SPECTROSCOPIC STUDIES ON COMPLEX COMPOUNDS OF TRANSITION METALS

A Thesis

submitted for the Degree of Doctor of Philosophy of the University of London by

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Department of Chemistry, Imperial College.
To my parents, in gratitude.
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I should also like to thank Dr. D. F. Evans, Dr. W. P. Griffith, and Dr. L. Pratt for helpful discussions, and Dr. A. J. Poë and Mr. E. J. Bounsall for informing me of results before publication. I thank Miss C. M. Ross for typing the manuscript, and for her help at other times.
ABSTRACT

Complex compounds of rhodium(III) containing co-ordinated halides and such weak-field ligands as amines, pyridine, and dioximes have been studied with particular reference to the nucleophilic replacement of the halide ions by hydride ion. Spectroscopic methods have been used, notably nuclear magnetic resonance and infra-red, and electronic spectral studies have utilized the d-d transitions of the rhodium(III) ion. The position of hydride ion in the spectrochemical series is shown to be between water and ammonia.

Several complexes reported in the literature to contain rhodium in an oxidation state lower than 3 have been re-examined, and have been shown to be either hydridic compounds of rhodium(III), or compounds of rhodium(III) whose formations have been catalysed by intermediate hydridic compounds. A large amount of spectroscopic information on complexes of rhodium(III) has been accumulated, and several new compounds are reported, including the first mixed cyanic complex of rhodium(III).

Studies have also been performed on analogous complexes of cobalt(III); although no cobalt(III)-hydrogen bonds were established, the novel catalytic isomerisation of the trans-dichlorobisethylenediaminecobalt(III) cation by hydride ion is investigated radiochemically. Spectroscopic data have been obtained.
Abstract (contd.)

Intramolecular hydrogen bonding in complexes containing the 
trans-bisdimethylglyoximato)cobalt(III) structure has been demonstrated by nuclear magnetic resonance. Infra-red spectral studies of adducts \([MA_xX_y]X.HX.2H_2O\), where \(M = \text{Co, Cr or Rh}\), and \(X = \text{Cl or Br}\), have revealed the existence of the \((H_5O_2)^+\) ion, which is compared with \((H_3O)^+\).
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INTRODUCTION

Hydrogen is a versatile element. The $1s^1$ electronic configuration of atomic hydrogen may become $1s^0$, giving the bare proton, $H^+$, with its enormous electron affinity, or $1s^2$, giving the extremely nucleophilic hydride ion, $H^-$. Hydrogen may also form covalent bonds, and is certainly far more common when so bonded than in either of its ionic forms. Indeed, compounds have been known for some time in which hydrogen is covalently bonded to a transition metal.

The first transition metal hydrides to be discovered were the carbonyl hydrides of iron$^1$ and cobalt.$^2$ Until about 1960, interest was concentrated on compounds containing $\pi$-bonding ligands, such as carbon monoxide, $\pi$-cyclopentadienyl, and tri-alkyl or tri-aryl phosphines. The chemistry of such "strong field" hydrides has been reviewed several times.$^3,4,5$ Many of these compounds are extremely stable; they are usually non-electrolytes, soluble in organic solvents, and many may be sublimed.

It was discovered$^6$ in 1955 that a hydrogen atom directly bound to a transition metal gave a signal at very high field in the proton resonance spectrum. A large amount of evidence for the generality of this property was rapidly accumulated, and the observation of the high-field line was taken as diagnostic of the presence of hydridic species which were too unstable to be isolated. It was shown$^7$ in
this way that the so-called "rhenide" ion in fact involved hydrogen directly bonded to rhenium, and, shortly afterwards, that the hydride ion would replace at least one cyanide ion in the hexacyanocomplexes of cobalt(III) and rhodium(III).

By 1960, a good deal was known about molecular hydrides, but there was very little connection between these stable compounds, containing π-bonding ligands, and the hydridic species which had been postulated in several systems on the basis of kinetic evidence. Typical cases where such transient metal-hydrogen bonds are thought to occur are those where molecular hydrogen is activated, and its reactions in solution are catalysed, for example by tetrachloropalladate(II) ion, where the hydridic intermediate thought responsible for catalytic activation is the hydridotrichloropalladate(II) ion.

One purpose of the present work was to attempt a junction between the known stable molecular hydrides and the transient hydridic species which occur in certain aqueous solutions, treated with molecular hydrogen and, presumably, in certain enzymic processes.

Several methods have been used for showing the presence of metal-hydrogen bonds. The spectroscopic methods have relied either on the extremely shielded nature of a hydrogen bonded to a metal, which gives rise to a signal at unusually high field in nuclear resonance, or on the metal-hydrogen stretching vibration, which gives rise to an absorption in the infra-red around 2100 cm\(^{-1}\) for monohydrides, and around 1800 cm\(^{-1}\) for trans-dihydrides.
There are certain drawbacks to these methods. The observation of a high-field line requires a fairly large concentration of the hydride, so that solubility may prove a limiting factor, particularly if the hydride has a large molecular weight. In certain cases, such as some hydridotriphenylphosphineplatinum complexes, the metal-hydrogen stretching frequency is not observed in the usual region (though there is now some doubt as to the hydridic nature of such compounds). The infra-red spectra of inorganic compounds are usually taken in mulls, requiring that the hydride be sufficiently stable to isolate as a solid. This requirement also exists in the method involving reaction of the hydride with bromine or iodine to form hydrohalic acid which may then be titrated.

In view of these difficulties, a second aim of this work was to examine the use of electronic spectra as a means of detecting hydridic species in solution, without necessarily isolating the compound. The position of hydride ion in the spectrochemical series is prerequisite to this method. The most suitable compounds for such work are those in which the Laporte-forbidden d-d transitions are quite separate from allowed bands due to charge-transfer or intra-ligand transitions.

Rhodium was chosen as a suitable transition metal for several reasons:

(a) the stable rhodium nucleus (Rh\textsuperscript{103}) has a nuclear spin of \( \frac{1}{2} \), giving rise to splitting of the proton resonance signal of a hydrogen atom attached directly to rhodium.
(b) complexes of rhodium(III) were fairly well known, and the analogous compounds of the iso-electronic cobalt(III) extremely well known.

(c) hydridic compounds of rhodium(III) had been reported.

(d) while a number of rhodium compounds in which the rhodium had a valence state lower than 3 had been claimed in the literature, none of them had been characterized in detail. It would be expected that rhodium(II) with the d^{7} configuration would be paramagnetic. However, the only report \(^1\) of magnetic measurements on "rhodous" compounds showed them to be diamagnetic. In view of the very large differences in the third ionisation potentials of cobalt and rhodium, the very existence of rhodium(II) was dubious, and a re-examination of "reduced" species derived from rhodium(III) was desirable.

A number of preparative methods are now available for forming hydrido-complexes, apart from protonation by acids or acidification of sodium salts:

(a) Direct synthesis:\(^1\)

\[
[(n-C_3H_7)_3P]_2PtCl_2 + H_2 \xrightarrow{\text{Pressure}} [(n-C_3H_7)_3P]_2PtHCl.
\]

(b) Reduction of halide complexes by complex hydrides:\(^2\)

\[
[(C_2H_5)_3P]_2PtCl_2 \xrightarrow{\text{LiAlH}_4, \text{THF}} [(C_2H_5)_3P]_2PtHCl
\]

(c) Introduction of hydride ions from alkaline alcohols:\(^3\)

\[
[(C_2H_5)_3P]_2PtCl_2 + KOH + C_2H_5OH \rightarrow [(C_2H_5)_3P]_2PtHCl + CH_3CHO + KCl + H_2O.
\]

This method has been used\(^6\) to obtain \([(C_2H_5\cdot P\cdot Ph_2)_3P]_3RhHX_2\), where X = Cl, Br, or I.
In this work, emphasis has been on nucleophilic replacement of halide ions by hydride, as in (b) above. No hydrides have yet been obtained using methods (a) or (c), though reduced species have been obtained in several cases from (c). Less common methods of producing metal-hydrogen bonds are:

(d) With hydrazine as a reducing agent; it has been said that the complexes formulated as hydrido-triphenylphosphineplatinum(II) compounds are not hydridic, but compounds of platinum(0).

(e) With hypophosphorous acid as a reducing agent; it was first reported in 1931 that hypophosphorous acid reduced hexacyanorhodate(III) to a rhodium(I) species. The solution produced was later shown to contain rhodium-hydrogen bonds, and in the present work, other reduced species of rhodium(III) produced by using hypophosphorous acid have been shown to involve rhodium-hydrogen bonds.

In this thesis, the discussion section is divided into four chapters, the first two dealing with complexes of rhodium with nitrogenous ligands, the third with related work on complexes of cobalt(III), and the last drawing some general conclusions.
CHAPTER I

Complexes of Rhodium(III) with Aliphatic Amines

Introduction

Although the trisethylenediaminerhodium(III) cation was first characterized by Werner,\textsuperscript{19} the isomers of the dichlorobisethylenediaminerhodium(III) complexes have been prepared only recently.\textsuperscript{20} The preparations earlier described by Meyer and Kienity\textsuperscript{21} were shown\textsuperscript{20} not to be reproducible. Basolo and Anderson\textsuperscript{20} obtained both isomers of dichlorobisethylenediaminerhodium(III) cation, and based their assignment of stereochemistry on the resolution of the cis-isomer (λ\textsubscript{max} 352 μ) by means of π-camphorsulphonic acid.

Evidence of a very different kind for the assignment of trans-configuration to the isomer absorbing at 407 μ is that, from a solution of its chloride in 1:1 hydrochloric acid, plate-like crystals of an adduct with hydrochloric acid, trans-[Rhen\textsubscript{2}Cl\textsubscript{2}]Cl.HCl.2H\textsubscript{2}O, were obtained. In the course of this work, it had become clear that a number of complex salts of the type trans-[MA\textsubscript{4}X\textsubscript{2}]X, where M = Cr, Co or Rh, A = \textsuperscript{1/2} en or py, and X = Cl or Br, formed adducts with the formula trans-[MA\textsubscript{4}X\textsubscript{2}]X.HX.2H\textsubscript{2}O. This work is discussed in detail in Chapter III; the relevant compounds here are trans-[Rhen\textsubscript{2}Cl\textsubscript{2}]Cl.HCl.2H\textsubscript{2}O and its bromo-analogue, which, it will be shown later, are best formulated [Rhen\textsubscript{2}X\textsubscript{2}](H\textsubscript{2}O\textsubscript{2})X\textsubscript{2}. Trans-dichlorotetramminerhodium(III)
chloride was also prepared by Basolo and Anderson, who found that the directions of Lebedinski led to trichlorotriamminerhodium(III). While the electronic spectrum confirms the trans-stereochemistry of this cation, no hydrogen chloride adduct has been isolated from it in this work, despite numerous attempts.

trans-Isomers

When yellow trans-dichlorobisethylenediaminerhodium(III) chloride in aqueous solution is treated carefully with a solution of sodium borohydride, the solution becomes pale brown, and the presence of a hydrido-species was shown by the observation of a high-field line in the proton resonance spectrum. It was originally thought that the reaction occurring was

$$[\text{Rhen}_2\text{Cl}_2]^+ + \text{H}^- \longrightarrow [\text{Rhen}_2\text{ClH}]^+.$$  

However, two reactions in fact occur consecutively:

$$\text{trans-}[\text{Rhen}_2\text{Cl}_2]^+ + \text{H}^- \longrightarrow \text{trans-}[\text{Rhen}_2\text{ClH}]^+ + \text{H}^- \longrightarrow \text{trans-}[\text{Rhen}_2\text{H}_2]^+.$$  

The proton resonance spectra of these systems might be expected to show high-field signals arising from both mono- and di-hydrides, but in no experiments using trans-dihalo-isomers have both signals been observed in the same solution. The reaction has been extended to the analogous dibromo- and di-iodo-complexes. In the iodo-case, on first addition of borohydride, a high-field line is observed at 1420 c/s relative to water, whereas on further addition of borohydride this disappears, and the final hydridic product shows a high-field line at 1500 c/s, due to the dihydride.
Some confusion arose because it was not realized for some time that both the hydridic species were formed. In early work, it was found that the addition of a solution of sodium tetraphenylborate to the hydridic solution gave a precipitate which showed an absorption in the infra-red at 2100 cm⁻¹. A subsequent experiment showed that the final product, using excess borohydride, gave a precipitate with sodium tetraphenylborate which contained no chlorine. It was eventually realized that these two experiments refer to different hydridic species; it is the monohydride, [Rhen₂ClH]⁺, which is responsible for the νₚₚₜ-H at 2100 cm⁻¹, whereas the final product, containing no chlorine, is, of course, [Rhen₂H₂]⁺. All the solid compounds isolated in this work (usually tetraphenylborates) have been extremely unstable, both to oxidation and to heat. Reliable analytical data are, in general, not available because of this instability, and the ready explosion of the dihydrides in particular in the presence of oxygen.

Although the hydridic species readily deposit rhodium metal at about 10°C, it proved possible to obtain reproducible electronic spectra by working with slightly alkaline solutions (pH 8-9) at 2°C under nitrogen. By successive additions of very small amounts of strong borohydride solution to solutions of the dihalobisethylenediamine-rhodium(III) salts, the details of the reactions occurring became clear. For example, using the trans-dibromo-compound, two isosbestic points were immediately apparent, as shown in Figure 1, at 405 μm and 310 μm, suggesting the reaction

\[
\text{trans-}[\text{Rhen}_2\text{Br}_2]^+ + \text{H}^- \rightarrow \text{[Rhen}_2\text{BrH}]^+.
\]
After the disappearance of the absorption bands due to the dibromo-compound, a second isosbestic point appeared, when more borohydride was added, indicating

\[ [\text{Rhen}_2\text{BrH}]^+ + \text{H}^- \rightarrow [\text{Rhen}_2\text{H}_2]^+ \]

as the second reaction.

Similar results were obtained for all three trans-dihalo-compounds. The reaction scheme outlined was supported by several distinct lines of evidence.

(a) The two sets of isosbestic points suggest two successive reactions of the general type \( A \rightarrow B; \ B \rightarrow C \).

(b) The final product from all three dihalo-compounds had the same electronic spectrum, that of \([\text{Rhen}_2\text{H}_2]^+\).

(c) The intermediate hydridic compounds had electronic spectra which varied in a regular way with the original dihalo-compound, as expected for \([\text{Rhen}_2\text{XH}]^+\).

The spectroscopic evidence available is summarized in Table 1. Data for chloropentamminerhodium(III) cation treated with borohydride are also given; the pale-brown solution obtained is too dilute for observation of a high-field line.

Early directions in the literature for preparing complexes containing the bis-ethylenediaminerhodium(III) moiety are inaccurate. For example, when trans-dichlorotetrapyridinerhodium(III) chloride is made into a paste with ethylenediamine and warmed till no more pyridine is lost, the product is not \([\text{Rhen}_2\text{pyCl}]\text{Cl}_2\), claimed by Meyer and
### TABLE 1

Spectroscopic data for trans-complexes of rhodium(III)

Electronic spectra in mμ, infra-red spectra in cm⁻¹, n.m.r. spectra in Ω values

<table>
<thead>
<tr>
<th>Formula</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \lambda \times \lambda \times \Omega \times \Omega )</th>
<th>( \nu_{\text{Rh-H}} )</th>
<th>( \lambda \times \lambda \times \Omega \times \Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{trans-}[\text{Rh}2\text{Cl}_2]^+]</td>
<td>406</td>
<td>365 85 - - -</td>
<td>2100</td>
<td>254 (340) 350 290 680 31.6</td>
</tr>
<tr>
<td>[\text{trans-}[\text{Rh}2\text{Br}_2]^+]</td>
<td>425</td>
<td>371 150 296 350</td>
<td>2120</td>
<td>260 (340) 350 291 700 31.6</td>
</tr>
<tr>
<td>[\text{trans-}[\text{Rh}2\text{I}_2]^+]</td>
<td>462</td>
<td>385 350 - - 30.2</td>
<td>2140</td>
<td>244 (340) 400 291 850 31.6</td>
</tr>
<tr>
<td>[\text{Rh(NH}_3\text{)}_5\text{Cl}]^{2+}]</td>
<td>348</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</table>

- **a.** Isosbestic point(s) for the process \([\text{Rh}A_4X_2]^+ + H^- \rightarrow [\text{Rh}A_4XH]^+\).
- **b.** Isosbestic point for the process \([\text{Rh}A_4XH]^+ + H^- \rightarrow [\text{Rh}A_4H_2]^+\).
Kienity, but $[\text{Rhen}_3]\text{Cl}_3$. However, the electronic spectra of a reasonable number of authenticated complexes containing the trans-bisethylenediaminerhodium(III) moiety are now available. These are used in Tables 2–4 to locate the hydride ion in the spectrochemical series.

### TABLE 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{1}A_{2g}, ^{1}E_g \leftarrow ^{1}A_{1g}$</th>
<th>$^{1}B_{2g}, ^{1}E_g \leftarrow ^{1}A_{1g}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Band I</td>
<td>Band II</td>
<td></td>
</tr>
<tr>
<td><strong>trans-[Rhen$_2$I$_2$]$^+$</strong></td>
<td>$\lambda$ 21,650 260</td>
<td>$\lambda$ - - -</td>
<td>a,b</td>
</tr>
<tr>
<td><strong>trans-[Rhen$_2$Br$_2$]$^+$</strong></td>
<td>425 23,530 100</td>
<td>- - -</td>
<td>a,b</td>
</tr>
<tr>
<td><strong>trans-[Rhen$_2$Cl$_2$]$^+$</strong></td>
<td>406 24,630 75</td>
<td>286 34,970 130</td>
<td>a,b</td>
</tr>
<tr>
<td><strong>trans-[Rhen$_2$(N$_3$)$_2$]$^+$</strong></td>
<td>375 26,670 780</td>
<td>- - -</td>
<td>b</td>
</tr>
<tr>
<td><strong>trans-[Rhen$_2$H$_2$]$^+$</strong></td>
<td>340 29,410 250</td>
<td>290 34,480 500</td>
<td>a</td>
</tr>
<tr>
<td><strong>trans-[Rhen$_2$(NO$_2$)$_2$]$^+$</strong></td>
<td>300(sh) 33,330 590</td>
<td>- - -</td>
<td>b</td>
</tr>
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</table>

a. This work.  
b. Ref. 20.
### TABLE 3

Electronic spectra of complexes of the type trans-[Rhen$_2$XCl]$^+$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$A$_{2g}$, $^1$E$<em>g$ $\leftrightarrow$ $^1$A$</em>{1g}$</th>
<th>$^1$E$_{2g}$, $^1$E$<em>g$ $\leftrightarrow$ $^1$A$</em>{1g}$</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>trans-[Rhen$_2$ICl]$^+$</td>
<td>$\lambda$ 440, $\nu$ 22,730, $\epsilon$ 154</td>
<td>- - -</td>
<td>a</td>
</tr>
<tr>
<td>trans-[Rhen$_2$BrCl]$^+$</td>
<td>$\lambda$ 413, $\nu$ 24,210, $\epsilon$ 98</td>
<td>- - -</td>
<td>a</td>
</tr>
<tr>
<td>trans-[Rhen$_2$Cl$_2$]$^+$</td>
<td>$\lambda$ 406, $\nu$ 24,630, $\epsilon$ 75</td>
<td>$\lambda$ 286, $\nu$ 34,970, $\epsilon$ 130</td>
<td>b,c</td>
</tr>
<tr>
<td>trans-[Rhen$_2$(H$_2$O)Cl]$^{2+}$</td>
<td>$\lambda$ 382, $\nu$ 26,180, $\epsilon$ 66</td>
<td>$\lambda$ 280, $\nu$ 35,710, $\epsilon$</td>
<td>a</td>
</tr>
<tr>
<td>trans-[Rhen$_2$HCl]$^+$</td>
<td>$\lambda$ 365, $\nu$ 27,400, $\epsilon$ 84</td>
<td>- - -</td>
<td>b</td>
</tr>
<tr>
<td>trans-[Rhen$_2$(NCS)Cl]$^+$</td>
<td>$\lambda$ 363, $\nu$ 27,550, $\epsilon$ 340</td>
<td>- - -</td>
<td>c</td>
</tr>
<tr>
<td>trans-[Rhen$_2$(NH$_3$)Cl]$^{2+}$</td>
<td>$\lambda$ 342, $\nu$ 29,240, $\epsilon$ 95</td>
<td>$\lambda$ 295, $\nu$ 36,360, $\epsilon$ 120</td>
<td>c</td>
</tr>
<tr>
<td>trans-[Rhen$_2$(NO$_2$)Cl]$^{2+}$</td>
<td>$\lambda$ 310, $\nu$ 32,360, $\epsilon$ 310</td>
<td>- - -</td>
<td>c</td>
</tr>
</tbody>
</table>

a. Bounsall and Poe, private communication.  
b. This work.  
c. Ref. 20.

### TABLE 4

Electronic spectra of complexes with C$_{4v}$ symmetry

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$A$_{2g}$, $^1$E$<em>g$ $\leftrightarrow$ $^1$A$</em>{1g}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-Rhen$_2$BrI</td>
<td>$\lambda$ 455, $\nu$ 21,980, $\epsilon$ 260</td>
<td>a</td>
</tr>
<tr>
<td>trans-[Rhen$_2$ClI]$^+$</td>
<td>$\lambda$ 440, $\nu$ 22,730, $\epsilon$ 154</td>
<td>a</td>
</tr>
<tr>
<td>trans-[Rhen$_2$HI]</td>
<td>$\lambda$ 385, $\nu$ 25,970, $\epsilon$ 220</td>
<td>b</td>
</tr>
<tr>
<td>trans-[Rhen$_2$HBr]$^+$</td>
<td>$\lambda$ 371, $\nu$ 26,950, $\epsilon$ 160</td>
<td>b</td>
</tr>
<tr>
<td>trans-[Rhen$_2$HCl]</td>
<td>$\lambda$ 365, $\nu$ 27,400, $\epsilon$ 84</td>
<td>b</td>
</tr>
</tbody>
</table>

a. Bounsall and Poe, private communication.  
b. This work.
The hydride ion can be seen to fit into the series as
\[ \text{H}_2\text{O} < \text{H}^- \sim \text{NCS}^- < \text{NH}_3 \ldots \ldots \]. This is directly opposed to an earlier conclusion, reached on the basis of compounds containing such ligands as phosphines, where curve analysis was necessary. The conclusion from that work was that \( \text{H}^- \sim \text{CN}^- \). A discussion of the chemical information implicit in the low ligand-field strength of the hydride ion is postponed till Chapter IV.

A most important practical point is that the electronic spectra of weak field hydrides may now be used as a fingerprint method of detecting them. In Table 5 is shown the electronic spectrum of trans-dichlorotetramminerhodium(III) cation and the monohydride produced from it by treatment with aqueous borohydride. Although this hydridic species decomposes extremely rapidly to rhodium metal, and is not isolable as a tetraphenylborate (this appears to decompose immediately) its presence is demonstrated by the magnitude of the electronic spectral shift.

**TABLE 5**
Spectra of trans-[RhA₂ClH]⁺

<table>
<thead>
<tr>
<th>Compound</th>
<th>[RhA₂Cl₂]⁺</th>
<th>[RhA₄ClH]⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>λ</td>
</tr>
<tr>
<td>trans-[Rhen₂Cl₂]⁺</td>
<td>407</td>
<td>365</td>
</tr>
<tr>
<td>trans-[Rh(NH₃)₄Cl₂]⁺</td>
<td>410</td>
<td>365</td>
</tr>
</tbody>
</table>
The reduction of chloropentamminerhodium(III) cation at the dropping mercury electrode occurs as $\text{Rh}^{\text{III}} \rightarrow \text{Rh}^{\text{I}}$. This suggested that the equivalent process $\text{Rh}^{\text{III}} - \text{Cl} \rightarrow \text{Rh}^{\text{III}} - \text{H}$ might in fact occur, and, indeed, on treating at 0°C a saturated aqueous solution (pale yellow) of the chloride with aqueous borohydride, a pale-brown colour is observed, which, even under nitrogen, rapidly disappears with the formation of rhodium metal. The pale brown solution was too dilute for a high-field line to be observed, but from it a tetraphenylborate may be precipitated. This exploded on heating, but was shown to contain no chlorine. It shows a band in the infra-red spectrum at 2079 cm$^{-1}$, and the electronic spectrum of the solution shows the disappearance of the band at 348 m$\mu$ due to the chloropentamminerhodium(III) cation, and the appearance of a new band at 315 m$\mu$, due to the hydridopentamminerhodium(III) cation. Table 6 collects electronic spectral data for complexes of the type $[\text{Rh}(\text{NH}_3)_5X]^{n+}$; again, it is clear that $\text{H}_2\text{O} < \text{H} \approx \text{NH}_3$.

### TABLE 6

Electronic spectra of $[\text{Rh}(\text{NH}_3)_5X]^{n+}$ species

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{1}E_g$, $^{1}A_{2g} \leftarrow ^{1}A_{1g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$, $\nu$, $\xi$</td>
</tr>
<tr>
<td></td>
<td>Ref.</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NH}_3)_5\text{I}]^{2+}$</td>
<td>388, 25,800, 230</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NH}_3)_5\text{Br}]^{2+}$</td>
<td>359, 27,800, 122</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$</td>
<td>349, 28,700, 100</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NH}_3)_5\text{OH}]^{2+}$</td>
<td>321, 31,200, 124</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$</td>
<td>316, 31,600, 105</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NH}_3)_5\text{H}]^{2+}$</td>
<td>310, 32,250, 120</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NH}_3)_5]^3+$</td>
<td>306, 32,700, 135</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$</td>
<td>296, 33,800, 330</td>
</tr>
</tbody>
</table>

a. This work.
cis-Isomers

The longest wavelength transition of the cis-dichlorobisethylenediaminerhodium(III) cation is at 349 μm; on treatment with hydride ions, this band disappears, the process being characterized by an isosbestic point at 331 μm, with a new band appearing as a shoulder at 340 μm. This may be attributed to

$$\text{cis-} \left[ \text{Rhen}_2 \text{Cl}_2 \right]^+ + \text{H}^- \rightarrow \text{cis-} \left[ \text{Rhen}_2 \text{ClH} \right]^+ + \text{Cl}^-.$$  

When more borohydride is added, the shoulder at 340 μm due to the monohydride in turn disappears, and the longest wavelength band is now observed at 295 μm. This has a broad tail to longer wavelength, and is rather strong for a d-d band ($\varepsilon \sim 1000$). The final solution, containing cis-[Rhen$_2$H$_2$]$^+$, shows a high-field signal at 1525 c/s relative to water ($\tau \sim 32$), but no high-field line has been observed for the monohydridic compound. By adding sodium tetraphenylborate to the reduced solutions at the requisite stages, precipitates of the hydridic tetraphenylborates may be obtained. The monohydride shows the Rh-H stretching mode at 2105 cm$^{-1}$, and cis-dihydridobisethylenediaminerhodium(III) tetraphenylborate has a strong absorption at 1969 cm$^{-1}$. This latter salt, which rapidly reduces silver nitrate to the metal, contains no chlorine. The NH$_2$ deformation region of the infra-red spectrum supports the cis-configuration; the occurrence of several absorptions in this region is characteristic of the cis-bisethylenediaminerhodium(III) moiety; the cis-dihydrido-salt shows bands at 1610, 1577 and 1560 cm$^{-1}$. 

The *cis*-isomer of dichlorotri-ethylenetetraminerhodium(III) cation behaves in a similar way. The process

\[
\text{cis-}[\text{RhtrienCl}_2]^+ + \text{H}^- \rightarrow \text{cis-}[\text{RhtrienClH}]^+ + \text{Cl}^-
\]

is characterized by isosbestic points at 340 μm and 305 μm. The band due to the dichloro-compound at 347 μm (ɛ = 250) begins to disappear and a new band appears at 331 μm (ɛ = 290), due to the *cis*-chloro-hydridotri-ethylenetetraminerhodium(III) cation. The tetraphenylborate of this cation shows ν\text{Rh-H} at 2081 cm\(^{-1}\). When more borohydride is added, the process

\[
\text{cis-}[\text{RhtrienClH}]^+ + \text{H}^- \rightarrow \text{cis-}[\text{RhtrienH}_2]^+ + \text{Cl}^-
\]

occurs, the band at 331 μm of the monohydride being replaced by a stronger band at 320 μm (ɛ = 400). *cis*-Dihydridotriethylentetramine-rhodium(III) tetraphenylborate shows an infra-red absorption at 1969 cm\(^{-1}\).

This was the sole case where the growth of a signal in the N.M.R. spectrum due to the dihydridic species was observed at the expense of the signal due to the monohydride. During the successive additions of borohydride ion, a high-field line at \(\tau = 28\) first appeared, due to *cis*-\[\text{RhtrienClH}\]^+, which subsequently became weaker, while, simultaneously, a second high-field line at \(\tau = 32.5\) (due to *cis*-\[\text{RhtrienH}_2\]^+) became stronger.

Spectroscopic data for the *cis*-complexes are given in Table 7.
TABLE 7

Spectroscopic data on cis-complexes of rhodium(III)
Electronic spectra in μ, infra-red in cm\(^{-1}\), n.m.r. spectra in \(\tau\) values

<table>
<thead>
<tr>
<th>Formula</th>
<th>(\lambda_{max})</th>
<th>(\lambda)</th>
<th>(\varepsilon)</th>
<th>(\tau)</th>
<th>(\nu_{\text{Rh-H}})</th>
<th>(\lambda)</th>
<th>(\varepsilon)</th>
<th>(\tau)</th>
<th>(\nu_{\text{Rh-H}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{cis-[RhA}_4\text{Cl}_2]^+)</td>
<td>349</td>
<td>340</td>
<td>-</td>
<td>2105</td>
<td>295</td>
<td>1000</td>
<td>32.0</td>
<td>1969</td>
<td></td>
</tr>
<tr>
<td>(\text{cis-[RhA}_4\text{H}_2]^+)</td>
<td>347</td>
<td>331</td>
<td>331</td>
<td>290</td>
<td>28.0</td>
<td>2081</td>
<td>32.0</td>
<td>1969</td>
<td></td>
</tr>
</tbody>
</table>

a. Isosbestic point for the process \([\text{RhA}_4\text{Cl}_2]^+ + \text{H}^- \rightarrow [\text{RhA}_4\text{ClH}]^+\).
CHAPTER II

Complexes of Rhodium(III) with Pyridine

Preparation and characterisation

Although complex compounds which contain both halogen and pyridine co-ordinated to rhodium have been known for many years (trans-dichlorotetrapyridinerhodium(III) chloride was made by Jorgensen\textsuperscript{26}) there is a good deal of confusion in the literature, so that it was necessary to clarify several points before considering the reduced species.

The hexapyridinerhodium(III) cation is unknown, though Klixbull-Jorgensen estimated\textsuperscript{27} that the \( ^{1}T_{1g} \leftarrow ^{1}A_{1g} \) transition would occur at 30,000 cm\(^{-1}\). In the course of this work, no evidence for either this or a pentapyridinerhodium(III) was obtained. The highest stable species is trans-dichlorotetrapyridinerhodium(III) cation; when treated with excess of pyridine (aqueous; anhydrous; refluxing; or in a sealed tube at 150°C) this ion, as its chloride salt, slowly loses pyridine, forming 1,2,6-trichlorotripyridinerhodium(III). Indeed, even under the most forcing conditions used, the reactions of rhodium trichloride, or of a mixture of 1,2,3- and 1,2,6-trichlorotripyridinerhodium(III), or of trans-dichlorotetrapyridinerhodium(III) chloride, with excess of dry pyridine in a Carius tube at 150-180°C for up to 8 days, gave only 1,2,6-trichlorotripyridinerhodium(III).
No evidence was obtained for the formation of hexapyridinerhodium(III) or pentapyridinerhodium(III) species; catalysis by hypophosphorous acid or ethanol was unsuccessful. Dichlorotetrapyridinerhodium(III) nitrate was recovered unchanged after refluxing with excess of pyridine for 12 hours. Dichlorotetrapyridinerhodium(III) chloride was treated under reflux with aqueous silver nitrate. All the chlorine was thus slowly removed, but the resultant aqueous solution, presumably of trans-bisaquotetrapyridinerhodium(III) nitrate, showed no change of absorption spectrum after refluxing with excess of pyridine for four days. When the reaction mixture was heated with hydrochloric acid, trans-dichlorotetrapyridinerhodium(III) cation was regenerated. Finally chloropentamminerhodium(III) chloride may be recrystallized from boiling pyridine; this result was not unexpected since the observation\textsuperscript{28} that ammonia readily displaces pyridine from dichlorotetrapyridinerhodium(III) chloride was also confirmed. It seems possible that some kind of steric hindrance operates to prevent hexaco-ordination of rhodium(III) by pyridine. The most stable species in the reaction of rhodium tribromide or of trans-dibromotetrapyridinetribromomesitylenehexaamine complex with excess pyridine was found to be 1,2,6-tribromotripyridinerhodium(III).

Foulenc\textsuperscript{29} reported that, when an ethanolic solution of trans-dichlorotetrapyridinerhodium(III) chloride (A) is heated, 1,2,6-trichlorotripyridinerhodium(III) (B) is formed. This was confirmed, and it was also found that heating the hexahydrate of (A)
in vacuo at 75°C gives the anhydrous compound, which subsequently loses pyridine when the temperature reaches 105°C, forming (B). The non-electrolyte B may be separated from the salt A by virtue of its solubility in dichloromethane or chloroform, with both of which it forms red solvates. Poulenc also claimed that the action of sunlight on trans-dichlorotetrapyridinerhodium(III) chloride gave 1,2,3-trichlorotripyridinerhodium(III), but this was not confirmed.

The reaction of aqueous rhodium trichloride with pyridine has been examined several times previously. The principal features, with which the present work agrees, are (i) that the initial precipitate is a mixture (X) of 1,2,3- and 1,2,6-trichlorotripyridinerhodium(III), and (ii) that the yellow filtrate from (X) gives crystals of (A). In one case, it was reported that after removing these crystals the filtrate (containing excess pyridine) was refluxed, when unidentified orange crystals were formed. These orange crystals have been obtained in exactly this way, and shown to be pure 1,2,6-trichlorotripyridinerhodium(III). The analytical value for rhodium (25.4%) was rather high [B requires Rh, 23.04%]. This unexpected formation of a tripyridine-species from the tetrapyridine-species with excess pyridine agrees with the preparative results above.

In both literature accounts of the attempted separation of isomers in (X), a pink residue is mentioned, which apparently remains after extraction of (X) with ethanolic chloroform. The residue was not characterised in one case, and was formulated as
[Rhpy₂(H₂O)(OH)Cl₂] in the other, a band due to OH stretching being observed in the infra-red spectrum. This rose-pink compound may be obtained from 1,2,6-trichlorotripyridinerhodium(III), B, by several routes:

(i) heating in vacuo;
(ii) refluxing with chloroform;
(iii) exposing a solution of B in rigorously dried dichloromethane, in a closed container, to light for some days.

The third process was studied spectrophotometrically; the concentration of (B), measured by its lowest energy absorption band at 425 μm, had fallen to half its initial value after one week. The absorption profile from 300 μm to higher wavelengths remained unchanged during this process; it was clear that the only species present which contained rhodium were the original trichloro-isomer (B) and the insoluble pink polymer. After a few days, free pyridine could be detected in the solution. This photochemical reaction is most likely a charge-transfer process, involving the so-called "pyridine bands" at about 280 μm, due probably to a delocalisation of an electron from the (t₂g)⁶ shell of the rhodium atom to a modified antibonding orbital of pyridine. It is obvious that the pink polymer, reported as a preparative by-product, is actually an artefact of the method (involving boiling chloroform) used for working up the mixture (X) of 1,2,3- and 1,2,6-trichlorotripyridinerhodium(III).
Infra-red and electronic (reflectance) spectra of the pink products (P) obtained in this work are identical. No bands due to water or hydroxyl occur in the infra-red spectrum. A pink compound is formed when $[\text{Rhpy}_2\text{Cl}_3(\text{H}_2\text{O})]$ is heated; this pink polymer has properties identical with those of P. Analytical data for this pink compound, formulated $[\text{Rhpy}_2\text{Cl}_3]_n$, are given in Table 8. The reaction scheme 1 given below accounts for the formula, the formation from $1,2,6-[\text{Rhpy}_3\text{Cl}_3]$ by loss of pyridine, or from $1,2,4$-trichloro-3,5-dipyridine-6-aquorhodium(III) by loss of water, and the reformation of $1,2,6-[\text{Rhpy}_3\text{Cl}_3]$ by refluxing the pink polymer with pyridine. The rhodium atoms in (P) have the environment 2,3,4,5-tetrachloro-1,6-dipyridine, as shown (Table 9) by the electronic spectrum, which is very similar to that of $\text{trans-}[\text{Rhpy}_2\text{Cl}_4]^-$. Schmidtke$^{32}$ formulated the pink residue from treating (X) with chloroform (just the conditions which give $[\text{Rhpy}_2\text{Cl}_3]_n$) as $[\text{Rhpy}_2\text{Cl}_2(\text{H}_2\text{O})(\text{OH})]$, and reported that it dissolved in dimethylsulphoxide, being reprecipitated by water. In fact, a dispersion is formed in dimethylsulphoxide, which deposits the pink compound unchanged when water is added. If the dispersion is heated, a true solution results, but the pink polymer is disrupted. The yellow solution shows an electronic spectrum ($\lambda_{\text{max}}$ 430 m$\mu$) rather similar to that of $\text{trans-}[\text{Rhpy}_2\text{Cl}_4(\text{H}_2\text{O})]$ in dimethylsulphoxide ($\lambda_{\text{max}}$ 420 m$\mu$); presumably, a chlorine bridge is broken by the polar solvent. Although pyridine also ruptures a chlorine bridge, giving 1,2,6-trichlore-
### TABLE 8

Analytical data for the pink polymeric $\text{[Rhpy}_2\text{Cl}_3\text{]}_n$  

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Required</th>
<th></th>
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<th></th>
<th>Found</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>Cl</td>
<td>N</td>
<td>O</td>
<td>Rh</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>$\text{[Rh}_2\text{py}_4\text{(H}_2\text{O)}\text{Cl}_6\text{]}^{83}$</td>
<td></td>
<td>31.9</td>
<td>2.95</td>
<td>28.25</td>
<td>7.4</td>
<td>2.1</td>
<td>27.3</td>
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</tr>
<tr>
<td>$\text{[Rhpy}_2\text{Cl}_3\text{(H}_2\text{O)}\text{Cl}_2\text{]}^{32}$</td>
<td></td>
<td>32.7</td>
<td>3.5</td>
<td>19.3</td>
<td>7.6</td>
<td>8.7</td>
<td>28.0</td>
<td>34.0</td>
<td>3.1</td>
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</tr>
<tr>
<td>$\text{[Rhpy}_2\text{Cl}_3\text{]}_n^a$</td>
<td></td>
<td>32.7</td>
<td>2.7</td>
<td>28.9</td>
<td>7.6</td>
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<td>32.9</td>
<td>3.0</td>
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</tbody>
</table>

a. This work; full analytical results on four preparations are given in the Experimental section.  
b. Delépine$^{85}$ pointed out that this analysis of the final product of heating $\text{[Rhpy}_2\text{Cl}_3\text{(H}_2\text{O)}\text{]}$ indicated $\text{Rhpy}_2\text{Cl}_3$.  
c. Based on combustion residue.
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_1$</th>
<th>$\epsilon_1$</th>
<th>$\lambda_2$</th>
<th>$\epsilon_2$</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-$[\text{Rhpy}_4\text{Cl}_2]^+$</td>
<td>411</td>
<td>80</td>
<td>305sh</td>
<td>200</td>
<td>ethanol</td>
</tr>
<tr>
<td>1,2,3-$[\text{Rhpy}_3\text{Cl}_3]^+$</td>
<td>407</td>
<td>140</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1,2,6-$[\text{Rhpy}_3\text{Cl}_3]^+$</td>
<td>425</td>
<td>81</td>
<td>368sh</td>
<td>-</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>&quot;</td>
<td>438</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>reflectance</td>
</tr>
<tr>
<td>$[\text{Rhpy}_2\text{Cl}_3]_n$</td>
<td>518</td>
<td>c</td>
<td>451</td>
<td>c</td>
<td>reflectance</td>
</tr>
<tr>
<td>trans-$[\text{Rhpy}_2\text{Cl}_4]^-$</td>
<td>500</td>
<td>40</td>
<td>432</td>
<td>90</td>
<td>water</td>
</tr>
<tr>
<td>cis-$[\text{Rhpy}_2\text{Cl}_4]^-$</td>
<td>448</td>
<td>91</td>
<td>348</td>
<td>118</td>
<td>water</td>
</tr>
</tbody>
</table>

a. Ref. 33 gives: $\lambda$, 411, $\epsilon$, 70.

b. Ref. 33 gives $\lambda$, 422, $\epsilon$, 76; ref. 32 gives $\lambda$, 428, $\epsilon$, 72.

c. $\epsilon_2$ is certainly greater than $\epsilon_1$. 

TABLE 9

Electronic spectra of chloropyridinerhodium(III) complexes
($\lambda$ in m\u)
tripyridinerhodium(III), triphenylphosphine, either molten or in ethanol, is without action on the pink polymer.

A second so-called "pink" by-product which is occasionally found\textsuperscript{31} in the preparation of chloropyridinerhodium(III) complexes is actually yellowish-pink. Its properties agree exactly with those of the salt \textit{trans}-dichlorotetrapyridinerhodium(III) \textit{trans}-tetrachlorodipyridinerhodate(II), originally characterised by Delépine.\textsuperscript{30} This salt has $\lambda_{\text{max}}$ 500, 432 and 411 \textmu m (E 45, 90 and 102, respectively).

Reactions of rhodium trichloride with aqueous pyridine are summarized in Scheme 2, and the interconversions now known within the series of pyridine complexes in Scheme 3. Infra-red spectra are given in Table 10; the spectra of the trichloro-isomers were reported earlier,\textsuperscript{31} but those compounds were impure; their spectra are very much more distinct than appeared. The weak band reported\textsuperscript{31} at 720 cm\textsuperscript{-1} for rhodium trichloride (of unspecified provenance) was probably due to the Nujol used as mulling agent.
Scheme 1  Formation and reactions of the pink polymer.

Scheme 2  Reactions of rhodium(III) chloride hydrate with aqueous pyridine.

Scheme 3  Interconversions of pyridine complexes of rhodium(III).
### TABLE 10

**Infrared spectra of chloropyridinerhodium(III) complexes**

(frequencies in cm⁻¹)

<table>
<thead>
<tr>
<th><strong>1,2,3-[Rhpy₃Cl₃]</strong></th>
<th><strong>1,2,6-[Rhpy₃Cl₃]</strong></th>
<th><strong>1,6-[Rhpy₂Cl₂]Cl</strong></th>
<th><strong>[Rhpy₂Cl₃]ₙ</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1604s</td>
<td>1610m</td>
<td>1609s</td>
<td>1607m</td>
</tr>
<tr>
<td>1481w</td>
<td>1485w</td>
<td>1485w</td>
<td>1486w</td>
</tr>
<tr>
<td>1472w</td>
<td>1478w</td>
<td>1480sh</td>
<td>1479w</td>
</tr>
<tr>
<td>1446s</td>
<td>1450s</td>
<td>1450s</td>
<td>1449s</td>
</tr>
<tr>
<td></td>
<td>1340w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1231w</td>
<td>1235m</td>
<td>1242w</td>
<td>1240w</td>
</tr>
<tr>
<td>1205s</td>
<td>1212vs</td>
<td>1208s</td>
<td>1206s</td>
</tr>
<tr>
<td>1150w</td>
<td>1153m</td>
<td>1149s</td>
<td>1149m</td>
</tr>
<tr>
<td></td>
<td>1679sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1062s</td>
<td>1071s, 1067s</td>
<td>1062s</td>
<td>1067s</td>
</tr>
<tr>
<td>1009m</td>
<td>1016w</td>
<td>1014m</td>
<td>1017m</td>
</tr>
<tr>
<td></td>
<td>781m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>760s</td>
<td>762s</td>
<td>764sh</td>
<td></td>
</tr>
<tr>
<td>752sh</td>
<td>754m</td>
<td>760s</td>
<td>758s</td>
</tr>
<tr>
<td></td>
<td>699sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>692s</td>
<td>692s</td>
<td>689s</td>
<td>689s</td>
</tr>
<tr>
<td>684w</td>
<td>686s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The hexahydrate has extra bands at 3300 vbd, s, 2700w, sp, 1641m, bd, 980w, bd, and 869w, bd cm⁻¹.
Hypophosphorous acid and pyridine solutions of rhodium trihalides

The action of reducing agents on rhodium(III) compounds in the presence of pyridine was studied\textsuperscript{34} twenty years ago, before the recognition of the possibility of the formation of metal-hydrogen bonds in reductions. Several pyridine complexes were isolated, which, naturally enough, were thought to contain rhodium(II). Although, in a few cases, hydrido-complexes are involved, the most usual action of reducing agents on systems containing rhodium(III) and pyridine is to catalyse the formation of rhodium(III) complexes, through labile hydridic intermediates. All the compounds which had been thought to contain rhodium(II) in fact involve rhodium(III). Some of these complexes of rhodium(III) had actually been characterised previously by Poulenc,\textsuperscript{29} who noted the catalytic effect of alcohol in the formation of complexes of rhodium(III). Similar catalytic effects have also been noted recently\textsuperscript{35} in the formation of malonato- and diethylidithiocarbamato-complexes of rhodium(III).

It was assumed in the early work\textsuperscript{34} that the solutions of rhodium(III) chloride or bromide in aqueous pyridine, after heating, contained the hexakispyridinerhodium(III) cation. This is not so; as shown earlier, such solutions contain 1,2,6-trihalotripyridinerhodium(III). When hypophosphorous acid was added to such solutions of rhodium trichloride containing excess pyridine, yellow crystals of reported stoichiometry $[\text{Rhpy}_6]X_2$ ($X = \text{Cl}$ or $\text{Br}$) were obtained.
"Oxidation" (that is, crystallization of the "reduced" species in air) gave $\text{trans-}[\text{Rhpy}_4X_2]X_5\text{H}_2\text{O}$. Accepting the original formula, it was thought that the yellow crystals were probably hydridic, readily oxidized to the rhodium(III) compound.

It was next found that the yellow crystals are diamagnetic, the solutions showing no high-field line, and crystallization in the absence of air still gave the dichlorotetrapyridinerhodium(III) salt. It became clear that the action of hypophosphorous acid on 1,2,6-trichlorotripyridinerhodium(III) in presence of excess pyridine is merely to catalyse the formation of the $\text{trans-}[\text{Rhpy}_4\text{Cl}_2]^+$ ion; the original yellow "hexakispyridinerhodium(II) chloride is identified as $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}.5\text{H}_2\text{O}$. The corresponding system involving bromide is exactly analogous, and the "rhodous" compound $[\text{Rhpy}_6]\text{Br}_2$ is actually $\text{trans-}[\text{Rhpy}_4\text{Br}_2]\text{Br}$.

In the early work, the reaction products of $[\text{Rhpy}_6]\text{Br}_2$ with hydrobromic acid were studied in detail. $[\text{Rhpy}_6]\text{Br}_2$ with hydrobromic acid gave "golden yellow flat plates" which have been shown to be $\text{trans-}[\text{Rhpy}_4\text{Br}_2]\text{Br}.\text{HBr}.2\text{H}_2\text{O}$, analogous to the well known chloride, and containing the ion $<\text{H}_2\text{O}_2>^+$; the water washing of these crystals removes the acid addend, so that the final product $[\text{Rhpy}_5\text{Br}]\text{Br}$ is actually $\text{trans-}[\text{Rhpy}_4\text{Br}_2]\text{Br}$. Potassium iodide when added to an aqueous solution of $[\text{Rhpy}_5\text{Br}]\text{Br}$ gives a precipitate which is not $[\text{Rhpy}_5\text{Br}]\text{I}$, as originally thought, but $\text{trans-}[\text{Rhpy}_4\text{Br}_2]\text{I}$, first
described by Jorgensen. Similarly, 

\[[\text{Rhyp}_5\text{Br}]\text{Br}\] when refluxed with 2N hydrobromic acid gave a yellow solution from which 1,2,6-tribromotripyridinerhodium(III) may be isolated; on boiling for a longer period, a pale buff precipitate, originally formulated "\text{Rhyp}_4\text{Br}_2" appeared, which is in fact the salt \text{trans-[Rhyp}_4\text{Br}_2\text{]}\text{trans[Rhyp}_2\text{Br}_4\text{]}\text{,}

originally described by Poulenc.\text{\textsuperscript{29}} It is obvious that the reactions of 

\[[\text{Rhyp}_6]\text{Br}_2\] with hydrobromic acid described in the early work simply involve the successive removal of coordinated pyridine. The processes involved had been correctly described by Poulenc.

Reactions in the chloro-series are analogous; a summary of the original and revised formulations of the various compounds is given in Table 11. It is perhaps noteworthy that the original analyses for rhodium agree with both the original and revised formulae, because the molecular weights of bromine and pyridine are approximately equal. The compounds in Table 11 show no reducing properties except that those involving \text{[Rhyp}_4\text{X}_2\text{]}\text{+} slowly "reduce" alcoholic silver nitrate, as previously\text{\textsuperscript{34}} reported; this may be put down to the formation, by the alcohol, of transient hydridic species, which then interact with the silver ion. Substances described in the early work but not given here are "\text{[Rhyp}_3\text{Br}_2\text{]}_2\text{" and "(pyH)}_2\text{[Rh}_2\text{py}_4\text{Br}_6\text{]" which were very likely mixtures.}
### TABLE 11

Reformulation of "rhodous" complexes with pyridine

<table>
<thead>
<tr>
<th>Original (a)</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rhpy₆]Br₃; orange</td>
<td>1,2,6-Rhpy₃Br₃</td>
</tr>
<tr>
<td>[Rhpy₆]X₂; yellow</td>
<td>1,6-[Rhpy₄Cl₂]Cl₄·5H₂O</td>
</tr>
<tr>
<td></td>
<td>1,6-[Rhpy₄Br₂]Br</td>
</tr>
<tr>
<td>[Rhpy₅]X; yellow</td>
<td>1,6-<a href="H%E2%82%82O%E2%82%82">Rhpy₄Cl₂</a>Cl₂</td>
</tr>
<tr>
<td></td>
<td>1,6-[Rhpy₄Br₂]Br</td>
</tr>
<tr>
<td>[Rhpy₅Br]; yellow</td>
<td>1,6-[Rhpy₄Br₂]I</td>
</tr>
<tr>
<td>Rhpy₄Br₂; pink-yellow</td>
<td>1,6-[Rhpy₄Br₂] 1,6-[Rhpy₂Br₄]</td>
</tr>
<tr>
<td>(pyH)₂[Rh₂py₂Cl₆]; pink-yellow</td>
<td>1,6-[Rhpy₄Cl₂] 1,6-[Rhpy₂Cl₄]</td>
</tr>
<tr>
<td>(pyH)₄[Rh₂py₂X₄]; orange-red</td>
<td>(pyH)₁,₆-[Rhpy₂X₄]  (X = Cl, Br)</td>
</tr>
</tbody>
</table>

(a) Ref. 34.
Hydridorhodium(III) complexes

Cold aqueous solutions of trans-dichlorotetrapyridinerhodium(III) cation or of its bromo-analogue react with borohydride ion or with hypophosphorous acid forming hydridic complexes. The yellow solution of the dihalogeno-complex first becomes pale brown, and a high field proton resonance line at \( \tau \sim 28.5 \) was observed in all four cases. The brown solution from the bromo-compound gave crystals which showed a strong band at 2000 cm\(^{-1}\), arising from the Rh-H stretching mode. The brown solutions with excess pyridine and reducing agent became colourless on boiling; these colourless solutions again show a high-field line at \( \tau \) ca. 29; no solid complexes have been isolated in the chloro- or bromo-cases, except that in one case, when a brown solution of [Rhpy\(_4\)Br\(_2\)]Br in aqueous pyridine containing borohydride was allowed to stand under \( \text{N}_2 \) overnight, pale brown acicular crystals which analysed reasonably for [Rhpy\(_5\)H]Br\(_2\) were obtained. However, when the iodide system was used, extremely air-sensitive crystals of "hexakis-pyridinerhodium(II) iodide", which is nearly white, may be obtained. These show a strong band at 1980 cm\(^{-1}\), and a band at 822 cm\(^{-1}\), owing to the Rh-H stretch and bend respectively. The results may be explained by:

\[
[Rhpy_4X_2]^+ + H^- \rightarrow [Rhpy_4HCl]^+ \rightarrow [Rhpy_5H]^2^+
\]

yellow \hspace{1cm} brown \hspace{1cm} almost colourless

The formulation of the brown species as tetrapyridine complexes is supported by the observations that:
(i) yellow \([\text{Rhy}_4\text{Br}_2]\)Br crystallized from a brown solution containing excess bromide;

(ii) the brown solutions treated with carbon tetrachloride gave the \([\text{Rhy}_4\text{Cl}_2]^+\) ion;

(iii) the formation of the brown monohydridic species from the yellow dihalo-species was characterised by an isosbestic point;

(iv) the electronic spectra of the monohydridic species are exactly what one would predict, as shown in Table 12.

**TABLE 12**

<table>
<thead>
<tr>
<th>Formula</th>
<th>(\lambda_{\text{max}})</th>
<th>(\lambda)</th>
<th>(\varepsilon)</th>
<th>(\gamma)</th>
<th>(\nu_{\text{Rh-H}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rhy}_4\text{Cl}_2]^+)</td>
<td>410</td>
<td>355</td>
<td>120</td>
<td>28.5</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Rhy}_4\text{Br}_2]^+)</td>
<td>432, 353</td>
<td>365</td>
<td>160</td>
<td>28.5</td>
<td>1976</td>
</tr>
</tbody>
</table>

*Isosbestic points for the conversion process.*

There appears to be an alternative reaction of the monohydride, when no excess pyridine is present:

\[
\text{trans-[Rhy}_4\text{HCl}]^+ \rightarrow [\text{Rhy}_4]^+ + \text{HCl}
\]

The final product, containing rhodium(I), is diamagnetic and very dark brown; for \(\text{trans-[Rhy}_4\text{Cl}_2]^+\), on treating with borohydride,
the $d-d$ bands of the dihalo-compound and the monohydridic species derived from it are rapidly swamped by an intense broad featureless absorption rising into the ultraviolet. The brown tetrphenylborate which is precipitated from a dark-brown fully reduced solution of \([\text{Rhpy}_4\text{Br}_2]\text{Br}\) by the addition of sodium tetrphenylborate contains no bromine.

The system involving iodine as the halogen has also been studied; the only compound isolated other than the unstable hydride mentioned above is brown, water-insoluble tri-iodotripyridinerhodium(III), which forms by loss of pyridine from the first product of the reaction of rhodium(III) iodide with pyridine and catalytic amounts of hypophosphorous acid. This initial product, which forms brown-yellow crystals, is most likely trans-di-iodotetrapyridinerhodium(III) iodide, but loses pyridine extremely readily, being stable only in the presence of excess pyridine.

**A reaction with cyanide ion**

In view of the high degree of nucleophilic character evinced by the cyanide ion, the reactions of a number of halo-complexes of rhodium(III) with cyanide ion were studied. While, from electronic spectral studies, it was clear that such compounds as trans-dichloro-bisethylenediaminerhodium(III) chloride indeed reacted fairly rapidly with cyanide ion, a solid "mixed" cyanide complex was isolated only
from the reaction

\[ \text{trans-}[\text{Rhpy}_4\text{Cl}_2]\text{Cl} + 2\text{CN}^- + 2\text{H}_2\text{O} \rightarrow \text{Rhpy}_2(\text{CN})_2\text{Cl}_2\text{.H}_2\text{O} + 2\text{Cl}^- \]

The stoichiometry given is confirmed by analysis, but the pale yellow compound is probably polymeric, being insoluble in all solvents tried. Also, its infrared spectrum shows bands characteristic of both terminal (2150 cm\(^{-1}\)) and bridging (2201 cm\(^{-1}\)) cyanide groups. Since the first cyanide group to displace a pyridine molecule will lead to the subsequent replacement of the trans-pyridine molecule, the repeat unit is quite possibly

\[ \begin{array}{c}
\text{CN}^- \\
\hline
\text{Py} \\
\hline
\text{Cl} \\
\hline
\text{Py} \\
\hline
\text{CN}
\end{array} \] \hspace{1cm} \text{CN}^- \\
\hline
\text{Py} \\
\hline
\text{Cl} \\
\hline
\text{Py} \\
\hline
\text{CN}

This is the first "mixed" cyanide complex of rhodium(III). Reactions of cyanide ion with other complexes of rhodium(III) have either given the hexacyanorhodate(III) ion, as with rhodium(III) ammines, or have been unsuccessful, as with the ethylenediamine complexes.

\[ \text{trans-Dichlorotetrapyridinerhodium(III) chloride is a reactive compound; its reaction}^{36} \text{ with oxalate ion,} \]

\[ [\text{Rhpy}_4\text{Cl}_2]\text{Cl} + \text{ox}^{2-} \rightarrow [\text{Rhpy}_3\text{oxCl}] + 2\text{Cl}^- + \text{py}, \]
has been confirmed. The product is unfortunately too insoluble in all solvents tried for electronic spectral work. The reaction of trans-[Rhpy₄Cl₂]Cl with ethylenediamine, described by Meyer and Kienity²¹ as forming chloropyridine bisethylenediaminerhodium(III) chloride, in fact gives rise to a colourless compound with $\lambda_{\text{max}}$ 299 and 254 μm, which is actually trisethylenediaminerhodium(III) chloride dihydrate.
CHAPTER III

Studies on Cobalt(III) and related Rhodium(III) Complexes

In every case where a hydridic species is formed by a rhodium(III) complex, the analogous complex of cobalt(III) has been examined. In no case has evidence for a cobalt-hydrogen bond been obtained, but several interesting observations have been made. The most common pattern of behaviour when a cobalt(III) species is treated with a hydridic reagent is formation of cobalt(II), which with further hydride forms cobalt metal. In some cases, the intermediate cobalt(II) compound was not observed.

**trans-cis Isomerisation of [Coen₂Cl₂]^+.**

Green trans-dichlorobisethylenediaminecobalt(III) chloride, in excess, when treated carefully with borohydride ion in ice-cold aqueous solution formed the purple cis-isomer very rapidly; even at -30°C in aqueous methanol, no evidence for a hydridic species was obtained. When sodium tetraphenylborate was added to the purple "reduced" solution, any unchanged trans-isomer was precipitated as its pale green tetraphenylborate. cis-Dichlorobisethylenediaminecobalt(III) cation could be recovered from the purple mother liquor. This difference in solubilities of the tetraphenylborates of cis- and trans-isomers is due presumably to a difference in lattice energies, though the expected
higher energy of solvation of the \textit{cis}-cation might also play a part.

The difference is by no means a general phenomenon; the solubilities of the tetraphenylborates of the \textit{cis}- and \textit{trans}-isomers of dichlorobisethylenediaminerrhodium(III) are similar, as are those of the salts of the isomers of dinitrobisethylenediaminecobalt(III). \textit{cis}-Dichlorotriethylenetetraminecobalt(III) tetraphenylborate is slightly soluble in water; the \textit{trans}-isomer is instantly isomerised by water. Tetraphenylborate salts of the monopositive cations \textit{trans}-dichlorotetramminecobalt(III) and bisdimethylglyoximato- bisamminecobalt(III) and of their rhodium(III) analogues are all very insoluble in water.

The mechanism of this catalysis by hydride ion of \textit{trans}-\textit{cis} isomerisation is obscure. Hypophosphorous acid at 65°C is also effective, but solutions of chromous compounds have no apparent effect on the green solution of \textit{trans}-dichlorobisethylenediaminecobalt(III) chloride. Radiochemical exchange experiments with $^{36}$Cl reveal that only one of the coordinated chloride ions in the \textit{trans}-dichloro-cation is involved in the reaction. After the isomerisation had occurred, and the complex ion had been removed, the supernatant liquid contained 60% of the initial activity; the displacement of one chloride would require 59.3%. If no chloride were displaced, 33% only of the initial activity should be in the supernatant liquid; if both, 81%. The scheme may be represented

\[
\text{trans-}[\text{Coen}_2\text{Cl}_2]^+ + H^- \rightarrow \text{cis-}[\text{Coen}_2\text{ClH}]^+ + \text{ox} + \text{Cl}^- \]

\[
\downarrow
\]

\[
\text{cis-}[\text{Coen}_2\text{Cl}_2]^+
\]
The reaction occurs with equal facility under nitrogen, so that "ox" represents a general oxidant. The intermediate hydride is assigned cis-stereochemistry, since if a chloride were trans to the hydride, it would be displaced very readily; in that case, both co-ordinated chloride ions would participate in the radiochemical exchange, and this is not observed.

When a solution containing the trans-chlorohydridobisethylenediamine-rhodium(III) cation is allowed to oxidise in the presence of chloride ion, the product is the cis-dichlorobisethylenediaminerhodium(III) cation, as shown by the electronic spectrum.

Adducts of protonic acids with complexes

trans-Dichlorobisethylenediaminecobalt(III) chloride forms\(^3^7\) mica-like plates of the formula trans-[Coen\(_2\)Cl\(_2\)]Cl.HCl.2H\(_2\)O, which are discussed below. One report\(^3^8\) mentions that the cation forms certain other "adducts", some of which were alleged to contain protonic acids and water of crystallization. The infrared spectrum of trans-dichlorobisethylenediaminecobalt(III) hydrogen oxalate dihydrate shows no bands characteristic of the hydroxonium ion; the best formulation is trans-[Coen\(_2\)Cl\(_2\)](HCO\(_2\)O\(_2\))\(_2\)H\(_2\)O. Oxalic acid dihydrate itself was shown\(^3^9\) by solid-state proton magnetic resonance not to involve hydroxonium ions. Price and Brazier\(^3^8\) also described the compound [Coen\(_2\)Cl\(_2\)][CH\(_2\)(COO)(CO\(_2\)H)] [CH\(_2\)(CO\(_2\)H)\(_2\)],2H\(_2\)O as dark green crystals made by mixing aqueous solutions of malonic acid and the complex chloride. The infra-red spectrum of
this compound is quite individual, indicating the presence of non-hydrogen bonded OH \((3500 \text{ cm}^{-1})\), non-hydrogen bonded \(-\text{NH}_2 \ (3328 + 3250 \text{ cm}^{-1})\) as in \text{trans-}[\text{Coen}_2\text{Cl}_2]\text{Cl}\), unusually strong unsymmetrical hydrogen bonds \(\text{broad absorption at 2480 and 1940 cm}^{-1}\) and symmetrical hydrogen bonding, indicated by a very broad strong absorption from \(1400 \text{ cm}^{-1}\) to lower frequencies, centred around \(750 \text{ cm}^{-1}\), with obvious "absorption windows" at \(1100 \text{ cm}^{-1}\) \(\text{due to an intense absorption of the cation}\) and at \(940 \text{ cm}^{-1}\) \(\text{due to absorption in the malonate residue}\). Carboxylate absorption occurs at \(1700 \text{ cm}^{-1}\) only, indicating that all the carboxylate groups are involved in hydrogen bonding. Similar compounds of other \text{trans-}dichlorotetraminecobalt(III) salts could not be made.

Several other adducts reported by Price and Brazier were not confirmed; another compound from the malonic acid system, said to be possibly \text{trans-}[\text{Coen}_2\text{Cl}_2]\text{Cl,CH}_2(\text{CO}_2\text{H})_2,H_2\text{O}\), has an infra-red spectrum which is a superposition of those of malonic acid and the complex chloride; no water is present, and the composition is variable; the alleged adduct is probably a mixture. The compound said to be \text{trans-}[\text{Coen}_2\text{Cl}_2](\text{CH}_2\text{Cl}.\text{COO})(\text{CH}_2\text{Cl}.\text{CO}_2\text{H})\) was prepared and found to be simply the chloracetate salt, \text{trans-}[\text{Coen}_2\text{Cl}_2][\text{CH}_2\text{Cl}.\text{COO}].

Salts of the type \text{trans-}dihalogenotetramminemetal(III) halide, where the metal is chromium, cobalt or rhodium, and the halogen is chlorine or bromine, are well known to form adducts with hydrogen halides and water, with the formulae \([\text{MA}_4X_2]X,HX,2\text{H}_2\text{O} \ (M = \text{Cr, Co or Rh} \)
A = \frac{1}{2}en, \frac{1}{2}pn, or py; X = Cl or Br. The sole disagreement with this formula was on the basis of a thermogravimetric study, when the hydrogen chloride adduct of trans-[Coen\textsubscript{2}Cl\textsubscript{2}]Cl was formulated\textsuperscript{40} as a hexahydrate. Extensive analyses in this and previous work,\textsuperscript{37,41,42} with the X-ray molecular weight,\textsuperscript{43} leave no doubt that the formulation as a dihydrate is correct.

There is a marked discrepancy between the infra-red results\textsuperscript{44} recorded for trans-dichlorobisethylenediaminecobalt(III) chloride hydrogen chloride dihydrate, [Coen\textsubscript{2}Cl\textsubscript{2}]Cl,HCl,2H\textsubscript{2}O and the earlier X-ray data\textsuperscript{43} for the same compound. The infra-red spectrum was claimed\textsuperscript{44} to show the presence of hydroxonium ions, while the X-ray results\textsuperscript{43} showed the presence of isolated pairs of oxygen atoms, with 0-0 = 2.66 \text{\AA}. Infra-red\textsuperscript{44} and X-ray studies\textsuperscript{45} of the analogous bromo-compound (0-0 = 2.60 \text{\AA}) also led to differing conclusions. The protons were not located in the X-ray work, but it was tentatively suggested that [H\textsubscript{5}O\textsubscript{2}]\textsuperscript{+} ions were present. This may be called the bisaquo-hydrogen ion.

The infra-red spectra of nine compounds of the type [MA\textsubscript{2}X\textsubscript{2}]X,X,HX,2H\textsubscript{2}O, including three new compounds of rhodium(III), have been measured. In the regions due to the added "HX,2H\textsubscript{2}O", all the spectra are very similar; in no case is absorption observed characteristic of molecular hydrogen halide, or the HCl\textsubscript{2}  ion, or the [H\textsubscript{5}O]\textsuperscript{+} ion; most notably, for the last case, the \nu\textsubscript{2} vibration at 1050-1100 cm\textsuperscript{-1} is not observed. If the formulation\textsuperscript{44} [Coen\textsubscript{2}Cl\textsubscript{2}] (H\textsubscript{5}O)Cl\textsubscript{2},H\textsubscript{2}O held, bands due to the crystal water\textsuperscript{46} should appear.
No such bands are observed. For the diamine complexes, in the OH and NH stretching region, no absorption occurs in the adducts higher than the highest N–H stretching mode of the parent compounds; the H₂O deformation region is less clear for complexes containing diamines, since, as Curtis assumed to be true, the NH₂ deformation frequency would possibly overlap the OH₂ deformation. More conclusively, in the case of the dichlorotetrapyridinerhodium(III) cation, the highest absorption, which is notably sharp, is at 1608 cm⁻¹. One would expect to see clearly the deformation frequency of the "spare" crystal water in any molecule [Rhpy₄Cl₂](H₂O)Cl₂H₂O. The spectrum from 1600–1650 cm⁻¹ actually shows only one absorption at 1606 cm⁻¹, due to the pyridine vibration. Above 3000 cm⁻¹, the spectrum provides cogent evidence for the absence of crystal water, since no absorption at all can be seen above the 2910 cm⁻¹ band. Crystal water is not present. Therefore, the structural unit containing the proton is, in fact, the bisaquo-hydrogen ion, (H₂O₂)⁺, first postulated by Huggins as a component of acid solutions.

The infra-red spectrum of the (H₂O₂)⁺ ion, deduced from differences between spectra of adducts and parents shows four broad absorptions, at much lower frequencies than those observed for hydroxonium ions, except the ν₄ mode of (H₃O)⁺, which is comparable with band III of (H₂O₂)⁺. Results are collected in Table 13, from which it is obvious that the adducts contain no hydroxonium ions, and must be formulated trans-[MA₂X₂](H₂O₂)X₂. Typical spectra of (H₂O₂)⁺ and (H₃O)⁺ are shown in Figure 2.
### TABLE 13

Infra-red spectra of $\left(\text{H}_2\text{O}_2\right)^+$ (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound$^a$</th>
<th>Band I</th>
<th>Band II</th>
<th>Band III</th>
<th>Band IV$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Coen$_2$Cl$_2$</a>Cl$_2$</td>
<td>2850</td>
<td>2240</td>
<td>1670</td>
<td>950</td>
</tr>
<tr>
<td>2. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Coen$_2$Br$_2$</a>Br$_2$</td>
<td>2880</td>
<td>2240</td>
<td>1670</td>
<td>960</td>
</tr>
<tr>
<td>3. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Co($\mp$)pn$_2$Cl$_2$</a>Cl$_2$</td>
<td>2920</td>
<td>2230</td>
<td>1680</td>
<td>1000</td>
</tr>
<tr>
<td>4. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Co(-pn)$_2$Cl$_2$</a>Cl$_2$</td>
<td>2915</td>
<td>2230</td>
<td>1682</td>
<td>1002</td>
</tr>
<tr>
<td>5. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Rhen$_2$Cl$_2$</a>Cl$_2$</td>
<td>2810</td>
<td>2205</td>
<td>1684</td>
<td>950</td>
</tr>
<tr>
<td>6. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Rhen$_2$Br$_2$</a>Br$_2$</td>
<td>2830</td>
<td>2215</td>
<td>1680</td>
<td>960</td>
</tr>
<tr>
<td>7. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Rhpy$_4$Cl$_2$</a>Cl$_2$</td>
<td>2910</td>
<td>2210</td>
<td>1660</td>
<td>970</td>
</tr>
<tr>
<td>8. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Rhdipy$_2$Cl$_2$</a>Cl$_2$</td>
<td>2990</td>
<td>2215</td>
<td>1700</td>
<td>970</td>
</tr>
<tr>
<td>9. trans-<a href="$%5Ctext%7BH%7D_2%5Ctext%7BO%7D_2$">Cren$_2$Cl$_2$</a>Cl$_2$</td>
<td>2860</td>
<td>2255</td>
<td>1668</td>
<td>972</td>
</tr>
<tr>
<td>10. ($\text{H}_3\text{O}$)$^+$ $^c$</td>
<td>3380-3150</td>
<td>2650-2468</td>
<td>1705-1670</td>
<td>1150-1130, 1060-1048</td>
</tr>
</tbody>
</table>

$^a$ This column gives the formula of the adduct; the bands given are for trans-$\left[\text{MA}_4\text{X}_2\right]($H$_2$O$_2$)X$_2$-trans-$\left[\text{MA}_4\text{X}_2\right]$X = (H$_2$O$_2$)X.

$^b$ Band IV is extremely broad in all cases, e.g. for compound 1 it extends from 775 to 1400 cm$^{-1}$; however, the maximum intensity may be located to ± 10 cm$^{-1}$.

Infrared spectra of (H$_5$O$_2$)$_+$ and (H$_3$O)$_+$ ions.

Full curve, (H$_5$O$_2$)$_+$ in *trans*-Co$\text{en}_2\text{Cl}_2$(H$_5$O$_2$)Cl$_2$. Dotted curve, (H$_3$O)$_+$.
The new adducts, prepared by allowing the parent salt to crystallize slowly from the relevant acid, are trans-dichlorobis-ethylenediaminerhodium(III) bisaquohydrogen chloride, \( \text{trans-}[\text{Rhen}_2\text{Cl}_2] (\text{H}_2\text{O}_2)\text{Cl}_2 \), and its bromo-analogue, \( \text{trans-}[\text{Rhen}_2\text{Br}_2](\text{H}_2\text{O}_2)\text{Br}_2 \); this gives a novel proof of the trans-stereochemistry of these cations. 

\( \text{trans-Dichlorobisbipyridylrhodium(III) bisaquohydrogen chloride} \) has also been made; it is very similar to the known \( \text{trans-}[\text{Rhpy}_4\text{Cl}_2](\text{H}_2\text{O}_2)\text{Cl}_2 \). The bisbipyridyl complex had previously\(^4\) been assigned cis-stereochemistry on the unreliable basis of the splitting of the in-phase out-of-plane C-H vibrations in the infra-red spectrum. No cation with cis-stereochemistry is recorded as forming adducts with hydrogen halides, nor have any such adducts been prepared in this work from cis-species corresponding to the trans-isomers in Table 13.

Water appears to be essential for such hydrogen halide adducts to form; there are two reports of hydrogen halides forming anhydrous adducts with \( \text{trans-}[\text{MA}_4\text{X}_2]\text{X} \). Drew and Pratt\(^5\) claimed to have made \( \text{trans-}[\text{Coen}_2\text{Cl}_2]\text{Cl}.\text{HCl} \); the short, blocky crystals obtained by following their method are in fact \( \text{trans-}[\text{Coen}_2\text{Cl}_2]\text{Cl} \). In the preparation\(^6\) of \( \text{trans-dibromotriethylenetetraminecobalt(III) bromide} \), the isolation of an apparently anhydrous adduct with hydrogen chloride was reported. However, the very dark green product contains water, as shown by direct oxygen analysis, and absorption in the infra-red spectrum at 3550 cm\(^{-1}\), due to an O-H stretching mode; the product on close examination proved to be a mixture of colourless needles and nearly black plates.
Although the first reported case\textsuperscript{52} where the product of crystallization from hydrochloric acid differed from that in water was trans-dichlorotetramminecobalt(III) chloride, \(\text{trans-}[\text{Co(NH}_3)_4\text{Cl}_2]\text{Cl}\), and the "shiny grass-green crystals on washing with water become matted and leek green", exactly paralleling the behaviour of the adducts in Table 13, these shiny grass-green crystals have not yet been obtained in this work. Nor have those of the adduct of \(\text{trans-}[\text{Rh(NH}_3)_4\text{Cl}_2]\text{Cl}\) or \(\text{trans-}[\text{Cpy}_4\text{Cl}_2]\text{Cl}\). The formation of the so-called "chlorhydrates" appears\textsuperscript{53,54} to be quite general for \(\text{trans-}[\text{Co(diamine)}_2\text{Cl}_2]\text{Cl}\).

**Hydrogen bonding in complexes of dimethylglyoxime with cobalt(III)**

An absorption band in the infra-red occurring around 1750 cm\(^{-1}\) in several bisdimethylglyoximato-cobalt(III) compounds has been attributed to hydrogen bonding; it has been said\textsuperscript{55} that "the presence of the hydrogen bonding is a proof of the trans-character of the molecule". The literature shows a number of discrepancies. In a few cases, even though the characteristic hydrogen-bonded frequency was observed, \(\text{cis}\)-stereochemistry is postulated, and elsewhere the \(\text{cis}\)-configuration was deduced for the bis-dioximato-cobalt(III) moiety on the basis of dubious resolutions into optical isomers. Spectroscopic data have been extended and good evidence for the \(\text{trans}\)-configuration in all \(\text{bis}\)-dioximato-cobalt(III) compounds is presented.

The available infra-red spectral data for complexes of cobalt(III), including deuterated species, are collected in Table 14. \(\nu_{\text{O-H}}\) occurs
TABLE 14

Infra-red spectra of complexes of cobalt(III) with dimethylglyoxime
(frequencies in cm⁻¹)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu_0\text{-H str.} )</th>
<th>( \nu_0\text{-D str.} )</th>
<th>( 0\text{-H} \cdots 0 )</th>
<th>( 0\text{-D} \cdots 0 )^a</th>
<th>( \nu_{OH} ) def.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(DMG)}_2(\text{NO}_2)(\text{H}_2\text{O})])</td>
<td>3546^b</td>
<td>2530</td>
<td>1770</td>
<td>1783</td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>([\text{Co(DMG)}_2(\text{NO}_2)(\text{D}_2\text{O})])</td>
<td></td>
<td>2530</td>
<td>1700</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Co(DMGd)}_2(\text{NO}_2)(\text{D}_2\text{O})])</td>
<td></td>
<td>2530</td>
<td></td>
<td>ca. 1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;([\text{H[Co(DMG)}_2(\text{NO}_2)]_2])&quot;^c</td>
<td>3550</td>
<td>2350</td>
<td></td>
<td>1630</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Na[Co(DMG)}_2(\text{NO}_2)]_2, \text{H}_2\text{O})]</td>
<td>3540^b</td>
<td>1740</td>
<td></td>
<td>1631^b</td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>([\text{NH}_4[\text{Co(DMG)}_2(\text{NO}_2)]_2])</td>
<td>d</td>
<td></td>
<td>1701</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Co(DMG)}_2(\text{NH}_3)\text{Cl}])</td>
<td>3550, 3400</td>
<td>321^d, 310^d</td>
<td>1751</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Co(DMG)}_2\text{PyCl}])</td>
<td></td>
<td></td>
<td>1710</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Co(DMG)}_2(\text{NH}_3)_2]\text{Cl, 5H}_2\text{O})</td>
<td></td>
<td></td>
<td>1695</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{Co(DMG)}_2(\text{NH}_3)_2</a>)</td>
<td></td>
<td></td>
<td>1703</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;([\text{H[Co(DMG)}_2\text{Cl}_2])&quot;^c</td>
<td>3200</td>
<td></td>
<td>1725</td>
<td></td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>&quot;([\text{D[Co(DMGd)}_2\text{Cl}_2])&quot;^c</td>
<td></td>
<td>2300</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Co(DMG)}_2(\text{NH}_3)(\text{NO}_2)])</td>
<td></td>
<td></td>
<td>1766</td>
<td></td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>([\text{Co(DMG)}_2])</td>
<td></td>
<td>3000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. In the deuterated compounds, the band assigned to \( 0\text{-H} \cdots 0 \) disappears, but in no case was the \( 0\text{-D} \cdots 0 \) frequency located exactly because of the large number of absorptions in the 1200-1300 cm⁻¹ region.
b. Absorption due to co-ordinated or crystal water.
c. The formulation of these compounds is discussed in the text.
d. Absorption due to N-H stretching modes.
e. In dichloromethane.
f. In chloroform; the compound was recovered unchanged from both these solutions.
in dimethylglyoxime itself at 3170 cm$^{-1}$. DMGH represents dimethylglyoxime and DMG its anion.

The compound usually formulated "$\text{H}[\text{Co(DMG)}_2\text{Cl}_2]"$, which has been named \textsuperscript{56} "hydrogen dichlorobis(dimethylglyoximato)cobaltate(III)" , shows absorptions due to free OH stretching and deformation, as does "$\text{H}[\text{Co(DMG)}_2(\text{NO}_2)_2]"$. Since no water of crystallization is present, these compounds do not contain hydroxonium ions. The structure shown in Figure 3 is preferable, in the solid state at least. The

![](image)

\textbf{Figure 3 (X = Cl)}

\textbf{trans}-configuration is implicit in the hydrogen-bonded OH frequency in both the parent compounds, and the salts obtained from them by proton loss. The compounds are strong monobasic acids; the electronic spectra of their solutions are identical with those of the sodium salts, so that the species present in aqueous solution are presumably the symmetrical anions containing two similar hydrogen bonds.

The structure of bisamminebisdimethylglyoximato(cobalt(III)) nitrate is known \textsuperscript{57} from X-ray crystallography; O-H...O = 2.65 Å, and the typical $\nu_{0-H...O}$ occurs at 1703 cm$^{-1}$. The spectrum of the corres-
ponding chloride pentahydrate is rather complex, as is that of its rhodium(III) analogue. The band at 3100 cm\(^{-1}\) is due most likely to water of crystallization, but the peak at 2600 cm\(^{-1}\) and the broad bands at 2150, 1950, 1750 and 1690 cm\(^{-1}\) indicate the large number of possible hydrogen bonds in this compound in the solid state. The assignment\(^{55}\) of the band at 1690 cm\(^{-1}\) as the characteristic hydrogen-bonded frequency is rather arbitrary. The electronic spectra of the nitrate and the chloride are extremely similar, so that the \textit{trans}-configuration for the chloride is certain. The resolution allegedly obtained by means of optically active quartz\(^{58}\) is undoubtedly spurious; so is the peculiar resolution said to be achieved\(^{59}\) by making solutions of opposite quarters of the same crystal, when opposite rotations were allegedly observed.

The conclusions from infra-red spectra are reinforced by the novel observation that the intramolecular hydrogen bonds give rise to a broad line in the proton magnetic resonance spectrum around 1000 c./sec. on the low-field side of tetramethylsilane. The position of this line shows no dependence on concentration, confirming the assignment as due to a proton in an \textit{intramolecular} bond. Compounds showing such absorptions are collected in Table 15, with the result for potassium hydrogen phthalate for comparison.
### TABLE 15
Nuclear magnetic resonance evidence for intramolecular hydrogen bonds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(DMG)$_2$(NH$_3$)Cl]</td>
<td>DMSO$^a$</td>
<td>1043$^b$</td>
<td>-8.47</td>
</tr>
<tr>
<td>[Co(DMG)$_2$pyCl]</td>
<td>DMSO$^a$</td>
<td>1032</td>
<td>-8.28</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>1017</td>
<td>-8.01</td>
</tr>
<tr>
<td></td>
<td>DMF$^e$</td>
<td>1000$^d$</td>
<td>-</td>
</tr>
<tr>
<td>[Co(DMG)$_2$(NO$_2$)(H$_2$O)]</td>
<td>DMF$^o$</td>
<td>1042</td>
<td>-8.45</td>
</tr>
<tr>
<td>KH phthalate</td>
<td>DMSO$^a$</td>
<td>-</td>
<td>-10$^g$</td>
</tr>
</tbody>
</table>

a, Dimethylsulphoxide.  
b, In c./sec. below TMS.  
c, Dimethylformamide.  
d, Too dilute for accurate measurement.  
e, Forsen (J. Chem. Phys., 1959, 31, 852) measured this value relative to external water, together with that of the analogous maleate.

The resolution of chloro-ammine bisdimethylglyoximatocobalt(III) by differential absorption on optically-active quartz has been claimed, although its crystals show no enantiomorphic faces; cis-stereochemistry was postulated, on the grounds of the very slight optical activity of the fractions obtained. However, the infra-red spectrum shows the characteristic O-H...O absorption at 1750 cm$^{-1}$; this has been confirmed, and the n.m.r. absorption due to strong intramolecular hydrogen bonding is also observed. The compound is
thereby proved to be trans; the resolution claimed is spurious. The formulation of the compound is confirmed by analysis, by its diamagnetism, and by its non-conductance in water. The sole remaining possibility is that it exists as the trans-isomer in the organic solvents used here for n.m.r. work, but as the cis-isomer in the aqueous solution used for the work with active quartz. The electronic spectra, however, in water and dimethylsulphoxide are identical; the compound is trans-chloro-amminebisdimethylglyoximatocobalt(III).

Complexes of rhodium(III) with dimethylglyoxime

The best known complex is that formulated \(^{31,61,62}\) as "hydrogen dichlorobisdimethylglyoximatorhodate(III)". This formulation is undoubtedly correct in aqueous solution, as shown (Table 16) by the coincidence of the electronic spectra of the monobasic acid and its salts. However, the formulation is incorrect for the solid state, since an O-H stretching mode is apparent at 3400 cm\(^{-1}\). This was recorded \(^{31}\)

<table>
<thead>
<tr>
<th>TABLE 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic spectra of salts of the (\text{[Rh(DMG)\textsubscript{2}Cl\textsubscript{2}]^-}) anion</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\lambda)</th>
<th>(\varepsilon)</th>
<th>(\lambda)</th>
<th>(\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;(\text{H[Rh(DMG)\textsubscript{2}Cl\textsubscript{2}]})&quot;</td>
<td>H(_2)O</td>
<td>292</td>
<td>717</td>
<td>273</td>
<td>847</td>
</tr>
<tr>
<td>(\text{NH}_4\text{[Rh(DMG)\textsubscript{2}Cl\textsubscript{2}]})</td>
<td>H(_2)O</td>
<td>292</td>
<td>717</td>
<td>273</td>
<td>847</td>
</tr>
<tr>
<td>((\text{GH})\text{[Rh(DMG)\textsubscript{2}Cl\textsubscript{2}]})(^a)</td>
<td>H(_2)O</td>
<td>292</td>
<td>728</td>
<td>274</td>
<td>860</td>
</tr>
</tbody>
</table>

\(^{a}\), GH = guanidinium.
by Holtzclaw and Collman, but not discussed. It leads to the formulation of the compound in the solid state as "dichlorodimethylglyoximato(dimethylglyoxime)rhodium(III)", as in the analogous compound of cobalt(III). This formulation is confirmed by (a) the shift of $\nu_{OH}$ to 2400 cm$^{-1}$ on deuteration, giving $\nu_{OH}:\nu_{OD} = 1.38$, and (b) the disappearance of $\nu_{OH}$ on formation of the silver salt. The hydrogen-bonded O-H...O frequency has been located only in the original acid, and its silver salt; in a strong mull, an extremely broad band occurs centred at 2440 cm$^{-1}$, which, in the acid, on deuteration (by several recrystallizations from heavy water) shifts; $\nu_{O-D...O}$ occurs as a very broad weak band centred at 1840 cm$^{-1}$, giving $\nu_{O-H...O}:\nu_{O-D...O} = 1.33$.

Results for complexes of dimethylglyoxime with rhodium(III) are collected in Table 17; measurements were made in Nujol, hexachlorobutadiene, and Fluorolube mulls. Although [Rh(DMG)(DMGH)Cl$_2$] is fairly soluble in dimethylformamide, and gives beautiful crystals by slow evaporation of this solvent, no hydrogen-bonded proton resonance signal was observed in the solution.

Although the formation of several compounds of the type [Rh(DMG)$_2$XCl] has been claimed by refluxing the dichloro-compound with the ammonium salt of the anion, X, the sole product obtained in this work when such reactions were repeated has been the ammonium salt of the dichloro-compound, (NH$_4$)[Rh(DMG)$_2$Cl$_2$]. The absence of
TABLE 17
Infra-red spectra of dimethylglyoxime complexes of rhodium(III)
(in cm⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>&quot;H[Rh(DMG)₂Cl₂]&quot;</th>
<th>Ag[Rh(DMG)₂Cl₂]</th>
<th>NH₄[Rh(DMG)₂Cl₂]</th>
<th>[GH][Rh(DMG)₂Cl₂]a</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν_OH</td>
<td>3400m</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ν_NH</td>
<td>-</td>
<td>-</td>
<td>3460</td>
<td>3410sh</td>
</tr>
<tr>
<td>ν_CH</td>
<td>-</td>
<td>2900w</td>
<td>2874w</td>
<td>-</td>
</tr>
<tr>
<td>ν_OH₂</td>
<td>-</td>
<td>-</td>
<td>1616</td>
<td>1660s</td>
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<td>ν_OH</td>
<td>1600m,b</td>
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</tr>
<tr>
<td>ν_NO</td>
<td>1508m</td>
<td>1515s</td>
<td>1520</td>
<td>1510s</td>
</tr>
<tr>
<td>ν_CH</td>
<td>-</td>
<td>1420m</td>
<td>1424</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1328m</td>
<td>1321m</td>
<td></td>
<td>1327m</td>
</tr>
<tr>
<td></td>
<td>1240s</td>
<td>1241s</td>
<td>1245</td>
<td>1240s</td>
</tr>
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<td></td>
<td>1129m</td>
<td>1129m</td>
<td>1124m</td>
<td>1124m</td>
</tr>
<tr>
<td></td>
<td>1078s</td>
<td>1075s</td>
<td>1074s</td>
<td>1065s</td>
</tr>
<tr>
<td>ν_OHX?</td>
<td>1019w</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>986w</td>
<td>-</td>
<td>977</td>
<td>997m</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>880s,b</td>
</tr>
<tr>
<td></td>
<td>860m,vb</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ν_NH₄⁺</td>
<td>-</td>
<td>-</td>
<td>839</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>737s</td>
<td>733s</td>
<td>734s</td>
<td>732s</td>
</tr>
</tbody>
</table>

a, GH = guanidinium.
substitution is particularly clear when ammonium thiocyanate is the reactant; the product shows no infra-red absorption characteristic of thiocyanate, and, on treatment with dilute hydrochloric acid, gives the original acid "H[Rh(DMG)₂Cl₂]".

Studies of the reaction of the anion [Rh(DMG)₂Cl₂]⁻ with hydridic reagents have been performed. A hydridic species (17.7 p.p.m. relative to t-butanol, i.e. Δ₂̅ ~26.4) occurs when the aqueous solution is treated with sodium borohydride. This was observed only under optimum conditions, and the high-field line was too weak for splitting to be observed. On addition of excess borohydride, a blue precipitate is obtained, extremely similar to that observed in the analogous complex of bipyridyl; it may therefore tentatively be assumed to be rhodium(I). Reaction with alkaline ethanol also gives the blue compound, which is immediately decomposed by air or water, and does not dissolve in organic solvents. The green hydridic solution obtained with borohydride ion rapidly turned brown, depositing metallic rhodium. No solid salt was obtained. Although compounds formulated as containing rhodium(II) were obtained by the action of hypophosphorous acid on "H[Rh(DMG)₂Cl₂]", these red-brown solutions do not show high-field signals, through they are diamagnetic, suggesting the presence of rhodium(III) or rhodium(I).
While a number of scattered reports of the effect of reducing agents on rhodium(III) complexes exist, there is no well authenticated case of a monomeric rhodium(II) compound. The classes of reduced compound formed are discussed briefly.

**Dimeric rhodium(II)**

Such compounds as the green formates and acetates formed by reaction of hexachlororhodate(III) solutions with the relevant acid have empirical formulae $\text{Rh(RCOO)}_2\text{B}$, where B is a donor molecule such as water or pyridine. Although formally containing rhodium(II), these compounds are diamagnetic and dimeric. Their structures are presumably similar to that of cupric acetate hydrate, and the diamagnetism explained by a large singlet-triplet separation in the rhodium cases.

**Compounds with a rhodium-mercury bond**

These may be prepared by treating a hydridic complex of rhodium(III) with mercuric salts; the formulae are $(\text{Ph}_2\text{AsMe})_3\text{RhCl}_2\cdot\text{HgR}$, where $R = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and $\text{OAc}$; while these may be looked on as complexes of rhodium(II), they are diamagnetic, and essentially analogous to the homonuclear dimers above.
Hydrido-rhodium(III) complexes

It is now clear that a large number of "reduced" rhodium species are, in fact, hydrides of rhodium(III); these include

\[ \text{[Rh(Ph}_2\text{AsMe)}_3X_2\text{H}] \], where \( X = \text{Cl, Br, or I} \)

\[ \text{[Rhpy}_3\text{H}]\text{I}_2 \],

and \[ \text{[HRh(CN)}_5\text{]}^3-. \]

Transient hydridic species have been invoked to explain the homogeneous activation of molecular hydrogen by metals, and the reduction of rhodium trichloride by hydrogen is presumably initiated by such a species. It is interesting that the pink solution of rhodium trichloride in methanol/water at \(-50^\circ\text{C}\) becomes pale brown on treatment with borohydride ion, suggesting the intervention of a hydridic species; the system is unstable above \(-45^\circ\text{C}\), rapidly forming rhodium metal.

Rhodium(I)

Complexes of rhodium(I) with strongly \( \pi \)-bonding ligands are reasonably well known, e.g., \[ \text{[Rh(PPh}_3\text{)}_2(\text{CO)}\text{Cl}] \] and \[ \text{[Rh(CNR)}_5\text{]}\text{I}. \] Complexes of nitrogenous ligands containing rhodium(I) are less certain. The reactions with borohydride ion of complexes of chelating \( \pi \)-bonding ligands of the type \[ \text{[Rh}^{\text{III}}\text{(AA)}_2\text{Cl}_2 \], where AA is bipyridyl, o-phenanthroline, or dimethylglyoxime, are remarkably similar; evidence has been offered\(^{67}\) that, in the bipyridyl case, the red-blue compound finally obtained contains the cation \[ \text{[Rh(bipy)}_2]^+. \] In this
work, no high-field line has been observed in such complexes, nor do their infra-red spectra show rhodium-hydrogen stretching modes, so that they are not hydridic. Their remarkable insolubility is hardly explained by an ionic formula, nor is their rather striking red-blue dichroism. It is not unusual for a d$^8$ compound to manifest such behaviour, nickel dimethylglyoxime being a classic case. This suggests the presence of metal-metal bonding. Supporting this is the observation that [Rh(DMG)(DMGH)Cl$_2$], when refluxed with alkaline 2-methoxyethanol gives a red-blue dichroic solution, with absorption bands similar to those found in other d$^8$ systems with metal-metal bonds.

The reduction of the yellow dichlorobisbipyridylrhodium(III) cation with borohydride gives, first, a brown solution, which is found to be diamagnetic, then the blue product$^{67}$ $^{[\text{Rh(bipy)}_2]\text{ClO}_4,3\text{H}_2\text{O}}$. From the brown solution, a solid brown tetraphenylborate was obtained, with a weak peak at 2016 cm$^{-1}$, possibly due to $\nu_{\text{Rh-H}}$. In one experiment, a brown solution made from [Rh(bipy)$_2$Cl$_2$]$^+$ with hypophosphorous acid showed a high-field line at 1130 c./sec. relative to water. Since the analogous dichlorotetrapyridinerhodium(III) cation gives a hydride on treatment with borohydride ion, a common first step may occur, of the type

$$\text{yellow } [\text{Rh}^{\text{III}}\text{B}_4\text{Cl}_2]^+ + \text{H}^- \rightarrow \text{brown } [\text{Rh}^{\text{III}}\text{B}_4\text{ClH}]^+.$$

A second stage then appears to occur only with the chelating ligands:

$$\text{brown } [\text{Rh}^{\text{III}}\text{B}_4\text{ClH}]^+ \rightarrow \text{blue } [\text{Rh}^{\text{I}}\text{B}_4]^+ + \text{HCl}.$$
This presumably reflects the greater π-bonding capacity of bipyridyl, o-phenanthroline, and dimethylglyoximate, and, possibly, the existence of rhodium-rhodium bonds in the blue complexes.

Hydridorhodium(I)

The complex Rh(PPh₃)₃(CO)H is known, and from its trigonal bipyramidal structure, this may be thought of as iso-electronic with iron pentacarbonyl.

Other studies on reduced rhodium species

Polarographic work on complexes of rhodium(III) has led to several discrepant results. However, it can safely be said that reliable work has, in every case, led to the electrode process Rh³⁺ → Rh⁺, a 2-electron step. In the cases of chloropentamine-rhodium(III) cation and hexacyanorhodate(III) anion, polarographic results have indicated a 2-electron step, and chemical work has shown that the reduced product is hydridic. No evidence has arisen from polarography for the existence of Rh²⁺, and the conclusion from polarographic work is that it does not exist. A relevant observation is that while trisethylenediamine complexes of cobalt(III) and platinum(IV) racemize on active charcoal, through an electron transfer mechanism, the analogous rhodium(III) complex does not racemize, suggesting that no electron transfer can occur, because Rh²⁺ is too unstable. It is noteworthy that the third ionisation potentials of
the gaseous ions are 33.49 ev for cobalt, but 31.05 ev for rhodium; the process

\[ \text{M}^{3+}(g) + e^- \rightarrow \text{M}^{2+}(g) \]

thus releasing more energy for cobalt than for rhodium.

The reported reduced species of rhodium require re-examination. The products of "reducing" rhodium trichloride solutions with hypophosphorous acid and with sodium formaldehyde sulfoxylate are probably complexes of rhodium(III), since in neither case is a high-field line observed in the proton magnetic resonance spectrum, although both solutions are diamagnetic.

**The hydride ion in rhodium(III) complexes**

Since hydridic complexes are preparable through nucleophilic replacement at rhodium(III) of halide by hydride, the assumption that hydride ion is present in the complexes is apparently reasonable. However, there has been a good deal of speculation about the nature of hydrogen bonded to rhodium; the limiting descriptions \( \text{Rh}^{\text{III}} - \text{H}^- \) (I) and \( \text{Rh}^{\text{I}} - \text{H}^+ \) (II) are available. Since the high-field line observed in nuclear resonance is believed to arise through the availability of low-lying excited states of the metal ion, no distinction is possible from \( \Upsilon \) values. Similarly, the infra-red stretching frequency is a function of the mass of the bonded vibrators, and is unable to distinguish (I) from (II). However, from the present
work, it is clear that the electronic states in hydridic complexes may
be considered as arising from the spin-paired $d^6$ configuration, not
from the $d^8$ configuration of Rh$^{I}$. The description (I) therefore seems
preferable, the complexes containing hydride ion as the prototype
halide. Supporting evidence for this Rh$^{III}$ – H$^-$ formulation arises
from polarographic studies; Vleck$^{69}$ found that the hydridic complex
[Rh(Ph$_2$AsMe)$_3$Cl$_2$H] behaved polarographically like other rhodium(III)
complexes such as [Rh(Ph$_2$AsMe)$_3$Cl$_3$], giving rise to a two-electron
step at the dropping mercury electrode.

Two theories of the trans-effect are extant; one$^{74}$ is based on
polarizability, and takes account of hydride as a small source of charge,
and the other$^{75}$ utilizes the theory of $\pi$-bonding, which seems
inappropriate, at present, for hydrogen. Hydride ion without a doubt
exerts a high trans-effect, and in view of the present work which
reveals that bonds between hydride and rhodium(III) are not abnormal,
this must arise from a polarizability effect.

It is known from X-ray analysis$^{68,76,77}$ that hydrogen occupies a
normal stereochemical position, and, considering the spectrochemical
and polarographic evidence that hydride is a normal halide ligand,
there seems no reason to postulate the "short" bonds which have been
assumed$^{78}$ to occur in such complexes.
EXPERIMENTAL

1. General

Analyses were by the Microanalytical Laboratory, Imperial College, except that analyses for rhodium were performed by igniting a weighed sample of the compound, finishing the ignition in the hottest part of the flame of a Meker burner. This proved unreliable in the presence of nitrate or perchlorate ion, presumably through sputtering.

Nuclear magnetic resonance spectra were generally obtained in non-spinning tubes of 15-mm. outside diameter, in a Varian Associates V-4311 spectrometer, operating at 56.43 Mc/sec. Infra-red spectra were measured either on a Perkin-Elmer Model 21 spectrophotometer with calcium fluoride or sodium chloride optics, or on a Grubb-Parsons "Spectromaster" grating instrument. Mulls were prepared in Nujol, Fluorolube, or hexachlorobutadiene, in a dry box flushed with nitrogen for the hydridic compounds. Electronic spectra in solution were initially determined using a Perkin-Elmer model 4000 spectrophotometer; later measurements used a Perkin-Elmer Model 350 spectrophotometer. Electronic spectra of solids were measured using the reflectance attachment to a Unicam SP500 spectrophotometer.

In preparative work on hydridic compounds, solvents used were degassed, then saturated with nitrogen, and all operations were conducted under nitrogen.
2. Complexes of Aliphatic Amines

trans-Dihalobisethylenediaminerhodium(III) salts and trans-dichlorotetramminerhodium(III) nitrate. - These were prepared by the method of Basolo and Anderson.20 The infra-red and electronic spectra of the products agreed well with those published, except that a new singlet-triplet band was discovered in a strong solution of trans-[RhenaCl₂]Cl at 488 μm, ε 6.6.

The nucleophilic replacements by borohydride were studied in 1-cm. silica cells maintained at 0-2°C by circulating water from an ice-salt bath. All solvents were degassed. Successive additions of ice-cold borohydride solutions were made by an ice-cooled syringe.

The borohydride solutions were rendered slightly alkaline (pH ~ 8) by addition of sodium hydroxide which prevents much bubble formation which would have prevented accurate measurements of electronic spectra. Control runs were performed without the borohydride to ensure that base hydrolysis was not a competing process. In no case did the initial spectrum alter in less than an hour with hydroxide alone present. For the initial measurements, the cell compartments of the spectrophotometer were flushed by a rapid stream of dry nitrogen. However, this subsequently proved necessary only in the case of chloropentamminerhodium(III) chloride.

Hydridic species were isolated as their tetraphenylborate salts where possible; the procedure is illustrated by the following example.
trans-Dihydridobisethylenediaminerhodium(III) tetraphenylborate. — trans-Dichlorobisethylenediaminerhodium(III) chloride (0.31 g., 1 mmole) in water (5 ml.) at 0°C. was treated dropwise with an ice-cold solution (5 ml.) of sodium borohydride (0.18 g., 5 mmoles). The solution was stirred for ten minutes, with occasional venting to remove excess hydrogen. An ice-cold solution (5 ml.) of sodium tetraphenylborate (0.75 g., 2 mmoles) was added slowly, and the very pale brown precipitate of the desired salt was collected, washed with ice-cold water, and dried in a rotary drier at 15°C. The salt contained no chlorine (Found: C, 65.0; H, 7.0; N, 9.0. C$_{28}$H$_{38}$BN$_4$Rh requires C, 62.0; H, 7.0; N, 10.4%).

This procedure was repeated with 0.0132 g. of the dichloro-complex. After the addition of sodium tetraphenylborate and removal of the precipitate, an excess of silver nitrate solution was added to the filtrate, giving a mixed precipitate of silver chloride and silver tetraphenylborate, contaminated with a small amount of metallic silver, presumably formed by residual borohydride ions. The precipitate was collected, washed several times with acetone (which dissolves out the silver tetraphenylborate), and redissolved in ammonia. The resultant solution was made acid with nitric acid, and the precipitate of silver chloride collected, washed with water, dried and weighed (0.0158 g.; calc. for complete chlorine displacement from complex, 0.0166 g.).
When the pale brown solution of trans-dihydridobisethylenediamine-rhodium(III) chloride (prepared from the trans-dichloro-compound) was allowed to stand under nitrogen, a mirror of metallic rhodium slowly formed, and, after three days, the solution was yellow. The rhodium was removed by filtration, and the absorption spectrum of the filtrate was measured (this is given in Table 18).

**TABLE 18**

trans-cis-Isomerisation in \([\text{Rhen}_2\text{Cl}_2]^+\) via the hydride

(\(\lambda\) in m\(\mu\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{max}})</th>
<th>(\epsilon_1)</th>
<th>(\lambda_{\text{max}})</th>
<th>(\epsilon_2)</th>
<th>(\lambda)</th>
<th>(\epsilon)</th>
<th>(\lambda)</th>
<th>(\epsilon)</th>
<th>(\epsilon/\epsilon_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Rhen(_2)Cl(_2)](^+)</td>
<td>350</td>
<td>130</td>
<td>292</td>
<td>170</td>
<td>-</td>
<td>-</td>
<td>210</td>
<td>10(^4)</td>
<td>1.30</td>
</tr>
<tr>
<td>trans-[Rhen(_2)Cl(_2)](^+)</td>
<td>407</td>
<td>75</td>
<td>289</td>
<td>130</td>
<td>240</td>
<td>1500</td>
<td>210</td>
<td>10(^4)</td>
<td>1.73</td>
</tr>
<tr>
<td>&quot;oxidized&quot; trans-[Rhen(_2)H(_2)](^+)</td>
<td>350</td>
<td>-</td>
<td>293</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>210</td>
<td>-</td>
<td>1.35</td>
</tr>
</tbody>
</table>

**Chloropentamminerhodium(III) chloride.** - This was prepared by the method of Lebedinski\(^79\) (exhaustive treatment of rhodium trichloride with ammonia on a steam bath), and recrystallized from dilute hydrochloric acid (Found: Rh, 34.7. Calc. for [Rh(NH\(_3\))\(_5\)Cl]Cl\(_2\): Rh, 34.9%). The electronic spectrum agreed with that previously recorded.\(^27\)
The reaction$^{21}$ of ethylenediamine with trans-dichlorotetrapyridinerhodium(III) chloride. - The directions$^{21}$ of Meyer and Kienity were followed exactly, except that the temperature used in this work was 100°C, whereas the pyridine was removed at 120°C in their directions. The whitish crystals obtained were dissolved in water, the electronic spectrum taken, and alcohol was added till crystallization ensued.

The electronic spectrum was then taken again, and proved to be identical with that$^{27}$ of tris-ethylenediaminerhodium(III) chloride ($\lambda$ 299 mµ, $\varepsilon$ 101; $\lambda$ 253 mµ, $\varepsilon$ 107). The infra-red spectrum was identical with that of an authentic sample of $[\text{Rhen}_3]\text{Cl}_3.2\text{H}_2\text{O}$, and showed that no pyridine was present. Analytical data agreed well (Found: C, 16.8; H, 5.8; N, 19.8. Calc. for $C_6H_{28}Cl_3N_6O_2\text{Rh}$: C, 16.9; H, 6.6; N, 19.7%).

cis-Dichlorobisethylenediaminerhodium(III) chloride was prepared by the literature method.$^{20}$ Infra-red and electronic spectra agreed well with those published.

cis-Dihydridobisethylenediaminerhodium(III) tetraphenylborate was prepared, by the general method outlined above, as an off-white powder; this had $\nu_{\text{Rh-H}}$ 1969 cm$^{-1}$ [Found: Cl, 0.3. $C_{28}H_{38}BN_4\text{Rh}$ (dihydride) requires: Cl, 0%. $C_{28}H_{37}BClN_4\text{Rh}$ (monohydride) requires 6.4%].

cis-Dichlorotriethylenetetraminerhodium(III) chloride was prepared both by the method outlined below and subsequently by the literature
Spectroscopic properties of both products were extremely similar to literature values.

Sodium hexachlororhodate(III) (1.9 g.) in water (10 ml.) and ethanol (200 ml.) was treated dropwise with redistilled triethylene-tetramine (0.85 g.). (The commercial triethylenetetramine was analysed:

- Found: C, 50.9; H, 12.3. Calc. for C₆H₁₈N₄: C, 49.4; H, 12.3%.
- After two distillations: Found C, 49.6; H, 12.3%.) The mixture was heated to reflux for 2 hr., after treatment with dilute hydrochloric acid to pH 4. After cooling, the reaction mixture was allowed to stand in the refrigerator overnight, and the yellow crystals were collected, redissolved in water, the solution treated with perchloric acid and cooled, when yellow crystals of cis-dichlorotriethylenetetramine-rhodium(III) perchlorate were formed. These were recrystallized from hot water; yield 1.2 g. (Found: C, 17.3; H, 4.7. C₆H₁₈Cl₃N₄O₄Rh requires C, 17.1; H, 4.3%). \( \Lambda \) = 102 mhos (10⁻³M in water). The perchlorate was converted to the chloride by means of ion exchange.

The chloride was isolated by evaporating the eluate and adding ethanol slowly with scratching (Found: C, 20.5; H, 5.2; N, 15.1. Calc. for C₆H₁₈Cl₂N₄Rh: C, 20.2; H, 5.1; N, 15.7%). By treating an aqueous solution of the chloride with a strong solution of sodium tetraphenylborate, a nearly white precipitate of cis-dichlorotriethylenetetramine-rhodium(III) tetraphenylborate was obtained, which was recrystallized from aqueous acetone (Found: C, 53.8; H, 5.9; Cl, 12.1. C₃₀H₃₈BCl₂N₄Rh requires C, 53.1; H, 5.9; Cl, 11.9%).
cis-Dihydridotriethylenetetraminerhodium(III) tetraphenylborate was prepared, using excess borohydride, by the general method, as a white powder, which had $\nu_{\text{Rh-H}}$ 1969 cm$^{-1}$ (Found: Cl, 0.1. The dihydride, C$_{30}$H$_{40}$BN$_4$Rh, requires Cl, 0%; the monohydride, C$_{30}$H$_{39}$BClN$_4$Rh, requires 6.0%).

Reduction of Quinone by Hydride Transfer. — Quinone (0.05 g., $5 \times 10^{-4}$ mole) in water (2 ml.) was added to a suspension of cis-dihydridotriethylenetetramerhodium(III) tetraphenylborate (0.58 g., $10^{-3}$ mole) in a mixture of water (3 ml.) and methanol (1.5 ml.). The mixture was shaken under nitrogen for 1 hr. at 30°C., cooled, and extracted with ether. On evaporation of the ether, white crystals of quinol (0.03 g.) were obtained, which, after recrystallization from ether, had m.p. and mixed m.p. 170° (lit. 170.3°). The aqueous layer had deposited a red gum, which contained all the rhodium.

Similar experiments were conducted on the reduction of nitrobenzene. Trisbipyridyloobalt(III) ion acts as a catalyst in the reduction of several aromatic nitro-compounds by borohydride. This is equally true for cis- and trans-dichlorobisethylenediaminerhodium(III) chlorides; in both cases, nitrobenzene was reduced to aniline, when an aqueous-methanolic solution of the rhodium complex was used to achieve homogeneity. Metallic rhodium produced by borohydride reduction of simple compounds of rhodium(III) is very effective in the hydrogenation of olefins. The hydridic complexes derived from complexes of
rhodium(III) with amines were treated with dec-1-ene, in aqueous alcohol, but no reduction of the olefin occurred, except in the case of cis-[Rhen₂Cl₂]Cl, where metallic rhodium was accidentally produced.

3. **Preparation of Rhodium-Pyridine Complexes.**

Reaction of Rhodium Trichloride with Aqueous Pyridine. — The procedure described by Holtzclaw and Collman was used. The first crop of crystals (X) were collected, but the separation of the isomers is unsatisfactory. Later work using electronic spectra showed that some 85% of the solid was 1,2,6-trichlorotripyridinerhodium(III). The filtrate from (X) afforded yellow needles of trans-dichlorotetrapyridinerhodium(III) chloride hexahydrate, which was reorocrystallized from hot water, there being a startling increase in solubility as the temperature is raised, as with the analogous complex of cobalt(III) (Found: C, 38.1; H, 4.9; N, 8.9. Calc. for C₄₀H₅₂Cl₃N₄O₆Rh: C, 37.9; H, 5.1; N, 8.8%). An authentic sample of the tetrapyridine complex was prepared by means of Delepine's procedure using alcohol catalysis. The water of crystallization could be removed by pumping at 75°C./1 mm. during 8 hr., when the loss in weight corresponded to 6H₂O.

When (X) (1.0 g.) was treated with excess of pyridine (15 ml.) in a sealed tube at 150°C. for 3 days and allowed to cool, red-orange crystals of 1,2,6-trichlorotripyridinerhodium(III) were obtained (0.93 g., 93%) (Found: C, 40.2; H, 3.4; N, 9.5. Calc. for C₁₅H₁₅Cl₃N₃Rh: C, 40.3;
H, 3.4; N, 9.4%). This compound was also recovered in good yield (0.42 g., 93%) when anhydrous trans-dichlorotetrapyridinerhodium(III) chloride (0.53 g., $10^{-3}$ mole) was treated with excess of pyridine (15 ml.) in a sealed tube at 160°C for 4 days. An earlier report said that 1,2,6-trichlorotripyridinerhodium(III) was reduced to the metal by refluxing with ethanol for 2 hr. This was not confirmed.

**Potassium trans-tetrachlorodipyridinerhodate.** - This was prepared by the method of Delepine; the electronic spectrum agreed with that in the literature.

**Pyridinium hexachlororhodate(III).** - This was obtained as small red crystals by the method of Gutbier and Bertsch (Found: C, 31.9; H, 3.4; N, 7.4. Calc. for $\text{C}_1\text{H}_8\text{Cl}_6\text{N}_2\text{Rh}$: C, 32.4; H, 3.3; N, 7.6%). The infra-red spectrum showed absorptions (in cm$^{-1}$) at: 3360s,bd, 2700m,bd, 1637m, 1606s, 1530s, 1240m, 1208s, 1192m, 1161m, 1147w, 1068s, 1049m, 768sh, 751s, 741sh, 694m, and 680s.

**Polymeric Trichlorodipyridinerhodium(III).** - Method 1: 1,2,6-Trichlorotripyridinerhodium(III) (0.45 g., 1 mmole) was kept in vacuo at 125°C till it had become substantially pink (1 hr.). The product, after cooling, was extracted repeatedly with dichloromethane, which served to remove the unchanged tripyridine complex. The rose-pink compound was collected and air-dried (0.27 g.) (Found: C, 32.9; H, 3.0; Cl, 28.5; N, 7.2; Rh, 28.1. $\text{C}_{10}\text{H}_{10}\text{Cl}_3\text{N}_2\text{Rh}$ requires C, 32.7; H, 2.7; Cl, 28.9; N, 7.6; Rh, 28.0%).
Method 2: A solution of 1,2,6-trichlorotripyridinerhodium(III) (0.23 g., 0.5 mmole) in chloroform (35 ml.) was refluxed for 2 hr., and then filtered while hot; the resulting pink solid (0.11 g.) was washed with hot chloroform (3 x 10 ml.) (Found: C, 32.3; H, 3.0; Cl, 28.6%).

Method 3: A solution of 1,2,6-trichlorotripyridinerhodium(III) (0.23 g., 0.5 mmole) in dichloromethane (15 ml.), which had previously been dried by molecular sieves, was kept under nitrogen during 8 days. The pink solid which resulted (0.12 g.) was collected and washed with dichloromethane (Found: Cl, 28.6%).

Method 4: Potassium trans-tetrachlorodipyridinerhodate(III) (0.5 g.) was aquated by the method of Delepine; the resulting orange 2,3,4-trichloro-1,6-dipyridine-5-aqourhodium(III) hydrate (0.4 g.) was kept in vacuo at 115°C. until it had become substantially pink. The product was allowed to cool, and then was washed with hot water (in which the orange aquo-compound is soluble) until no orange colour could be seen in the washings. The pink insoluble residue (0.32 g.) was washed with alcohol, then with ether, and air-dried (Found: C, 33.4; H, 2.9; Cl, 28.2%).


Compounds are listed below under the original names and numbers for convenience.
"II. Hexakispyridinerhodium(II) bromide". This was prepared under nitrogen as glistening yellow prisms, soluble in ethanol in agreement with the original description. The infra-red and electronic spectra were in complete agreement with those of an authentic sample of trans-dibromotetrapyridinerhodium(III) bromide, which was prepared by the literature method. These spectra in turn agreed well with reported values (Found: C, 36.2; H, 3.1; N, 8.42. Calc. for C$_{20}$H$_{20}$Br$_3$N$_4$Rh: C, 36.45; H, 3.06; N, 8.50%).

"III. Bromopentakispyridinerhodium(II) bromide". This was obtained by treating an ice-cold solution of II with concentrated hydrobromic acid. The golden-yellow plates first obtained are 1,6-[Rhpy$_4$Br$_2$](H$_5$O$_2$)Br$_2$, analogous to the chloride, 1,6-[Rhpy$_4$Cl$_2$](H$_5$O$_2$)Cl$_2$, as shown by the similarity in infra-red spectra. Bands occur (in cm$^{-1}$) at: 2900vs, 2200b, 1660b, 1601m, 1480w, 1207m, 1150m, 1060m, 1017m, 940vb, 771sh, 762s and 693s. Since washing removes the added HBr.2H$_2$O, the material analysed was probably [Rhpy$_4$Br$_2$]Br (Found: Rh, 15.6. Calc. for C$_{20}$H$_{20}$Br$_3$N$_4$Rh: Rh, 15.61%).

"IV. Bromopentakispyridinerhodium iodide". The pale yellow precipitate was identical with an authentic sample of trans-dibromotetrapyridinerhodium(III) iodide obtained by treating a solution of the bromide with potassium iodide (Found: Rh, 14.9%. Calc. for C$_{20}$H$_{20}$Br$_2$IN$_4$Rh: Rh, 14.6%).
"V. Dibromotetrakispyridinerhodium(II)". As described, when [Rhpy₄Br₂]Br was refluxed with 2N hydrobromic acid in the presence of a few drops of hypophosphorous acid a yellow solution gradually formed. In one experiment this solution was cooled and diluted with water, when 1,2,6-tribromotripyridinerhodium(III) separated (Found: C, 30.9; H, 2.8; N, 7.5; Br, 40.75. Calc. for C₁₅H₁₅Br₃N₃Rh: C, 31.06; H, 2.61; N, 7.25; Br, 41.35%). In acetone, λₘₐₓ 458 μm, εₘₐₓ 182 (literature λₘₐₓ 460 μm, εₘₐₓ 186). Other bands and the infra-red spectrum agreed with published data. However, 1,2,6-tribromotrispyridinerhodium(III) is not compound V of ref. 34 but an intermediate, since on prolonged refluxing of the yellow solution a buff precipitate is formed. This substance, of properties identical to V, is [Rhpy₄Br][Rhpy₂Br₄]₂₉ which is isomeric with Rhpy₃Br₃ (Found: C, 31.2; H, 2.8; N, 7.2; Rh, 17.8%. Calc. for C₃₀H₃₀Br₆N₆Rh₂ as above and Rh, 17.74%). The infra-red spectrum showed bands (in cm⁻¹) at: 1606m, 1480w, 1240w, 1218m, 1150m, 1070s, 1020m, 774s, 766m, 754m, 699s, 695sh and 693sh, agreeing with an authentic sample within 1 cm⁻¹.

"VIII. Tetrakispyridinium hexabromobispyridinedibromorhodium(II)". As described, the method is identical with that of Poulenc for pyridinium tetrabromobispyridinerhodate(III). The products of both methods are identical and the analyses fit very well.
"Hexakispyridinerhodous chloride". The glistening pale-yellow crystals, prepared either in air or under nitrogen, had electronic and infra-red spectra identical with those of trans-dichlorotetrapyridinerhodium(III) chloride pentahydrate.

"Chloropentakispyridinerhodium(II) chloride". The crystals given by the described method are identical in properties and in infra-red spectra with the acid adduct \(1,6-[\text{Rhpy}_4\text{Cl}_2]\)\(\cdot\text{HCl}\cdot2\text{H}_2\text{O}\). However, on being washed they lose hydrochloric acid so that the analysed material was of unknown composition.

"Bispyridinium tetrachlorotetrakispyridinedichlororhodium(II)". The product is identical with the salt \(1,6-[\text{Rhpy}_4\text{Cl}_2] 1,6-[\text{Rhpy}_2\text{Cl}_4]\) described by Delepine and so essentially is the method (Found: C, 40.6; H, 3.7; N, 9.8. \(\text{C}_{30}\text{H}_{30}\text{Cl}_6\text{N}_6\text{Rh}_2\) requires C, 40.3; H, 3.4; N, 9.4%). The electronic spectra agreed with those of an authentic sample, prepared by Delepine's method (Found: C, 40.4; H, 3.5; N, 9.4%) which had \(\lambda 501 \text{ m\u}, \varepsilon 45; \lambda 433 \text{ m\u}, \varepsilon 90; \) and \(\lambda 411 \text{ m\u}, \varepsilon 105;\) in solution in acetone.

"Tetrakispyridinium hexachlorobispyridine-\(\mu\)-dichlorodirhodium(II)". The product is identical with the pyridinium tetrachlorobispyridinerhodate(III) of Delepine. The electronic and infra-red spectra agreed with those previously reported.
"Hexakispyridinerhodium(II) iodide". Using the original procedure the extremely unstable air-sensitive pale-yellow crystals were obtained. Analyses are not satisfactory but the compound may be hydridopenta-pyridinerhodium(III) iodide (Found: I, 31.2; Rh, 12.6%. \(\text{C}_{26}\,\text{H}_{26}\,\text{I}_{2}\,\text{N}_{5}\,\text{Rh}\) requires I, 33.7; Rh, 13.7%). The infra-red spectrum showed bands (in cm\(^{-1}\)) at 1990s, 1601m, 1590m, 1490w, 1478w, 1239w, 1221m, 1160s, 1155sh, 1068s, 1047w, 1039m, 1020m, 997m, 987w, 960w, 941w, 822m, 779s, 769s, 749s, 702sh, and 698s.

Tri-iodotrispyridinerhodium(III). Rhodium trichloride solution (10 ml. containing 0.09 g. rhodium) was treated with potassium iodide (3 g. in 3 ml. \(\text{H}_2\text{O}\)). On heating, the dark iodorhodate(III) ion was formed and at this stage pyridine (12 ml.) and hypophosphorous acid (2 ml., 30%) were added. The mixture was warmed until the colour faded to brown, then rapidly cooled when trans-di-iodotetrapyridinerhodium(III) iodide began to crystallize. This yellow-brown compound was collected (a sample dried on a porous tile showed bands in the infra-red spectrum (in cm\(^{-1}\)) at 1610s, 1544m, 1482w, 1242m, 1220m, 1165s, 1082m, 1069m, 1048s, 1021m, 998w, 960w, 765s, 749m and 702s) and washed copiously with water; during washing, the colour changed to red-brown. When the washings no longer contained pyridine the red-brown residue of the compound was air-dried and crystallized from dichloromethane. Yield 0.2 g. (Found: I, 52.5; N, 6.1. \(\text{C}_{15}\,\text{H}_{15}\,\text{I}_{3}\,\text{N}_{3}\,\text{Rh}\) requires I, 52.84; N, 5.83%).
Reaction of trans-dibromotetrapyridinerhodium(III) bromide with reducing agents. Trans-[Rhpy₄Br₂]Br (0.66 g., 10⁻³ mole) in water (5 ml.) was treated with hypophosphorous acid (0.2 ml.) and the mixture heated to boiling, when the yellow solution became brown. The solution was cooled rapidly in an inert atmosphere, and allowed to stand in an ice-bath. After 6 hours, the brown acicular crystals which had appeared were collected in an inert atmosphere. Yield 0.2 g. Analytical results were inconclusive, because of the instability of the compound; formulation as a hydride is based on the observation of a high-field line in the brown solution (ζ = 28.5) and the infra-red spectrum, which shows bands at 1976 s, 1605 m, 1592 s, 1487 w, 1479 w, 1238 m, 1223 m, 1159 s, 1154 m, 1067 s, 1021 m, 996 m, 942 w, 781 s, 768 s, 747 s, 703 m and 698 s.

A brown solution showing a high-field line (ζ = 28.5) was also obtained by treating an aqueous (or alcoholic) solution of [Rhpy₄Br₂]Br with aqueous sodium borohydride, but in this case no crystals could be obtained. Similar experiments on the dichloro species, trans-[Rhpy₄Cl₂]Cl, gave brown solutions (showing high-field lines, ζ = 28.5) with hypophosphorous acid or borohydride ion, but no crystals were obtained in these cases. A brown solution from borohydride reduction of the trans-dibromo-complex was treated with a saturated solution of sodium tetraphenylborate; the resultant pale-brown precipitate was collected and washed by centrifugation, and was shown to contain no bromine. It decomposed very rapidly while wet, and
smelt strongly of phenol. In the presence of excess pyridine, the brown solutions became colourless on boiling and showed high-field lines at $\gamma = 29$. A puzzling observation, which has not been repeated despite numerous attempts, is that a solution of $[\text{Rhpy}_4\text{Br}_2]\text{Br}$ in aqueous pyridine, treated with sodium borohydride, and allowed to stand in a closed container under nitrogen overnight, gave brown acicular crystals, which analysed reasonably well for $[\text{Rhpy}_5\text{H}]\text{Br}_2$ (Found: N, 10.2; Br, 22.0. $C_{25}H_{26}\text{Br}_2N_5\text{Rh}$ requires N, 10.6; Br, 23.9%). The infra-red spectrum, however, showed bands, presumably due to $\nu_{\text{Rh-H}}$, at 2050 and 1966 cm$^{-1}$, of about equal intensities. Other bands were observed at 1604, 1582, 1240, 1217, 1150, 1069, 1036, 1018, 991, 780, 751 and 703 cm$^{-1}$. The electronic spectrum of trans-$[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$ shows a band at 408 μm with $\varepsilon = 75$; after treatment with excess borohydride, a broad featureless absorption rising into the ultra-violet was found for the brown solution; the extinction coefficient per g.-atom of rhodium at 408 μm is then $2 \times 10^3$.

5. Reactions of $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$.

**Chlorodiocyanobispyridinerhodium(III) dihydrate.** - trans-Dichlorotetrapyridinerhodium(III) chloride pentahydrate (0.616 g., 1 mmole) in water (25 ml.) was treated with an excess of potassium cyanide (0.65 g., 10 mmole). The yellow solution obtained on heating to ca. 80°C. will give crystals of trans-$[\text{Rhpy}_4\text{Cl}_2]\text{Cl}.5\text{H}_2\text{O}$ if allowed to cool. If the
solution is boiled, pyridine is lost, and a yellow oil may appear briefly (this is probably \( \text{[Rhpy}_3(\text{CN})_2\text{Cl]} \)) but in a few seconds redissolves, the solution subsequently depositing a precipitate of chlorodicyanobispyridinerhodium(III) dihydrate (0.37 g., 94%), which was washed with copious hot water, and dried in a vacuum desiccator (Found: C, 37.5; H, 3.67; Cl, 8.8%; N, 14.3%; Rh, 29.3).

\( \text{C}_2\text{H}_4\text{ClN}_4\text{O}_2\text{Rh} \) requires C, 37.4; H, 3.64; Cl, 9.2; N, 14.5; Rh, 29.3%). The infrared spectrum showed bands (in cm\(^{-1}\)) at 3400s,b, 2192s, 2145s, 1631m,b, 1606s, 1239m, 1217s, 1153s, 1071s, 1018s, 765s,b, and 693s,b, confirming the presence of water, cyanide (both bridging and terminal), and pyridine. The compound was insoluble in all solvents tried.

**Chloro-oxalato-tripyridinerhodium(III).** - This was prepared from trans-[\( \text{Rhpy}_4\text{Cl}_2 \)] \( \text{Cl}\cdot5\text{H}_2\text{O} \) and potassium oxalate as described\(^3\) by Tchugaev. The yellow needles of the product were washed with hot water, and dried over silica gel in a vacuum desiccator (Found: C, 44.1; H, 3.38; Cl, 7.8; N, 8.9. Calc. for \( \text{C}_{17}\text{H}_{15}\text{ClN}_3\text{O}_4\text{Rh} \): C, 44.0; H, 3.26; Cl, 7.6; N, 9.0%). The infrared spectrum showed bands (in cm\(^{-1}\)) at: 1701s, 1680s, 1605m, 1241m, 1214m, 1157m, 1072s, 1016m, 885w, 801s, 780s, 766w, 724m, 710m, 699m, and 689s. The only solvent in which the compound appeared to be even slightly soluble was pyridine. The compound showed no sharp melting-point, decomposing ca. 200° to pyridine and a black residue.
Reaction with dimethylglyoxime. - According to the literature, when trans-[Rhpy₄Cl₂]Cl in aqueous solution is refluxed for 36 hours with dimethylglyoxime, the product is chloro-bisdimethylglyoximato-pyridinerhodium(III). The reaction was repeated, and the product is, in fact, not [Rh(DMG)₂pyCl] but a mixture of orange and very pale yellow crystals, which were separated by extraction with dichloromethane, the orange component dissolving, and the pale yellow component being insoluble. By pumping down the dichloromethane solution, the orange component was obtained as crystals, which are probably 1,2,3-trichlorotripyridinerhodium(III), in view of the electronic maximum in dichloromethane solution at 407 m\(\mu\), and the coincidence of the infra-red spectrum with that of an authentic sample. The pale yellow crystals, which are soluble in water, certainly contain both pyridine and rhodium, but, from the infra-red spectrum, no dimethylglyoxime. Reproducible analytical data were not obtained.

When the reaction was performed in ethanol, in which both components are soluble, the product appeared to be pyridinium trans-dichlorobisdimethylglyoximatorhodate(III) (Found: C, 32.7; H, 4.16; N, 15.1. Calc. for C₁₃H₁₉ClN₅O₄Rh· C, 32.2; H, 4.13; N, 14.5%).
trans-cis Isomerisation of \([\text{Coen}_2\text{Cl}_2]^+\).

**trans-Dichlorobisethylenediaminecobalt(III) chloride**, in aqueous solution at 0°C., was treated with a little ice-cold sodium borohydride solution. After a short while, the originally green solution passed through a colourless stage and became purple. Study of the electronic spectra of this process revealed that the green **trans-**dichloro-compound was transformed directly into the purple product, isosbestic points being observed. Although diamagnetic, the purple solutions showed no high-field line in n.m.r., and, on addition of sodium tetraphenylborate, the precipitates obtained were always green **trans-**dichlorobisethylenediaminecobalt(III) tetraphenylborate, identified by analysis (Found: C, 58.9; H, 6.32. Calc. for \(\text{C}_{28}\text{H}_{36}\text{BCl}_2\text{N}_4\text{Co}\): C, 59.0; H, 6.31%).

It was then realized that the very characteristic electronic spectrum of the purple product was identical with that of the **cis-**dichlorobisethylenediaminecobalt(III) cation, and that the reaction was a catalysed **trans-cis** isomerisation. The mechanism of this reaction was studied radiochemically as follows.

**trans-Dichlorobisethylenediaminecobalt(III) chloride** (0.3 g.) was dissolved in \(^{36}\text{Cl}\)-labelled hydrochloric acid (A.E.R.E. Harwell, 4 ml., 2M, with an activity of 10 µc) and refluxed for 2 hr., the solution then being cherry-red. (Control experiments with unlabelled hydrochloric acid had shown that the cation present at this stage was disaquo-
bisethylenediaminecobalt(III).) The radio-active solution was allowed to evaporate to dryness, when green crystals of active trans-dichlorobisethylenediaminecobalt(III) chloride hydrochloride dihydrate were obtained. They were collected, and heated at 110°C.; the desired labelled compound trans-[Co(en$_2$$^3$Cl$_2$)]$^3$Cl was obtained.

After unsuccessful experiments on the purple final solution which involved (i) precipitating free chloride with silver nitrate (this removed all the chloride from the complex ion as well, leaving cherry-red bisaquobisethylenediaminecobalt(III) ion in solution) and (ii) precipitation of the complex cation with tetraphenylborate (this was incomplete, as shown by the marked purple colour of the filtrate), the following procedure was adopted to investigate the number of co-ordinated chloride ions involved in the isomerisation.

A solution (0.01M) of the labelled trans-complex in potassium chloride solution (0.1M) was counted. An ice-cold 5-ml. aliquot part was treated with freshly prepared sodium borohydride solution in excess; this was necessary because aged solutions of borohydride were sufficiently alkaline to promote the base-catalysed hydrolysis of the complex ions, which effectively increased the exchange of radio-chlorine. The solution was immediately made acid with concentrated nitric acid and shaken with Dowex 50 cation-exchange resin (0.5 g.) which removed all the complex ion from solution. The resin was removed by centrifugation and washed with ice-water, and the combined supernatant
solutions were made up to 10 ml. An aliquot part (5 ml.) was counted. The activity of the free chloride in the supernatant liquid was found to be 60% of the original (mean of 3 runs: 58, 66, 56%), indicating that only one of the two co-ordinated chlorides of the original had exchanged.

7. Adducts of Hydrohalic Acids.

trans-Dichlorobis(ethylenediamine)cobalt(III) hydrogen malonate malonic acid dihydrate. - This was prepared according to Price and Brazier\textsuperscript{38} (Found: C, 24.8; H, 5.7; Cl, 14.7. Calc. for C\textsubscript{16}H\textsubscript{26}Cl\textsubscript{2}CoN\textsubscript{4}O\textsubscript{10}: C, 24.4; H, 5.5; Cl, 14.4%).

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride hydrochloride dihydrate. - This was prepared following Jorgensen,\textsuperscript{37} as green micaceous plates (Found: 0, 8.8; weight loss (HCl.2H\textsubscript{2}O) at 110°C, 30.2. Calc. for C\textsubscript{4}H\textsubscript{2}Cl\textsubscript{4}CoN\textsubscript{4}O\textsubscript{2}: [Coen\textsubscript{2}Cl\textsubscript{2}]Cl.HCl.2H\textsubscript{2}O, 0, 9.0; weight loss, 30.3%).

trans-Dibromobis(ethylenediamine)cobalt(III) bromide hydrobromide dihydrate. - This was prepared in a similar way\textsuperscript{37} (Found: 0, 5.8; weight loss, 36.7. Calc. for C\textsubscript{4}H\textsubscript{2}Br\textsubscript{4}CoN\textsubscript{4}O\textsubscript{2}: 0, 6.0; weight loss, 36.7%).

trans-Dichlorobis(\textpm)propylenediamine)cobalt(III) chloride hydrochloride dihydrate. - This was prepared by the literature method,\textsuperscript{86} as
green flat plates (Found: weight loss, 27.8. Calc. for C₆H₂₅Cl₄CoN₄O₂: weight loss, 28.0%).

**trans-Dichlorobis(-)propylenediaminecobalt(III) chloride hydrochloride dihydrate.** - As described by Dwyer, Garvan and Shulman, commercial propylenediamine was converted, via the (+) tartrate, to (-)-propylenediamine, [α]_D in benzene = -34°. The desired cobalt(III) compound was then prepared by a method similar to that used for the racemic derivative above (Found: C, 18.5; H, 6.01; Cl, 36.3; N, 14.7; weight loss, 28.1. Calc. for C₆H₂₅Cl₄CoN₄O₂: C, 18.7; H, 6.23; Cl, 36.9; N, 14.5; weight loss, 28.0%).

**trans-Dichlorobisethylenediaminerhodium(III) chloride hydrochloride dihydrate.** - A saturated solution of trans-dichlorobisethylenediaminerhodium(III) chloride in concentrated hydrochloric acid at 90°C. was allowed to cool slowly to room temperature, during 3 hr., and then further cooled in ice. The shiny yellow plates of the separated compound were collected and dried (CaCl₂). The yield was 87% (Found: ionic Cl⁻, 18.3; weight loss, 26.6. C₄H₂₁Cl₄N₄O₂Rh, [Rhen₂Cl₂]Cl.HCl.2H₂O requires ionic Cl⁻, 17.7; weight loss, 26.9%). Ionic halide in this and subsequent analyses denotes the halide precipitated from aqueous solution of the compound by silver nitrate. Control experiments showed that no silver chloride was precipitated from an aqueous solution of trans-dichlorobisethylenediaminerhodium(III) nitrate at 20°C. in twenty minutes; only a slight opalescence was observed.
The compound was also obtained in a similar way from a hot solution of trans-dichlorobisethylenediaminerhodium(III) nitrate in concentrated hydrochloric acid. The infra-red spectrum in this case proved the absence of nitrate ions. This constitutes the best way of obtaining the pure trans-isomer from the trans-isomer contaminated with cis-isomer, since the hydrogen chloride adduct is the most insoluble species present.

trans-Dibromobisethylenediaminerhodium(III) bromide hydrobromide dihydrate. - This compound was obtained by allowing a solution of trans-dibromobisethylenediaminerhodium(III) nitrate in 1:1 hydrobromic acid at 80°C. to cool slowly over 5 hours. (The container was placed in an oven at 85°C. which was then switched off.) The orange-yellow plates of the desired compound were collected (52% yield) (Found: ionic Br⁻, 27.5; total Br, 54.8; O, 5.5. C₄H₂Br₂N₂O₂Rh, [Rhen₂Br₂]Br·HBr·2H₂O, requires ionic Br⁻, 27.6; total Br, 55.2; O, 5.6%).

trans-Dichlorotetrapyridinerhodium(III) hydrogen chloride dihydrate. - This was prepared by the literature method, as yellow flat plates (Found: ionic Cl, 11.6; weight loss, 18.1. Calc. for [Rhpy₂Cl₂]Cl·HCl·2H₂O: ionic Cl, 11.9; weight loss, 18.1%).

trans-Dichlorobisbipyridylrhodium(III) chloride hydrochloride dihydrate. - A mixture of dichlorobisbipyridylrhodium(III) chloride (0.5 g.), prepared by the literature method, and concentrated
hydrochloric acid was kept at 90° for 8 hr., allowed to cool, and the hydrochloric acid replaced with fresh acid. The mixture was again heated to 75° and kept at this temperature for 6 hr., with occasional shaking. The desired compound (yellow plates) was collected by filtration, washed with concentrated hydrochloric acid and dried (CaCl₂). The yield was 0.53 g. (Found: ionic Cl, 11.9; weight loss, 18.3. C₂₀H₂₁Cl₄N₂O₂Rh, [Rh(bipy)₂Cl₂]Cl·HCl·2H₂O, requires ionic Cl, 11.9; weight loss, 18.2%).

cis-Dichlorobisethylenediaminechromium(III) chloride hydrogen chloride dihydrate. — The method in the literature for preparing the cis-dichlorobisethylenediaminechromium(III) cation is inconvenient, so a much more rapid, small-scale method was developed, based on an observation by Pfeiffer. cis-Dichlorobisethylenediaminechromium(III) chloride (1.2 g., 5 x 10⁻³ mole) in water (12 ml.) was treated with mercuric chloride (2.72 g., 10⁻² mole), and the mixture allowed to evaporate to dryness on the steam-bath. Concentrated hydrochloric acid (5 ml.) was added, and the mixture kept on the steam-bath for 15 min., with occasional stirring. The mixture was filtered hot, and the green filtrate rapidly cooled to 20°, when mercuric chloride crystallized and was removed. The green filtrate was kept in a closed container overnight, when plate-like green crystals of the desired adduct were formed. These were collected, and washed with 1:1 hydrochloric acid (0.5 g., 32%) (Found: Cl, 40.2; O, 8.9; weight loss, 30.5. Calc. for C₄H₂Cl₄CrN₂O₂: Cl, 40.4; O, 9.1; weight loss, 30.8%).
The system trans-dibromotriethylentetraminecobalt(III) bromide-hydrogen chloride. - The product of reacting\textsuperscript{51} cis-dichlorotriethylentetraminecobalt(III) chloride with constant boiling hydrobromic acid was collected. The properties of the very dark green product obtained agreed closely with those reported.\textsuperscript{51} The formulation trans-[CotrienBr\textsubscript{2}]Br, HCl given\textsuperscript{51} is inaccurate; the infra-red spectrum of the dried material showed a strong band at 3550 cm\textsuperscript{-1}, due to water. Oxygen was present (Found: 0, 3.0\%). When examined under the microscope, the material was seen to be a mixture of two components, the major being green-black, and the other (15\%), colourless needles.

Other [MA\textsubscript{4}X\textsubscript{2}]X species. - No adducts were obtained from attempts on a variety of cis-[MA\textsubscript{4}X\textsubscript{2}]X with HX. In general, beautiful crystals of the original cis-compound were obtained. trans-Compounds from which no success resulted were trans-[Co(NH\textsubscript{3})\textsubscript{4}Cl\textsubscript{2}]Cl, trans-[Copy\textsubscript{4}Cl\textsubscript{2}]Cl, trans-[Co(NH\textsubscript{3})\textsubscript{4}Br\textsubscript{2}]Br, and trans-[Rh(NH\textsubscript{3})\textsubscript{4}Cl\textsubscript{2}]Cl.

Weight loss at 110°C. - The products of heating the adducts were the anhydrous compounds, except in the cases of trans-[Co(pn)\textsubscript{2}Cl\textsubscript{2}]Cl. HCl.2H\textsubscript{2}O, where with both (±) and (-) propylenediamine as the ligand, the product was the cis-isomer. trans-[Rhen\textsubscript{2}Br\textsubscript{2}]Br.HBr.2H\textsubscript{2}O readily decomposed when heated, and bromine was evolved. The nature of the residual solid is not known. The anhydrous precursors of the adducts could always be obtained by either precipitating a solution of the adduct in 95\% alcohol with ether, or by washing the adduct with hot alcohol.
8. **Complexes of Dimethylglyoxime with Cobalt(III).**

Conductivities were measured with a Mullard type E 7576 bridge, with a dipping cell, and were corrected for the conductivities of solvents.

**trans-Nitrobisdimethylglyoximato-aquo-cobalt(III).** - This was prepared by the literature method, and recrystallized from dilute acetic acid, as brown needles (Found: C, 27.1; H, 4.7; N, 19.6. Calc. for $\text{C}_8\text{H}_6\text{CoN}_5\text{O}_7$: C, 27.2; H, 4.51; N, 19.8%). $\Lambda = 4.2$ mhos ($10^{-3}$ M in water). The n.m.r. spectrum in dimethylformamide (5-mm. o.d. spinning tube) showed lines due to the intramolecularly hydrogen-bonded protons (1042 c/s below TMS, $\gamma$ -8.45), to co-ordinated water (202 c/s, $\gamma$ 6.42) and to the methyl protons of the dimethylglyoximate ligands (137 c/s, $\gamma$ 7.57).

**trans-Dinitrodimethylglyoximato(dimethylglyoxime)cobalt(III).** - This was obtained by the literature method (Found: C, 24.9; H, 4.0; N, 22.3. Calc. for $\text{C}_8\text{H}_5\text{CoN}_6\text{O}_8$: C, 25.1; H, 4.0; N, 22.0%).

**Sodium trans-dinitrobisdimethylglyoximatocobaltate(III) monohydrate.** - The compound was obtained as yellow crystals by the literature method (Found: C, 22.9; H, 3.7. Calc. for $\text{C}_8\text{H}_4\text{CoNaN}_6\text{O}_9$: C, 22.8; H, 3.8%). $\Lambda = 64.7$ mhos ($10^{-3}$ M in water). The compound was kept at 100°C. for 24 hr., but the composition was unaffected; in particular, no water was lost.
Ammonium trans-dinitro bisdimethylglyoximato-cobaltate(III). - This salt was prepared by the literature method\textsuperscript{90} (Found: C, 24.3; H, 4.4. Calc. for \(C_6H_6CoN_7O_8\): C, 24.0; H, 4.5%). \(\Lambda = 87.4\) mhos (10\(^{-3}\) M in water).

trans-Chloro-bisdimethylglyoximato-pyridinecobalt(III). - This non-electrolyte was made by the method of Tchugaev\textsuperscript{91} (Found: C, 38.4; H, 4.7; N, 17.1. Calc. for \(C_{13}H_{19}ClCoN_5O_4\): C, 38.7; H, 4.7; N, 17.4%). \(\Lambda = 0\) mhos (10\(^{-3}\) M in nitrobenzene); \(\Lambda = 6.9\) mhos (10\(^{-3}\) M in water). In dichloromethane, dimethylsulphoxide, or dimethylformamide, the compound was sufficiently soluble for the proton resonance of the intramolecularly hydrogen-bonded protons to be observed in 5-mm. o.d. spinning tubes, although the solution in dimethylformamide was too weak for accurate measurement. The compound was recovered unchanged from dichloromethane, and almost certainly from dimethylsulphoxide. Lines due to pyridine were observed in two groups in the n.m.r. spectrum as found\textsuperscript{92} in other complexes containing co-ordinated pyridine. In \([\text{Co(DMG)}_2\text{pyCl}]\), they were (i) at 506, 518 and 534 c/s below TMS (\(\tau \approx 1.04, 0.82, \text{ and } 0.54\)), and (ii) 627 and 637 c/s (\(\tau = -1.11 \text{ and } -1.13\)). The methyl protons in the dimethylglyoximate ligands gave a resonance at 177 c/s (\(\tau = 6.86\)).

Trisdimethylglyoximato-cobalt(III). - The method\textsuperscript{93} given in the literature was followed. The complex, which readily decomposes in boiling ethanolic solution, was obtained as golden-yellow needles
It was observed that, if in the course of recrystallization from dilute acetic acid the solution was boiled for longer than a very few seconds, a dark-brown insoluble compound was produced which was quite stable in air, diamagnetic, and most likely polymeric, since it dissolved completely only in glacial acetic or formic acids. The infra-red spectrum showed the presence of acetate groups and dimethylglyoximate radicals. Analytical data (Found: C, 27.8; H, 5.5%) suggested the presence of two dimethylglyoximate radicals per cobalt atom. When the compound was treated with concentrated hydrochloric acid, the known green compound trans-dichlorodimethylglyoximatodimethylglyoximecobalt(III) was obtained, identified by its infra-red and electronic spectra.

trans-Chlorobisdimethylglyoximato-amminecobalt(III). - This was prepared by the method given in the literature (Found: C, 28.3; H, 5.0; N, 20.8. Calc. for C₈H₇CoN₅O₄: C, 28.13; H, 5.0; N, 20.5%). \( \Lambda = 4.9 \text{ mhos (}10^{-3}\text{ M in water}) \). The compound was unaffected by keeping at 100°C. for 14 days.

trans-Bisdimethylglyoximato-di-amminecobalt(III) chloride pentahydrate. - This salt was prepared by the reported method, and recrystallized from water. \( \Lambda = 134.4 \text{ ohms (}10^{-4}\text{ M in water}) \) (Found: C, 21.1; H, 6.4; Cl, 7.8. Calc. for C₈H₃OClCoN₅O₄: C, 21.4; H, 6.7; Cl, 7.9%).
Deuteration procedures. Compounds were simply allowed to recrystallize from heavy water, except in the case of 
\([\text{Co(DMGd)}_2(\text{NO}_2)(\text{D}_2\text{O})]\), where DMGd represents the mono-deuterated anion of dimethylglyoxime. Dinitro-dimethylglyoximato-dimethylglyoxime-cobalt(III) (0.3 g., \(7.9 \times 10^{-4}\) mole) was warmed with an excess of deuterium oxide (5 ml.) at 80° for 15 min.; the resultant brown precipitate showed only a weak band at 3500 cm\(^{-1}\), but a fairly strong band at 1770 cm\(^{-1}\), and was thus mainly \([\text{Co(DMG)}_2(\text{NO}_2)(\text{D}_2\text{O})]\). The product was recrystallized twice from heavy water (2 ml.) containing acetic anhydride (0.1 g.). After the first recrystallization, the band at 3546 cm\(^{-1}\), due to free OH, had disappeared and the band at 1770 cm\(^{-1}\), due to the hydrogen-bonded protons, had become rather weak. After the second recrystallization, the band at 1770 cm\(^{-1}\) was not observed; the product was thus \([\text{Co(DMGd)}_2(\text{NO}_2)(\text{D}_2\text{O})]\), and showed a band due to co-ordinated D\(_2\)O at 2530 cm\(^{-1}\), and a band due to O—D—O at ca. 1200 cm\(^{-1}\).


**trans-Dichloro(dimethylglyoximato)dimethylglyoximerhodium(III).**

This monobasic acid was made by treating rhodium trichloride in aqueous solution with dimethylglyoxime in alcoholic solution; on heating, a yellow precipitate of the desired compound is obtained; this was collected, washed with water, and recrystallized from copious hot water (Found: Cl, 18.3. Calc. for C\(_8\)H\(_{15}\)Cl\(_2\)N\(_4\)O\(_4\)Rh: Cl, 18.2%). The
ammonium and guanidinium salts were prepared by the literature method; their infra-red spectra are recorded in the Discussion section. Electronic spectra of all three compounds were determined (1.2 - 1.4 \times 10^{-3} \text{M in water}). The silver salt was prepared also, and its infra-red spectrum taken.

**trans-Bis(dimethylglyoximato-di-amminerhodium(III) chloride pentahydrate.** - This was prepared by a modification of the method of Tchugaev and Lebedinski: chloropentamminerhodium(III) chloride (0.56 g.), dimethylglyoxime (0.66 g.), ammonium acetate (1.2 g.), and water (14 ml.), were heated overnight at 150°C in a sealed tube. After cooling, the solution was filtered (leaving 0.085 g. of dimethylglyoxime unreacted, identified by m.p. 240°C.) and the filtrate evaporated to dryness; the yellow product was recrystallized from water, collected, washed with a little water and dried in air at 100°C. (Found: C, 18.9; H, 5.8; N, 16.6. Calc. for C_8H_{30}ClN_6O_9Rh: C, 19.5; H, 6.1; N, 17.0%).

\[ \lambda = 122 \text{ mhos} \ (10^{-3} \text{M in water}). \] The electronic spectrum (3.1 \times 10^{-3} \text{M in water}) showed \( \lambda 335, \epsilon 214.0; \lambda 266, \epsilon 1230.0. \)

**Attempted substitution reactions.** - According to the literature, when \([\text{Rh(DMG)(DMGH)Cl}_2]\) is refluxed in aqueous solution with an excess of ammonium thiocyanate, the product is \(\text{NH}_4[\text{Rh(DMG)}_2(\text{SCN})\text{Cl}].\) This reaction was repeated, but the yellow-brown crystals obtained were actually \(\text{NH}_4[\text{Rh(DMG)}_2\text{Cl}_2],\) identified by the identity of the infra-red spectrum with that of an authentic sample; in particular, no absorption
due to the thiocyanato group was found. Bands occur (in cm\(^{-1}\)) at
3120, 2610w,b, 2100w,b, 1848w,b, 1656w,b, 1520, 1235s, 1118s, 1074s,
998w, 976m, 840m and 733s. When the product was warmed (70\(^\circ\)C.) with
1:1 hydrochloric acid, crystals of the original \([\text{Rh(DMG)(DMGH)}\text{Cl}_2]\) were
obtained. A similar result was obtained with pyridine; in this case,
the beautiful light-brown crystals obtained were the pyridinium salt of
the original acid, and, again, on treatment with hydrochloric acid,
\([\text{Rh(DMG)(DMGH)}\text{Cl}_2]\) was regenerated. Authentic pyridinium trans-dichloro-
bridimethylglyoximatoorthorhodinate(III) is very readily prepared by allowing a
solution of \([\text{Rh(DMG)(DMGH)}\text{Cl}_2]\) in pyridine to stand in the cold; after
14 days, large brown crystals of the desired compound are obtained
(Found: C, 32.8; H, 4.2; N, 14.9. \(\text{C}_3\text{H}_{20}\text{Cl}_2\text{N}_5\text{O}_4\text{Rh}\) requires C, 32.2;
H, 4.1; N, 14.5%).

Deuteriation. - The complex \([\text{Rh(DMG)(DMGH)}\text{Cl}_2]\) (0.1 g.) was
suspended in heavy water (3 ml.), and the suspension refluxed for 15 min,
then filtered hot. On cooling, yellow crystals were obtained, which
were almost completely deuterated \([\text{Rh(DMG)(DMGD)}\text{Cl}_2]\) from their infra-red
spectrum.

Dichloro-cyclohexanedioximato-cyclohexanedioximerhodium(III). -
Rhodium trichloride trihydrate (0.2 g.) in water (1 ml.) and ethanol
(9 ml.) was treated with cyclohexane-1,2-dionedioxime (0.3 g.) in
ethanol (10 ml.). The mixture was boiled for 1 min., then cooled
rapidly, when yellow crystals appeared. These were collected, and
recrystallized from copious amounts of hot water. Yield 0.2 g. 
(Found: C, 31.5; H, 4.3; N, 12.5. C_{12}H_{18}Cl_2N_4O_4Rh requires C, 31.6; H, 3.9; N, 12.3%). The compound, though soluble in alcohol, reacts rapidly with it when hot. Its infra-red spectrum shows bands at 3215s, 1611m, 1572m, 1511s, 1340m, 1305m, 1252w, 1227s, 1047s, 978s, 932w, 915m, 810m, and 751m cm\(^{-1}\). When treated with sodium borohydride in a water/ethanol mixture (1:10), a blue compound is obtained, analogous to the reaction observed with the dimethylglyoxime compound.

10. Miscellaneous Experiments.

Dichlorobis(bipyridyl)rhodium nitrate. - This was prepared by the literature method\(^49\) with the following slight modification which improves the yield: rhodium trichloride (0.2 g.) and bipyridyl (0.78 g.) were fused in a tube; the mass was kept molten for 10 mins., then cooled. The tube was broken into water (150 ml.) which was then boiled for 5 mins., and filtered hot. The filtrate was kept overnight in the refrigerator after potassium nitrate (1.5 g.) had been added. The resultant slush of product, potassium nitrate, and ice, was allowed to warm to 10\(^\circ\)C., then filtered; the solid thus collected contained some potassium nitrate, but after recrystallization from water, pure dichlorobis(bipyridyl)rhodium(III) nitrate was obtained as yellow spangles (Found: C, 46.2; H, 2.9; N, 10.8. Calc. for C_{20}H_{16}Cl_3N_4Rh: C, 46.0; H, 3.1; N, 10.7%). The electronic spectrum showed bands at
The infra-red spectrum showed bands (in cm\(^{-1}\)) at 3400s, 1651m, 1608s, 1493sh, 1350s, 1160s, 1106m, 1078m, 1040m, 895w, 832m, 778s, 769s, and 729s. In view of the bands at 3400 and 1651 cm\(^{-1}\), it appears that water of crystallization is present, and from other evidence this is probably 2H\(_2\)O. When an aqueous solution of [Rh(bipy)\(_2\)Cl\(_2\)](NO\(_3\)) was treated with a little sodium borohydride, a brown colour was observed. When a solution of sodium tetraphenylborate was added to the brown solution, a very pale brown precipitate was obtained, which was collected, washed with ice-water, and dried in a rotary drier at 16\(^{\circ}\)C. Although quite soluble in acetone, no high-field line was observed in the brown solution; however, the infra-red spectrum showed a weak band at 2014 cm\(^{-1}\), which may be due to \(\nu_{\text{Rh-H}}\).

Other indications that a hydridic species may well participate in the reduction of bipyridyl complexes of rhodium(III) were obtained. In the hope of preparing a bisbipyridyl-complex more easily, rhodium trichloride in water was mixed with bipyridyl in ethanol, both solutions being hot. A reddish precipitate formed immediately, but on addition of hypophosphorous acid a clear yellow solution at once resulted; on heating this became brown, but on cooling (even in the absence of air) yellow crystals were obtained. The infra-red spectrum showed bands at 3380m, 2300m, 1650w, 1605m, 1311m, 1248m, 1161m, 1139sh, 1126sh, 1113sh, 1075w, 1040m, 890s, vb, 773s and 729s cm\(^{-1}\). Since the
compound was found to contain phosphorus, the bands at 2300 and 890 could be due to P-H and P-O modes respectively. The compound may be recovered apparently unchanged from hot hydrochloric acid. When these yellow crystals are heated with hypophosphorous acid, a brown solution is first formed, which rapidly becomes yellow; at this stage, a definite high-field line was observed, at 1130 c/s relative to water, indicating the presence of an Rh-H bond. On cooling and standing, pale yellow crystals were obtained, apparently identical with those above.

Other "reduced" species. — (a) A solution of rhodium trichloride in hypophosphorous acid was boiled, and rapidly became yellow, as reported in the literature.\textsuperscript{72} The solution was cooled rapidly, in the absence of air, and the proton resonance spectrum examined. Apart from the P-H split resonance of $\text{H}_3\text{PO}_2$, there was a broad hump in about the position observed for t-butanol. The solution was diamagnetic, and probably contains complexes of rhodium(III).

(b) A similar experiment was performed using sodium dithionite\textsuperscript{72} as the reducing agent; the dark-red solution obtained was diamagnetic, but showed no high-field line.

(c) When sodium formaldehyde sulphoxylate was used to "reduce" slightly acidic rhodium trichloride, as described in the literature,\textsuperscript{72} a very intense red colour became apparent, the absorptions due to $d-d$ transitions in $[\text{RhCl}_6]^{3-}$ and similar ions being swamped by intense absorption rising into the ultra-violet. The dark-red diamagnetic
solution showed no high-field line. When methanol was added to the dark-red solution, a brown-red precipitate was formed, which was collected, and recrystallized from water, in which it was very soluble, by adding ethanol. It showed a broad, featureless absorption rising through the visible into the ultra-violet. The infra-red spectrum showed bands at 3400<sub>b</sub>, 2920<sub>m</sub>, 1620, 1300, 1150, 1070, 1030 and 920 cm<sup>-1</sup>. The compound contained both sodium and sulphur (Found 10.9%), and gave a solution in water which conducted electricity quite well, though no precipitates were obtained with tetra-alkylammonium or tetraphenylborate.

**Rhodium(I) species.** (a) When [Rh(DMG)(DMGH)Cl<sub>2</sub>] was allowed to reflux with alkaline 2-methoxyethanol, the solution rapidly became a beautiful purple-red. This was stable to water and air, and, assuming total conversion to the purple material, had electronic bands at 599 µ, ε 49; 559 µ, ε 33; 520 µ (sh), ε 17; 340 µ (sh), ε 450; 260 µ (sh), ε 2400 and 223 µ, ε 6,700. Extinction coefficients are calculated per g.-atom of rhodium present.

(b) **Trisacetylacetonatorhodium(III).** - This was prepared following Dwyer and Sargeson,<sup>95</sup> and recrystallized from methanol. M.p. 261<sup>o</sup> (lit.<sup>95</sup>, 260<sup>o</sup>). In ethanol (2.5 x 10<sup>-4</sup>M), electronic bands were observed at 319 µ, ε 8.83 x 10<sup>3</sup> and 260 µ, ε 7.75 x 10<sup>3</sup>. The infra-red spectrum in carbon tetrachloride solution showed absorptions (in cm<sup>-1</sup>) at: 3052w, 2978m, 2955sh, 2941sh, 2901m, 2810w, 1662m, 1565s, 1511s, 1384m, 1269m, 1201m, 1025vs, 936vs, 702m and 673s. The
n.m.r. spectrum in benzene solution was very simple, the methyl protons giving a signal at 105.0 c/s below TMS, and the -CH protons at 296.1 c/s below TMS. When rhodium(III) acetylacetonate was set to reflux with alkaline 2-methoxyethanol, a purple-red solution was obtained, whose electronic spectrum was similar to that described under (a) above.
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