_5\text{Cl})\text{Cl}_2\] \(128\).

\text{NH}_4\text{Cl} (15 gm) and (\text{NH}_4)_2\text{IrCl}_6 (1 gm) were added to a solution of (\text{NH}_4)_2\text{CO}_3 (25 gm) in water (60 mls). The covered solution was heated for six hours, during which time pale yellow crystals of the product were formed. The product was re-precipitated from hot water, using hydrochloric acid, as almost colourless crystals (Yield 0.6 gms). (Found N, 18.7%; Cl\text{3H}_15\text{IrN}_5 requires N, 18.3%).

Preparation of Dinitrogenpentammineosmium (II) dichloride
\[(\text{Os(NH}_3)_5\text{N}_2)\text{Cl}_2\] \(101\).

Method (a) (\text{NH}_4)_2\text{OsCl}_6 (0.5 gms) was added to hydrazine hydrate (5 mls) and the solution refluxed for six hours during which time the pale yellow product crystallised. (Yield 0.3 gms). Shorter refluxing times give varying amounts of \[(\text{Os(NH}_3)_4\text{N}_2)\text{Cl}_2\] (detected from infrared spectra) as an impurity.

Method (b) This reaction was identical to the above, except
[\text{Os} (\text{NH}_3)_5 \text{Cl}] \text{Cl}_2 \text{ was used as source of osmium. A six hour reaction is still required.}

(Found N, 25.9%; Cl$_2$H$_{15}$N$_7$Os required N, 26.1%).

**Preparation of Pentaaminechloroosmium (III) chloride, [Os(NH$_3$)$_5$Cl]Cl$_2$.**

[Os (NH$_3$)$_5$N$_2$]Cl$_2$ was dissolved in the minimum volume of cold water, then iodine, in alcohol, was added until dinitrogen evolution ceased and an excess of iodine was present. The solution was made 1:1 in concentrated hydrochloric acid and evaporated on a steam bath to give crystals of the yellow product. (Yield almost quantitative).

(Found N, 18.4%; Cl$_3$H$_{15}$N$_5$Os requires N, 18.4%).

**Preparation of Hexaammineruthenium (III) chloride [Ru(NH$_3$)$_6$]Cl$_2$.**

Commercial grade RuCl$_3$·nH$_2$O (5 gm) is "activated" by dissolving in concentrated hydrochloric acid (10 to 20 mls) and then evaporating the solution to dryness at 80°C on a steam bath. The chloride is dissolved in 0.880 ammonia (50 mls), excess A.R. zinc dust (1 gm) is added and the solution boiled for 7 minutes. Considerable effervescence occurs during the reaction. The excess zinc is filtered off and any crystallised yellow product is washed out, from the zinc, by dissolving in the minimum quantity of water. This solution is added to the filtrate. If any Zn(OH)$_2$ is precipitated during this process, a few drops of ammonia (0.880) are added to redissolve it. Small portions of solid ammonium chloride are added to the filtrate and dissolved until crystallisation of the product [Ru(NH$_3$)$_6$]Cl$_2$ commences. The solution is cooled in ice
until crystallisation is complete and the product is filtered and washed with a little cold 0.880 ammonia, then ethanol (yield 3 gm). (Found N, 30.3% Cl₂H₁₈N₆Ru requires N, 30.7%). (See also preparation below).

Preparation of Hexaammineruthenium (II) tetrachlorozinc (II)

\[ \text{[Ru(NH₃)₆]Cl₂•ZnCl₄} \]

The filtrate remaining, after collection of \([\text{Ru(NH₃)₆}]\text{Cl₂}\) above, is just neutralised with concentrated hydrochloric acid. Pale yellow leaflets of the product begin to separate (excess acid should be avoided). The product is filtered off and washed with a little cold water, then ethanol. (Yield 2 gm).

(Found N, 19.8%; Cl₄H₁₈N₆RuZn requires N, 20.4%).

In the two preparations above, the relative yields of both products depends on the ammonia concentration present. High concentrations give a greater relative yield of the first product \([\text{Ru(NH₃)₆}]\text{Cl₂}\). The total \([\text{Ru(NH₃)₆}]^{2+}\) precipitated as the chloride and ZnCl₂⁻ salts remains constant.

Preparation of Pentaamminechlororuthenium (III) chloride.

\[ \text{[Ru(NH₃)₅Cl]Cl₂} \]

\([\text{Ru(NH₃)₆}]\text{Cl₂} (3 gm) (or equivalent amount \([\text{Ru(NH₃)₆}]\text{ZnCl₄}\) is added to 20 mls of water, then bromine water is added until it is present in a slight excess. This is observed by the initial yellow solution first becoming paler, almost colourless, and then slightly orange as the excess bromine accumulates. Concentrated hydrochloric acid is added to give a 1:1 acid solution, and the solution is heated under reflux for two hours (excess bromine is allowed to escape). The
product \([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) is formed as yellow-orange crystals during the heating. The product is recrystallised from 0.1 molar hydrochloric acid. (Yield 3 gm.)

(Found N, 24.0%; Cl\text{3H}_{15}\text{N}_5\text{Ru requires N, 23.9%).}

Preparation of Hexaammineruthenium (III) bromide

\([\text{Ru(NH}_3\text{)}_6\text{}]\text{Br}_3\) \(129\)

\([\text{Ru(NH}_3\text{)}_6\text{]}\text{Cl}_2\) (1 gm) is oxidised with bromine water as described above in the preparation of \([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\). After oxidation, solid NaBr is dissolved in the neutral solution, until the product \([\text{Ru(NH}_3\text{)}_6\text{]}\text{Br}_3\) precipitates out as a yellow powder. The product was reprecipitated from aqueous solution with sodium bromide and washed with ethanol. (Yield 1 gm.)

(Found N, 18.8% \text{Br}_3\text{H}_{18}\text{N}_6\text{Ru requires N, 19.0%).}

Preparation of Dinitrogenpentaammineruthenium(II) tetrachlorozinc(II)

\([\text{Ru(NH}_3\text{)}_5\text{N}_2\text{]}\text{ZnCl}_4\text{-}

\([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) (0.5gm) and sodium azide (0.2 gm) were added to aqueous methylsulphonic acid solution (20 mls, 0.1 molar) and the solution heated to about 60\(^\circ\)C. The yellow \([\text{Ru(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) dissolves to give a yellow solution, which on further heating becomes bright red and a vigorous evolution of gas occurs. The solution is kept at this temperature (about 60\(^\circ\)C) until gas evolution stops (5 to 10 minutes), (at this stage the solution is pale orange). The solution was then cooled and \(\text{NH}_4\text{Cl/ZnCl}_2\) was added to precipitate the required product as off-white leaflets. (Yield 0.4 gms).

(Found N, \text{(NH}_3\text{)} 16.2%; \text{Cl}_4\text{H}_{15}\text{N}_2\text{RuZn requires N(NH}_3\text{), 16.5%).}
Other complexes such as the bromide, iodide (Chapter 7, ) and the perchlorate (Chapter 5) were prepared from the solution above, containing \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}_2\text{]}^{2+}\) by precipitation with the appropriate anion.

**Preparation of Dinitrogenpentaaammineruthenium(II) chloride**

\([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}_2\text{]}\text{Cl}_2\)

\([\text{Ru(NH}_3\text{)}_5\text{Cl} \text{]} \text{Cl}_2\) and azide were reacted together as above in the preparation of \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}_2\text{]} \text{ZnCl}_4\). After the reaction had finished, the solution was evaporated under vacuum, to a small volume (about 5 mls.) and the product precipitated out as a white solid. Any solid product not kept damp with the mother liquid, tends to become deep red because of slight decomposition but this red decomposition product is very soluble in the mother liquid. The product was filtered off and washed with a little cold 0.680 ammonia (1-2 mls.) then alcohol.

(Found N, \((\text{NH}_3)\), 24.5%; \(\text{Cl}_2\text{H}_5\text{N}_7\text{Ru}\) requires N(\(\text{NH}_3\)), 24.6%)

**Preparations of complexes**, used in only one section of the present work, are included in the appropriate chapters. These compounds are listed below.

**Ruthenium (II)** = \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}_2\text{]} \text{Cl}_2\) (hydrazine method), (P. 31).

\([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}_2\text{]}(\text{ClO}_4\text{)}_2\), (P 74); \([\text{Ru(NH}_3\text{)}_5\text{(N}_2\text{)}_2\text{]}X_2\ (X=\text{Br, I})\) (P 89);

\([\text{Ru(NH}_3\text{)}_5\text{]} \text{X}_2\ (X=\text{Br, I})\) (P 89);

\([\text{Ru(NH}_3\text{)}_5\text{(CO)}\text{]} \text{Cl}_2\), (P 52);
Ruthenium (III) \([\text{Ru(NH}_3\text{)}_3X]_2\text{Cl}_2\), \((X=\text{Br, Cl, } Y=\text{Br, Cl})\), (P 88);
\[\text{Ru(NH}_3\text{)}_6\text{Cl}_4\text{ZnCl}_4\], (P 32).
\[\text{cis-}[\text{Ru(en)}_2\text{Cl}_2\text{]}\text{Cl}_2\text{,} \quad \text{(P 55)}; \quad \text{cis-[Ru(NH}_3\text{)}_4\text{Cl}_2\text{]}\text{Cl}\]
\[3/2\text{H}_2\text{O}\]. (P 56).
\[\text{Ru(NH}_3\text{)}_4\text{(oxalate)}_2\text{S}_2\text{O}_6\], (P 55).

Osmium (II) \([\text{Os(NH}_3\text{)}_5(CO)]\text{Cl}_2\], (P 53)

Iridium (III) \([\text{Ir(NH}_3\text{)}_3\text{Cl}_3\] (P 54).

\[\text{Ir(NH}_3\text{)}_4\text{(CO)}\text{Cl}]\text{Cl}_2\], (P 53), \text{trans-}[\text{Ir(NH}_3\text{)}_4\text{Cl}_2\text{]}\text{Cl}\] (P 54)
\[\text{Ir(NH}_3\text{)}_5\text{Cl}]\text{Br}_2\], (P 89)

Rhodium (III) \([\text{Rh(NH}_3\text{)}_5\text{H}]\text{Br}_2\], (P 54)

Iron (II) and (III) \([\text{Fe(dtc)}]_3\], (P 55); \([\text{Fe(dtc)}_2\text{CO}]_n\) (P 56)

**Cobalt Complexes.** The two cobalt complexes used in the present work \text{trans-[Co(NH}_3\text{)}_4\text{Cl}_2\text{]}\text{Cl}\) and \([\text{Co(NH}_3\text{)}_6\]\text{Br}_3\) were obtained from Dr. D.A. House.

**Analysis.** Microanalysis for carbon, hydrogen and total nitrogen were kindly carried out by Dr. Campbell at the University of Otago.

Nitrogen, as coordinated ammonia, in the ruthenium and rhodium complexes, was analysed by means of the Kjeldahl Method. A known weight of complex was added to the apparatus together with an excess of 7.5M NaOH solution and Devarda's Alloy (0.2 gm). The solution was slowly warmed at such a rate that distillation did not start until the reaction of the alloy had finished. (If warming is more rapid, some alkali is always brought over). The distilled alkali (ammonia) was reacted with 5% boric acid, then ammonium borate was titrated with standard acid using bromocresol green/methyl
red as indicator.

Halide was determined as the silver salt gravimetrically.
In the case of the rhenium salts, the Re(IV) and Re(V) complexes were first oxidised with peroxide.

Physical Methods:

(1) Infrared Spectra:

Infrared spectra were recorded using a Shimadzu IR-27G Spectrophotometer 4000-400 cm\(^{-1}\) or on a Perkin-Elmer 337 Spectrophotometer; both instruments were calibrated using poly styrene film.

Solid samples were run using nujol mulls between KBr plates.
The spectra of aqueous solutions were recorded using AgCl plates.

Low frequency infrared spectra 400-40 cm\(^{-1}\) were recorded on a Research and Industrial Instru. Co. FS-720 Fourier Spectrophotometer using nujol mulls on polythene discs. In all cases two spectra of each compound were recorded. Spectra of compounds with absorptions above 250 cm\(^{-1}\) were also recorded on a Grubb Parsons D.M.4 spectrophotometer calibrated using water vapour. Positions of absorptions in the spectra obtained from the two low frequency instruments agreed within experimental error.

(2) Electronic Spectra:

Electronic spectra were recorded using a Shimadzu MGS Spectrophotometer. The spectra were obtained on aqueous solutions. Reflectance spectra were recorded on the above instrument or on a Beckman DK 2A spectrophotometer with a Beckman reflectance attachment, using magnesium oxide as standard.
\[ \text{[Ru(NH}_3\text{)}_5(N_2)\text{]} (ClO}_4\text{)}_2 \]

25 (theta angles, 1 inch = 5 degrees)

\[ \text{[Ru(NH}_3\text{)}_6\text{]} Cl \text{ ZnCl}_4 \]

25 (theta angles in degrees)

\[ \text{[Ru(NH}_3\text{)}_5(N_2)\text{]} ZnCl}_4 \]

25 (theta angles in degrees)

\[ \text{[Ru(NH}_3\text{)}_5(CO)\text{]} Cl}_2 \]

25 (theta angles in degrees)

\[ \text{[Ru(NH}_3\text{)}_5(N_2)\text{]} Cl}_2 \]

25 (theta angles in degrees)

\[ \text{[Ru(NH}_3\text{)}_5(N_2)\text{]} Cl}_2 / \text{[Ru(NH}_3\text{)}_5\text{Cl} \text{]} Cl}_2 \]

Physical Mixture

25 (theta angles in degrees)

\[ \text{[Ru(NH}_3\text{)}_5\text{Cl} \text{]} Cl}_2 \]

25 (theta angles in degrees)

\[ \text{trans[Ir(NH}_3\text{)}_4\text{Cl}_2 \text{]} Cl \]

25 (theta angles in degrees)
(3) **Magnetic Susceptibilities**

Magnetic measurements were determined by the Gouy Method\(^{130}\). The complex \([\text{Ni(en)}_3]_3 \text{S}_2 \text{O}_3\)\(^{131}\) was used as calibrant. The low temperature (103-270° K) moments for Ca\(_2\)ReO\(_4\)Cl\(_5\) were obtained with a Newport Low Temperature Cryostat and Balance using liquid nitrogen as coolant.

The magnetic moment \(\mu\) was calculated from the expression

\[
\mu = 2.34 \left( \chi_m^{\text{corr.}} \times T \right)
\]

where \(\chi_m^{\text{corr.}}\) is the molar susceptibility corrected for diamagnetism.

(4) **X-ray Powder Photographs**

X-ray powder photographs were obtained using a Philips 114.83 mm Debye Scherrer camera and CuK\(\alpha\) radiation. Finely ground samples were packed into glass capillary tubes. The diffraction patterns obtained are shown in figure 20.

(5) **Conductivity Measurements**

Conductivity measurements were made at 25° C using a Philips PR9500/01 bridge and a cell with removable dip-type platinum electrodes. The cell was calibrated with standard potassium chloride solution\(^{132}\).
APPENDIX

Preparation and Properties of Recently Reported Dinitrogen Complexes

1. Reactants used in Preparations

(a) from Dinitrogen

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactants</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>t- Mo(N₂)₂(diphos)₂</td>
<td>Mo(acac)₃ + diphos + N₂ +¹Bu₃Al</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>[Ru(N₂)H(diphos)₂]BPh₄</td>
<td>RuHCl(diphos)₂ + N₂</td>
</tr>
<tr>
<td></td>
<td>[Os(N₂)H(diphos)₂]BPh₄</td>
<td>OsHCl(diphos)₂ + N₂</td>
</tr>
<tr>
<td>mer- OsX₂(N₂)(QR₃)₃</td>
<td>OsX₃(QR₃)₃ + N₂ + Zn</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>(X = Cl, Br; Q = P, As)</td>
<td></td>
</tr>
<tr>
<td>c,t- W(N₂)₂(PR₃)₄</td>
<td>WC₁₄(PR₃)₂ + N₂ + Na/Hg</td>
<td>28</td>
</tr>
<tr>
<td>t- Mo(N₂)₂(diphos)₂</td>
<td>Mo(acac)₃ + diphos + N₂ +¹Bu₃Al</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>[Ru(diars)₂(N₂)Cl]PF₆</td>
<td>Ru(diars)₂(N₂)Cl + NOPF₆</td>
</tr>
<tr>
<td></td>
<td>[Ru(NH₃)₅(N₂)]²⁺/Ru(NH₃)₅(N₃)]²⁺ + H⁺</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Ru₂(NH₃)₁₀(N₂)]⁴⁺</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Cr(CN)₅(N₂)]⁴⁻ (impure)</td>
<td>K₃[Cr(CN)₆] + NaN₃ in DMSO</td>
</tr>
<tr>
<td></td>
<td>Rh₂(N₂)(CO)₂(PPh₃)₂</td>
<td>Rh(CO)(PPh₃)(acac) + HN₃</td>
</tr>
</tbody>
</table>

(b) from Azide

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactants</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>t- [Ru(diars)₂(N₂)Cl]PF₆</td>
<td>Ru(diars)₂(N₂)Cl + NOPF₆</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>[Ru(NH₃)₅(N₂)]²⁺/Ru(NH₃)₅(N₃)]²⁺ + H⁺</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Ru₂(NH₃)₁₀(N₂)]⁴⁺</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Cr(CN)₅(N₂)]⁴⁻ (impure)</td>
<td>K₃[Cr(CN)₆] + NaN₃ in DMSO</td>
</tr>
<tr>
<td></td>
<td>Rh₂(N₂)(CO)₂(PPh₃)₂</td>
<td>Rh(CO)(PPh₃)(acac) + HN₃</td>
</tr>
</tbody>
</table>

(c) from Hydrazine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactants</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(N₂)(CO)₃(NH₂)(PR₃)₁/Re(CO)₃(or₄)X(PR₃) + N₂H₄</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Re(N₂)(CO)₂(NH)(PR₃)</td>
<td>(X = Cl, Br.)</td>
<td></td>
</tr>
</tbody>
</table>

Ref. - References
(2) Properties

### Frequencies of $\nu$(NN) Absorptions

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(NN) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t- $[\text{RuCl}(\text{N}_2)(\text{diars})_2]/\text{PF}_6$</td>
<td>2130 ($\nu$(Ru-N$_2$) at 494)</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{N}_2)\text{H}(\text{diphos})_2]/\text{BPh}_4$</td>
<td>2160</td>
</tr>
<tr>
<td>$[\text{Os}(\text{N}_2)\text{H}(\text{diphos})_2]/\text{BPh}_4$</td>
<td>2136</td>
</tr>
<tr>
<td>mer- $\text{Os}(\text{N}_2)X_2QR_3)_3$</td>
<td>2056 - 2092 (Lower for X = Cl, Q = P, As, R = long alkyl)</td>
</tr>
<tr>
<td>t- $\text{Os}(\text{N}_2)\text{H}_2(\text{PETPh}_2)_3$</td>
<td>2085</td>
</tr>
<tr>
<td>t- $\text{Mo}(\text{N}_2)_2(\text{diphos})_2$</td>
<td>1970 (2020 weak)</td>
</tr>
<tr>
<td>o- $\text{W}(\text{N}_2)_2(PR_3)_4$</td>
<td>1931; 1998</td>
</tr>
<tr>
<td>t- $\text{W}(\text{N}_2)_2(PR_3)_4$</td>
<td>1953</td>
</tr>
<tr>
<td>ReCl$\text{N}_2(\text{PR}_3)_2(\text{CO})_2$</td>
<td>Three above 1900cm$^{-1}$</td>
</tr>
<tr>
<td>Re$\text{N}_2(\text{NH}_2)(\text{CO})_3(PR_3)$</td>
<td>2220 $\nu$(Re-N$_2$) at 520</td>
</tr>
<tr>
<td>Re$\text{N}_2(\text{NH})(\text{CO})_2(PR_3)$</td>
<td>2225</td>
</tr>
</tbody>
</table>

Other properties such as esr$^{35}$ or magnetic data$^{27}$ of these complexes are only reported for one or two compounds and references should be consulted.

The reported stabilities range from air stable for $[\text{Ru}(\text{N}_2)\text{H}(\text{diphos})_2]/\text{BPh}_4$ to very unstable and impure as for $[\text{Cr}(\text{N}_2)(\text{CN})_5]^{4-}(35)$. In many cases where a series of ligands have been used, only a few complexes could be obtained pure$^{28,33,39}$. 
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