STUDIES OF SOME AMINE AND RELATED

COMPLEXES OF RUTHERNIUM (III)

A Thesis presented for the Degree of
Doctor of Philosophy
in the University of London.

by
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A number of ruthenium (III) ammine complexes containing phosphate or oxalate groups have been prepared from previously known ruthenium (III) ammine compounds. In both cases only one oxyacid group could be introduced into the co-ordination sphere; and the complexes thus formed are the phosphato tetrammine ruthenium (III) and the oxalato tetrammine ruthenium (III) ion. All the other compounds prepared contain the phosphate and oxalate group in the ionised form. Attempts to prepare phosphato- and oxalato-pentammines have failed, indicating that both groups form stable complexes only - in the case of ruthenium ammines - when they act as bidentate ligands. The five-membered chelate ring formed between the metal and oxalate group was more easily formed and more stable than the four-membered phosphate - metal ring.

In connection with the above study it was necessary to investigate the various forms of ruthenium (III) chlorides, namely "commercial" - hydrated- and anhydrous-ruthenium (III) chlorides. Evidence has been found for the presence of both positively and negatively charged species, containing ruthenium, in aqueous solutions of commercial ruthenium chloride and hydrated ruthenium (III) chloride. The nature of these species has been determined by ion exchange methods. It is concluded from the evidence presented that the "commercial" ruthenium chloride which was previously
known to contain a nitrosyl group probably has structure of the type
\[ \text{[RuCl(H}_2\text{O)}_3]_3\text{[Ru(NO)Cl}_2]_4 \]. Possible structures have been proposed for the hydrated- and anhydrous-ruthenium (III) chlorides in the solid state.

Complex formation between ruthenium (III) and phosphoric acid has been investigated and ion exchange methods have shown the presence of both cationic and anionic complex phosphates of ruthenium (III). The existence of mixed chloro-phosphato ruthenium complexes has been also indicated. Possible structures for the complex phosphates have been suggested.
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SECTION 1.

GENERAL INTRODUCTION
1.1. Introductory

The present work is concerned with the preparation and properties of ruthenium compounds, most of which belong to the class of complex or co-ordination compounds. To understand, and account for, the properties of these substances a knowledge of co-ordination chemistry is obviously necessary; and in the present section the general principles governing the formation and nature of co-ordination compounds is outlined.

The concept of co-ordination compounds was first introduced by Werner in 1891. His theory was put forward to account for the phenomenon by which apparently stable molecules, capable of independent existence, can combine to form "molecular complexes". He suggested the possible existence of two types of valency, primary or ionizable valency and secondary or non-ionizable valency. The atoms held by the secondary valency are directly attached to the central ion forming a co-ordination sphere around it, whilst the ones held by primary valency are in the outer or ionization sphere. Neutral molecules or ions are co-ordinated around the central atom in the inner sphere, the number of these groups is the "co-ordination number" of the central ion, which is a fixed maximum number for each metal. While six and four are the most common co-ordination numbers, two, three, five, seven and eight are also known. He stated that if the co-ordination number is six, the groups occupy the corners of a regular octahedron, whilst if the co-ordination
number is four, either a tetrahedral or a planar configuration is possible. The assignment of definite positions in space to the groups, is one of the most important features of his theory. It provided an explanation for the existence of known isomeric compounds and also predicted the possible existence of hitherto unknown isomers.

The theory of co-ordination was further developed by Kossel (1920) and by Sidgwick (1923), each giving a different explanation for the formation of complex compounds. Kossel postulated that complexes are held together by the electrostatic attraction between oppositely charged ions and dipolar molecules. For example, in \([BF_4]^-\) or in \([\text{Fe(H}_2\text{O)}_6]^3+\) the constituents of the complex ion are held together by electrostatic forces. From considerations of elementary electrostatics he suggested that metal ions with high ionic charge and small ionic radius would form co-ordination compounds of greatest stability. This ionic model leads to a linear molecule for co-ordination number two, a planar structure for co-ordination number three, a tetrahedral molecule for co-ordination number four and a regular octahedron for co-ordination number six. Deviations from these have been attributed to polarisation effects.

Sidgwick interpreted co-ordination by introducing the concept of co-ordinate link defining it as a special case of covalent link, when both the electrons forming the bond are furnished by only one of the atoms concerned. However, when once the link is formed it is not different from...
the ordinary covalent bond. According to this theory a co-ordinate bond can be formed between any atom or ion which can furnish a pair of electrons (the donor), and any atom or ion, which can accept a pair of electrons (the acceptor). The donor may be part of a neutral molecule, such as nitrogen in ammonia, or oxygen in water, or part of an ion such as chloride or oxygen in the carbonate ion. Two or more types of donors may be present simultaneously and the complex may be a positive ion, like \( [\text{Ru(NH}_3\text{)}_6]^{3+} \), or negative ion, like \( [\text{Ru(NO)}\text{Cl}_5]^{3-} \), or a neutral molecule, like \( [\text{Ru(NH}_3\text{)}_2\text{Cl}_2]^{-} \). A donor atom having more than one pair of unshared electrons may combine with two metallic ions, thus binding them into a binuclear compound, for example \( [\text{Cl}_2\text{Ru} - \text{O} - \text{RuCl}_5]^{4-} \). There are cases when two or three "bridge" groups are present. If the co-ordinating molecule has two or more donor atoms, these may co-ordinate with the central ion to form a chelate ring. The stability of co-ordination is greatly enhanced by this chelation effect if the resulting ring is of suitable size. Sidgwick has postulated that the central ion of a complex will share electron pairs with the co-ordinating groups until the electronic configuration of the next higher inert gas is achieved. Ephraim has shown, however, that there are numerous complexes, some of which are very stable, where the number of electrons either does not attain or else exceeds the inert gas shell. He concluded, therefore, that an additional important tendency is the production of symmetrical structure irrespective
of the actual number of electrons involved. Although both of these theories have played an important part in the development of co-ordination chemistry, their interpretation of the formation of complexes is not entirely satisfactory. Kossel's model does not account for the formation of complexes with covalent link; whilst Sidgwick's picture of electron donation suggests an improbable accumulation of negative charge on the central ion. Furthermore, the electron pair available for co-ordination in many neutral molecule is the 2s$^2$ pair, which has no bonding characteristics, and to excite it to a higher level would require much more energy than is usually available in bond formation.

The answers to these problems were given by Pauling by the introduction of the concept of hybridised bond orbitals. He has shown that the availability of d, s and p orbitals of similar energy leads to the formation of hybrid orbital sets. His calculations indicate that the hybridisation process results in the formation of stronger bonds than would result from bonding with pure unhybridised orbitals. He has shown that a set of six equivalent bonding orbitals can be obtained by d$^2$sp$^3$ hybridisation and that these hybridised orbitals are directed towards the corners of a regular octahedron. A tetrahedral arrangement of orbitals around a central ion may be obtained by sp$^3$ hybridisation. When only one d orbital is available for bond formation d$^2$sp$^2$ hybridisation occurs and the resulting equivalent hybridised orbitals are directed in space toward the corners of
This theory provides a suggestive explanation of the experimental facts, and in particular of magnetic susceptibilities of the coordination compounds.

An interesting and useful method, for theoretical treatment of certain properties of complexes and crystals, is given by the "Ligand Field Theory". It has been mainly applied to octahedral complexes and especially in the discussion of their absorption spectra and magnetic properties. This theory is based on an ionic model in which a central transition-metal ion is surrounded by electric charges which may be either ions or electric dipoles. In the simple model covalent binding between the metal ion and the ligands is neglected.

In the free metal ion the nonbonding d electrons are distributed in five d orbitals, which are all degenerate. If six ligands are now allowed to approach the metal ion to form an octahedral complex then these electrons will suffer a repulsive force due to the electric fields of the ligand electrons. This results in an increase in energy of the d electrons of the metal. However, this increase is not uniform for all the electrons, since some will be nearer to the ligands and hence will be repelled more than others. In the octahedral complex this effect splits the nonbonding d orbitals into two different energy levels. This is known as the Ligand Field Splitting. If the splitting is large the nonbonding electrons tend to pair up in the lower energy level and hence produce
spin paired complexes. These complexes will possess magnetic moments lower than that of the free ion. Ligands causing a large splitting are in general those of low electronegativity or high polarizability. On the other hand, if the splitting is small then the metal electrons will tend to remain unpaired, and hence the complex will exhibit magnetic properties similar to those of the simple ion. Small energy separation is caused by ligands of high electronegativity or low polarizability.

Theories of co-ordination are still in a state of development, quantum mechanics now provide the framework for solution of valence problems. However, this approach is extremely complex unless many simplifying assumptions are made; therefore the simple molecular models suggested by Kossel, Sidgwick and others are still of great importance in correlating facts and theory. The various theories can be regarded as alternative explanations, each useful in its own sphere.
1.2. Chemistry of Ruthenium

Ruthenium belongs to group VIII of the periodic table being the first member of the platinum metals. Together with osmium it is relatively unknown compared to the other members of the group. The metal itself, which has an atomic weight of 101.1 and atomic number of 44, possesses properties similar to those of the other platinum metals, such as high melting point, great inertness towards acids and oxidising agents, catalytic power, etc. Being a second row transitional element it exhibits a great variety of valence states, from 0 to 8. The tervalent state is the most important one and that is from which the great majority of its compounds are derived. The simple compounds can rarely be isolated in a pure state, and as is usual with the platinum metals even the apparently simple salts are probably complex in nature, which explains why so many of them occur in different isomeric modifications. The complexes, on the other hand, are relatively well defined substances and some of them are very stable.

The electronic configuration in the tervalent state is $4s^2 4p^6 4d^5$ which permits the formation of either an octahedral $d^2 sp^3$ complex or a tetrahedral $sp^3$ complex. It is known, however, that among the transitional elements of the second row, the formation of octahedral bonds is usually favoured. In fact, in most of its complexes ruthenium (III) possesses a co-ordination number of six. On theoretical grounds it is
expected that the six-covalent complexes would be paramagnetic, and so far as the compounds have been examined it is so.

Amongst the "simple" halides of ruthenium (III) the chloride is the easiest compound to obtain in the pure state. Attempts to prepare the tri-fluoride have failed. However, complex fluorides, such as $K_2RuF_6^+$ and $K_2RuF_8^-$, have recently been reported and are the only known fluoro compounds of ruthenium. The tribromide has not been obtained in a pure state and the iodide, $RuI_3$, which is a black sparingly soluble substance, is not stable but is readily oxidised with the separation of iodine.

There are two main methods for the preparation of the chloride: (a) by the action of chlorine on the metal at high temperature in the presence of carbon monoxide, which probably catalyses the reaction by the formation of intermediate carbonyl compounds, and (b) by the evaporation of a solution of ruthenium tetroxide with hydrochloric acid. The two products obtained by the two methods mentioned above differ greatly in their physical and chemical properties and their nature has been much debated in the literature. The one, prepared by the "dry method", is a shiny black crystalline compound which is very inert and insoluble in organic or inorganic solvents. It is attacked, however, by concentrated ammonia, ethylene diamine, etc. The compound prepared by the "wet way" is a dark brown amorphous powder. It is very hygroscopic and readily
dissolves in water or alcohol. Some authors formulated this form as the trihydrate RuCl$_3$.H$_2$O$^5$, some as the monohydrate RuCl$_3$.H$_2$O$^6$, whilst it was also suggested that it is a mixture of ruthenium (III) and ruthenium (IV) chlorides$^7$. On the basis of the results of conductometric studies it was suggested that freshly prepared solutions contain no ionised chloride$^6$, and the chlorides are gradually split off by standing or heating the solution. To account for the colour change, from green to yellowish brown, of these solutions, it was suggested that the ion $[\text{RuCl}_2(\text{H}_2\text{O})_2]^{2+}$ is present in cis and trans isomeric forms. Recent investigators have reported that they obtained a soluble crystalline modification of RuCl$_3$, simultaneously with the insoluble form, by high temperature chlorination of the metal$^8$.

Ruthenium (III) forms numerous complex chlorides, pure chloro, aquo chloro and hydroxo chloro complexes. They are of the general types: $[\text{RuCl}_4]^{-}$, $[\text{RuCl}_5.\text{H}_2\text{O}]^{2-}$, $[\text{RuCl}_5]^{2-}$, $[\text{RuCl}_6]^{3-}$. These halide complexes show a strong tendency to hydrolyse and replace the halogen atoms with water or hydroxyl group in the co-ordination sphere. They are stabilised, however, by the introduction of a nitrosyl group to the central atom, thus $[\text{Ru(NO)}\text{Cl}_5]^{2-}$ is stable even in hot solutions. The free acid formed from the $[\text{RuCl}_4]^{-}$ ion has been reported to occur in two isomeric forms, which might be the cis and trans forms of the diaquo complex $[\text{RuCl}_4(\text{H}_2\text{O})_2]^{11}$. Aquo penta bromides are also known, but the existence of similar iodo complex...
is not mentioned in the literature. However, the fact that the insoluble ruthenium iodide dissolves in solutions of potassium iodide to a certain extent, suggests that some sort of complex formation must take place.

Ion exchange studies of solutions, containing ruthenium (III) and chloride ion, suggested the presence of $\text{Ru}^{3+}$, $(\text{RuCl})^{++}$ and $(\text{RuCl}_2)^+$. Potentiometric studies of the couple $\text{Ru(IV)}/\text{Ru(III)}$ in hydrochloric acid and hydrobromic acid solutions also indicated the existence of $(\text{RuX}_2)^+$ and $(\text{RuX})^{++}$ species.

Ruthenium has a very strong affinity for nitrogen, forming more nitrosyls than does any other element, and numerous ammine complexes with ammonia and organic amino compounds. It seems that it also readily coordinates with other members of group five, such as substituted phosphines and arsines to give compounds analogous to the amines. In its complex compounds ruthenium (III) bears more resemblance to cobalt and rhodium than to iron or osmium forming ammine complexes very similar to those given by Co (III) and Rh (III). The amines are amongst the most stable ruthenium(III) complexes, they cover the whole range from hexammine to triammine. They are of the general type:

\[
\begin{align*}
\text{Ru(NH}_3)_6 \text{Ru(NH}_3)_5^X \\
\text{Ru(NH}_3)_4^X \text{Ru(NH}_3)_4 \text{NO(OH)}^{++} \text{ and Ru(NH}_3)_3^X
\end{align*}
\]

where $X =$ halogen, water or hydroxyl group. The hexammines and halopentammines
are stable substances which are not easily attacked by acids, and decompose only by alkalies. The hydroxo- and aquo- pentammines cannot be isolated and exist only in solution, whilst the nitroso pentamine is a well defined solid; thus here again the introduction of nitrosyl group stabilises the complex ion. The cis and trans tetrammines are not interconvertible; they both are fairly stable to acids and produce triamine only after prolonged boiling with concentrated hydrochloric acid.

In agreement with the theory, all the amines listed above are paramagnetic with a moment of about 2 Bohr Magnetons. They are known through the work of Gleu and co-workers. Morgan and Burstall reported the preparation of "Ruthenium Red" and many of its derivatives, by the action of ammonia on insoluble ruthenium chloride. They formulated the compound as chlorotetrammine-hydroxo-ruthenium chloride hydrate: $[\text{Ru(OH)}\left(\text{NH}_2\right)_4\text{Cl}]\text{Cl.H}_2\text{O}$. The structure of this compound has been much debated since Gleu has shown that it was not identical with the tetrammines prepared by other methods, thus the formulae written above cannot be correct. Fletcher and co-workers suggested a polynuclear structure containing three ruthenium atoms joined with ammine and hydroxo bridges similarly to various cobalt complexes.

Tetrammines of ruthenium (III) containing ethylamine, ethylene diammine and pyridine have also been described. However, the results of the present work suggest that some of these compounds have polynuclear structure. Furthermore, complexes containing nitric oxide and polypyridyls
have been prepared by the action of bi-, tri- or tetra-pyridyl on potassium nitroso chlororuthenite $K_2\left[\text{Ru(NO)Cl}_5\right]$\textsuperscript{21,22}. A few representatives of the resulting complexes are: $\left[\text{NO Ru X}_3\text{dipy}^\text{t}\right]$, $\left[\text{NO Ru X}_2\text{tripy}^\text{t}\right]$, $\left[\text{NO RuX tetropy}^\text{t}\right]$. Among the oxygen complexes the oxalate derivatives are the most important. They occur both as "pure" complexes, such as $M_3\left[\text{Ru OX}_3\right]$\textsuperscript{23} and also in ammine complexes, such as $\left[\text{Ru(NH}_3)_4\text{ OX}^t\right]$\textsuperscript{t}. The acetylacetonate has long been known and a trinuclear acetate has been recently reported\textsuperscript{24}. It has the formula $\left[\text{Ru}_3(\text{OAc})_6(\text{OH})_2\right] (\text{OAc})_7 \text{H}_2\text{O}$. Complex formation between ruthenium (III) and gluconate ion has been established on the ground of polarographic and spectrophotometric studies\textsuperscript{25}. 
1.3. Purpose of the present work

It was evident from the survey of the literature reported in the preceding section that very little is known about the behaviour of ruthenium (III) ammines towards oxyacid ligands, such as phosphates, oxalates, etc. As there is a remarkable similarity between the ammine complexes of ruthenium (III), rhodium (III) and cobalt (III), it was expected that there would also be a similarity between the corresponding compounds formed by the combination of these complexes with oxy-acid ligands.

The purpose of the present work was to prepare some of these compounds and to study their behaviour in order to elucidate their structure.

It was found during the course of this investigation that the "commercial" ruthenium chloride, which served as starting material for most of the preparations, was not identical with either forms of ruthenium (III) chloride reported in the literature. Furthermore, the conclusions reached by previous workers as to the nature of these chlorides are often in conflict. Therefore, the research was extended into this field in order to acquire more information about the properties and composition of the soluble, insoluble, and "commercial" ruthenium chlorides. The preparation of pure, soluble ruthenium (III) chloride was also attempted.

In order to compare fully the behaviour of ruthenium with other tervalent metals towards phosphates as ligands, it was desirable to prepare a ruthenium phosphate as such compound has not been reported in the literature. However, while the ammine phosphate complexes could be obtained as solids, the "pure" ruthenium phosphate complexes could not be isolated from solutions. It was thus necessary to study them in solutions, and methods such as ion exchange have been used.
1.4. General Methods of Study

(a) Ion Exchange

Certain insoluble solids, when in contact with a solution containing ions, may exchange ions with this solution. The ions exchanged are of like sign and the process is known as ion exchange. For such an exchange to be possible the solid, called the ion exchanger, must contain ions of its own and for the exchange to proceed fast enough to be of practical use, the exchanger must have an open permeable structure so that ions and solvent molecules can move in and out.

Numerous substances, of both natural and synthetic origin, possess ion exchanging properties. The best known naturally occurring ones are the silicate minerals and soils. The exchange capacity of the silicates is, however, low, being only of the order of 0.03 to 1.5 meq. of cation per dry gramme of material, compared with the modern synthetic exchangers capacity of ca. 5 meq. per gramme.

The synthetic ion exchange resins consist of a cross-linked polymer network to which ionised or ionisable groups are attached. In cation exchange resins these are acidic groups and in anion exchange resins the groups are basic. Many types of resin have been prepared, such as strongly acidic (with \( \mathrm{SO}_3^+ \) group), weakly acidic (with \( \mathrm{COOH} \) group) cation ex-changers; strongly basic (quaternary ammonium group) and weakly or moderately basic (primary, secondary or tertiary ammine groups) anion exchangers.
The original types of cation exchangers were prepared by a polycondensation reaction of phenol or phenolsulphonic acid with formaldehyde. More recently the polymerisation resins have become very important. The cation exchangers are prepared by the sulphonation of a styrene divinyl benzene copolymer and the anion resins by chloromethylation of a cross-linked polystyrene. The chloromethyl group is subsequently treated with a primary, secondary or tertiary amine to form an exchanger of the required base strength. These modern resins have a high exchange capacity, exceptional stability and have a well defined chemical structure. Their molecular weight is very high and are, therefore, practically insoluble. They behave as hygroscopic gels, swelling and shrinking reversibly with absorption or desorption of moisture. The strongly acidic and strongly basic resins can be taken as fully ionised under all conditions and the exchange reactions between them and ionic solutions are completely reversible. Thus, if an anion resin R in form A is treated with sufficient quantity of \( \bar{B} \) (aq), it can be completely converted to form RB according to the reaction:

\[
RA + \bar{B} (aq) \rightarrow RB + \bar{A} (aq)
\]

as long as the \( \bar{A} \) released is continuously removed, e.g. in the column operation. If \( \bar{A} \) is not removed as in the batch technique, where RA is put into a limited volume of solution containing \( \bar{B} \), an equilibrium is set up:

\[
RA + \bar{A} (aq) \rightleftharpoons RB + \bar{B} (aq)
\]
\[ \text{RA} + \bar{B} \text{(aq.)} \rightleftharpoons \text{RB} + \bar{A} \text{(aq.)} \]
and the resin will exist as a mixture of forms RA and RB. This equilibriu
is reproducible and independent of the direction of the above reac
tion. The distribution of ions between the exchanger and solution
obeys the Law of Mass Action at first approximation, but is also influenced
by the selectivity or preference of the resin for one ion or the other.
Selectivity or affinity of resins can be expressed ideally as the concen-
tration ratio of ions on the resin and in solution, e.g. for the above reac
tion:

\[ K^B_A = \frac{[\overline{B}^+][\overline{A}^-]}{[\overline{A}^-][\overline{B}^+]} \]

where \( K^B_A \) is the selectivity coefficient and concentrations in the resin
phase are indicated by a bar above the symbol. However, we can arrive at
this expression by considering the resin as a concentrated solid electrolyte
solution with the resin ion large and non-diffusible. The wellknown Donnan
membrane equilibrium can then be applied. This requires that the ionic
activity product for any permeant electrolyte should be the same inside as
outside the semi permeable medium, i.e. :

\[ \overline{a} \frac{\overline{A}^-}{\overline{X}^+} = a \frac{A^-}{X^+} \]

where \( X^+ \) is the permeant cation.

For a system containing two anions \( \bar{A} \) and \( \bar{B} \) and the same cation \( X^+ \) this
becomes:
cancelling cation activities and introducing concentrations, the expression for the selectivity coefficient becomes:

\[
\frac{a^-_A \cdot a^+_X}{a^-_B \cdot a^+_X} = \frac{a^-_A \cdot a^+_X}{a^-_B \cdot a^+_X}
\]

The selectivity coefficient, calculated on this ground, shows the qualitatively correct direction of the relative affinity and the right order of magnitude, but not a quantitatively accurate value. For a given series of ions of similar type, the order of increasing affinity for the resin is generally the order of decreasing activity coefficients in concentrated solutions. Thus the factors influencing selectivity are those controlling activity in concentrated electrolyte solutions and although these are not completely known, the two main determinants seem to be the hydrated ionic radius and the polarisability of the ions.

Both column and batch methods have been used in the present work, the former for the separation of various ionic species, and the latter for the study of complex systems of ruthenium (III).

The exchangers used were the strongly acidic Zeo Karb 225 and the strongly basic DeAcidite FF resins in varying degrees of cross-linking.
(b) Conductivity measurements

Dilute solutions of electrolytes obey Ohm's Law under normal conditions. The law states that if an electromotive force of value \( E \) is applied to a conductor of resistance \( R \), then the current \( I \) which flows is:

\[
I = \frac{E}{R}
\]

(1)

The quantity \( \frac{1}{R} \) is called the conductance \( C \).

The electrical resistance is directly proportional to the length of the conductor \( l \) and inversely proportional to its cross section \( a \), e.g.

\[
R = \frac{\gamma l}{a} \text{ ohms}
\]

(2)

where \( \gamma \) is a constant, the specific resistance of the conducting material.

The specific conductance, designated by \( k \), of a given material is defined as \( 1/\gamma \) ohms\(^{-1}\) cm\(^{-1}\), thus the above expression can be written:

\[
R = \frac{1}{ka}
\]

(3)

and the conductance:

\[
C = \frac{1}{R} = \frac{ka}{l} \text{ ohms}^{-1}
\]

(4)

The equivalent conductance \( \Lambda \) is obtained by multiplying the specific conductance \( k \) by the volume \( v \) in millilitres which contains 1 g. equivalent of solute, that is by \( 1000/c \), where \( c \) is the number of gramme equivalents per litre.

\[
\Lambda = kv = \frac{1000k}{c} \text{ ohms}^{-1} \text{ cm}^{2}
\]

The term molar conductance is defined the same way except that the concentration is given in moles per litre.
It is seen from (3) that \( k = 1/aR \), where \( l \) may be taken as the distance between the two electrodes in the conductance cell and \( a \) is the area of each. For a given cell \( l \) and \( a \) are constant, and the quantity \( 1/a \) is called the cell constant.

Knowing the constant of the cell and measuring the resistance, the specific conductance and thus the equivalent or molar conductance can directly be obtained.

The equivalent conductance of many simple electrolytes is known, and these values may be compared with those obtained for complex compounds; thus providing a means of assessing the number of ions present in these substances.

In the present study, by such methods, it was possible to distinguish phosphato or oxalato complexes from the corresponding phosphates and oxalates. Furthermore, it was possible to follow the sequence of certain reactions by measuring the conductivity of the solution at various time intervals.

(c) Examination of the loss of water

The purpose of this study was to acquire information about the stability of the compounds, and to distinguish between water of crystallisation and water of co-ordination.

Co-ordination bond energy is generally greater than the energy of bonds associated with water of crystallisation; therefore the latter will
be more readily lost than the former. Thus, by measuring the loss of water at various conditions, indication as to the type of water may be obtained.

The methods used in the present work were:

(a) drying over calcium chloride or concentrated sulphuric acid in a desiccator, and

(b) heating at 90°C, 110°C and in some cases also above 110°C. Method (a) is expected to remove water of crystallisation, and method (b) would remove water of co-ordination.

In some cases, however, water was not the only volatile entity which could be lost during the process of heating. Therefore a complete analysis of the components was necessary after this treatment.

(d) Spectro photometry

The principle of this process is to allow a beam of light to pass through the solution or liquid under examination which is contained in a silica or glass cell according to the wave length used - the emergent beam enters a quartz prism or grating spectrograph; then by a suitable devise, usually a photosensitive cell, the extent of light transmission at each wavelength can be determined or read directly from the instrument.

Plotting the light transmitted against the wavelength gives curves characteristic of the substance or solution used. The absorption spectrum in the visible region is related to the colour of the substance
which arises from the energy changes associated with electronic transitions. Interaction between the solvent and solute also have an effect on the spectrum.

Since most of the ruthenium ammine complexes studied are coloured substances it seemed logical to investigate the system spectrophotometrically. However, very little information was obtained by this method because of the sparing solubility of most of the complexes prepared.
SECTION 2.

AMMINE COMPLEXES OF RUTHENIUM (III)
2.1. EXPERIMENTAL

2.1.1. Preparation of Starting Materials

The ruthenium ammine compounds used for the preparation of ruthenium (III) ammine phosphates and oxalates, and phosphato and oxalato ruthenium ammines were prepared either from hexaammine ruthenium (II) chloride or from insoluble ruthenium (III) chloride. (The preparation of the latter will be given in Section 3.1.(a))

(a) Hexaammine ruthenium (II) chloride

A concentrated solution of ammonia (25 ml.) was added to an aqueous solution of commercial ruthenium chloride (6 g. in 30 ml.) containing also ammonium chloride (12 g.). The solution was heated and zinc dust was added slowly to the strongly boiling solution, until the black solution changed colour passing through purple, finally to golden yellow colour. At this stage the hot solution was filtered off to remove the excess of zinc and a small amount of ruthenium metal which was formed during the reduction. The filtrate was cooled and the orange yellow crystals were filtered into a Buchner funnel under suction and washed with dilute ammonia until free from mother liquor. The crystals were finally washed with acetone to remove any water and placed in a vacuum dessicator over calcium chloride. All operations involving the wet solid were done as quickly as possible, as the wet compound decomposed easily changing colour to green or blue. The well dried product, when kept in a dessicator, was stable for at least a fortnight.
(b) Hexammine ruthenium (III) chloride

An excess of chlorine water was added to a freshly prepared solution of hexammine ruthenium (II) chloride (5 g.) dissolved in the minimum amount of water. The golden yellow colour of the solution disappeared and the solution became nearly colourless. At this stage it was evaporated on a water bath to about a quarter of the original volume and set aside to crystallise. The white crystals were collected in a Buchner funnel, washed with dilute ammonia and finally air dried. It was stable for any length of time.

(c) Chloropentammine ruthenium (III) chloride

Hexammine ruthenium chloride (5 g.) was boiled under reflux with 6N hydrochloric acid (100 ml.) until the solution turned deep yellow (usually 4-5 hours). Heating was stopped then and the solution was allowed to cool. The chloropentammine ruthenium (III) chloride which crystallised was separated by filtration at the pump and recrystallised, when necessary, from dilute hydrochloric acid. It was air-dried.

The compound could also be prepared directly from hexammine ruthenium (II) chloride. Hexammine ruthenium (II) chloride (5 g.) was dissolved in 6N hydrochloric acid (150 ml.) contained in a conical flask fitted with a rubber bung carrying an inlet tube from a chlorine cylinder and an outlet tube leading to a drying tower filled with calcium oxide. A stream of chlorine was passed through the solution for about 30 minutes.
During the chlorination the solution turned almost colourless and then yellow. Passage of chlorine was then stopped and the solution boiled under reflux for an hour. The solution was cooled and the crystals which were deposited were subsequently treated as described above.

(d) Cis dichloro tetrammine ruthenium (III) chloride

It was prepared from the oxalato tetrammine ruthenium (III) chloride, the preparation of which is given below (e).

Oxalato tetrammine ruthenium (III) chloride (6 g.) was boiled under reflux with 20 per cent hydrochloric acid (100 ml.) for about half an hour. The hot solution was filtered off from any unreacted material and set aside to crystallise. The orange yellow shiny crystals were collected in a Buchner funnel and recrystallised from a dilute hydrochloric acid solution in a mixture of water and ethanol 1 : 1. The product was air dried.

(e) Oxalato tetrammine ruthenium (III) chloride

Chloropentammine ruthenium (III) chloride (6 g.) was heated with concentrated ammonia until it all dissolved due to the formation of the hydroxopentammine ruthenium (III) ion. A solution of oxalic acid (2 g. in 20 ml.) was then added and the mixture heated for 30 minutes. The granular yellow precipitate was allowed to settle and the supernatant liquid was removed by decantation. The precipitate was stirred with a small amount of hot water and the liquid decanted again. It was filtered
then by suction, washed with water and finally with acetone. The pure oxalato tetrammine ruthenium (III) chloride is almost colourless.

(f) Nitroso hydroxo tetrammine ruthenium (III) chloride

It was prepared from ammonium nitroso chlororuthenite, the preparation of which follows. Ammonium nitroso chlororuthenite (6 g.) was dissolved in 1 : 1 ammonia (100 ml.) containing also ammonium chloride (5 g.). The solution was boiled until the violet colour had turned yellow. (A precipitate was formed while it was hot). It was filtered and the yellow crystals of nitroso hydroxo ruthenium chloride were washed first with dilute ammonium chloride solution and then with water. The product was air dried.

(g) Ammonium nitroso chlororuthenite

Commercial ruthenium chloride (30 g.) (preparation described in section 3.1.(a) was dissolved in water (100 ml.) and any insoluble residues were filtered off. It was heated to boiling and a saturated solution of ammonium chloride (150 ml.) was added slowly to it. Concentrated nitric acid (10 ml.) was added next, and the solution kept at 90°C for two hours. The solution was allowed to cool and the precipitated compound was filtered off. It was washed with a cold ammonium chloride solution (9 part saturated solution to 1 part of water) and finally washed quickly with water. It was dried at 110°C for 12 hours.

(h) Trans dichloro tetrammine ruthenium chloride

This was prepared from chloro-tetrammine ruthenium (III) chloride
by the following method. An excess of sodium hydrogen sulphite was added to a solution of chloropentammine ruthenium (III) chloride (5 g. in 200 ml. water) which resulted in the formation of dihydrosulphito tetrammine ruthenium (II). The precipitate of the divalent ruthenium compound was dissolved in 6N hydrochloric acid and oxidised with chlorine water. The orange yellow crystals of the trans dichloro tetrammine ruthenium chloride were filtered off and were recrystallised from dilute hydrochloric acid.

(i) **Ruthenium Red**

Insoluble ruthenium (III) chloride (2 g.) was added in small quantities to concentrated ammonia (50 ml.) at 0°C. The mixture was left at room temperature overnight, diluted with water (50 ml.) and heated at 40°C until no more solid dissolved. The purple red solution was filtered off from unreacted ruthenium chloride, evaporated to half of the volume and diluted with alcohol (200 ml.). The ruthenium red then precipitated in very fine purple crystals which were further purified by dissolving in water and precipitating with alcohol. The product was dried in a desiccator over concentrated sulphuric acid.

(j) **Chloro derivative of Ruthenium Red**

Ruthenium Red (2 g.) was treated with 2N hydrochloric acid (120 ml.)

The red colour of the solution changed instantly into brown. The mixture

*It was formulated by Morgan and Burstall as chloro tetrammino hydroxo ruthenium chloride. It was however suggested by other investigators and also from the results of the present work that the compound has a polynuclear structure.*
was warmed for several hours at 40°C and set aside to crystallise. The
brown crystalline powder was then collected and washed with a little
2N hydrochloric acid. Aqueous ammonia at once regenerated Ruthenium
Red from this derivative.

2.1.2. Preparation of phosphate complexes

(a) Phosphato tetrammine ruthenium (III) dihydrate

This was prepared from cis dichloro tetrammine ruthenium (III)
chloride by the addition of dihydrogen sodium phosphate.

Cis dichloro tetrammine ruthenium (III) chloride (3 g.) was
dissolved in water (50 ml.) and a solution of dihydrogen sodium phosphate
(1.2 g. in 10 ml.) was added in the cold, which was followed by the
addition of dilute ammonia (5 ml.). The mixture was kept in the re­
frigerator for a few days; the bright yellow crystalline precipitate
was filtered off, washed with dilute ammonia and air dried.

(b) Diaquo tetrammine ruthenium (III) phosphate

This was prepared similarly to the previous compound, except
that the mixture of cis dichloro tetrammine ruthenium (III) chloride and
dihydrogen sodium phosphate was boiled with ammonia for an hour.

Alternatively it could be prepared from phosphato tetrammine
ruthenium (III) dihydrate by suspending it in ammonia and boiling.

(c) Hexammine ruthenium (III) phosphate dihydrate

This was prepared similarly to the previous ones, except that
hexammine ruthenium (III) chloride was used as starting material instead
of cis dichloro tetrammine ruthenium (III) chloride. Hexammine ruthenium (III) chloride (3 g.) was dissolved in the minimum amount of water and a solution of dihydrogen sodium phosphate (1.2 g. in 10 ml.) was added to it in the cold. An immediate fine precipitation was observed. This precipitate coagulated on standing and the mixture was therefore set aside in the ice box for a day in order that precipitation should be complete. The pale yellow crystals of hexammine ruthenium (III) phosphate were collected in a Buchner funnel, washed with water and air dried.

(d) Nitroso hydroxo tetrammine ruthenium (III) phosphate

Nitroso hydroxo tetrammine ruthenium (III) chloride (3 g.) was dissolved in water (25 ml.) and disodium hydrogen phosphate (1.5 g.) in water (15 ml.) was added to it. The mixture was heated on the water bath for a few hours and then set aside to crystallise. The yellow precipitate was filtered under suction, washed with cold water and air dried.

(e) Hydroxopentammine ruthenium (III) phosphate

Chloropentammine ruthenium (III) chloride (3 g.) was heated with dilute ammonia until it all dissolved. This treatment converted it into hydroxopentammine ruthenium (III) chloride. The solution was now cooled and a solution of dihydrogen sodium phosphate (1.2 g. in 10 ml.) was added. The mixture was kept in the ice box for a few days. The deep yellow precipitate of the hydroxopentammine ruthenium phosphate was then filtered into a Buchner funnel, washed with dilute ammonia and air dried.
2.1.3. Preparation of oxalate complexes

(a) Dichloro tetrammine ruthenium oxalate dihydrate

This is prepared from trans dichloro tetrammine ruthenium (III) chloride. Trans dichloro tetrammine ruthenium (III) chloride (3 g.) was dissolved in the minimum amount of water and a solution of ammonium oxalate (1.2 g. in 20 ml. water) was added and the mixture was kept in the refrigerator for a few days. The brown crystalline precipitate was filtered into a Buchner funnel, washed and air dried.

(b) Oxalato tetrammine ruthenium (III) oxalate monohydrate

This is prepared from cis dichloro tetrammine ruthenium (III) chloride. Cis dichloro tetrammine ruthenium (III) chloride (2 g.) was dissolved in water (50 ml.) and heated to boiling. A solution of ammonium oxalate was then added and the solution boiled until the yellow colour turned into brown. At this stage the heating was stopped and the solution was set aside to crystallise. The brown microcrystalline powder was filtered off, washed with water and air dried.

(c) Oxalato derivative of Ruthenium Red

This was prepared from the chloro derivative of Ruthenium Red by the addition of cold oxalic acid. The brown precipitate was filtered off, washed thoroughly with water and air dried.

*When cis dichloro tetrammine ruthenium chloride was given the same treatment as the trans dichloro compound no precipitation occurred.
2.1.4. Analytical Methods

Whenever a quantitative analysis was performed, preliminary qualitative tests for the various groups expected to be present were carried out. When dealing with products described in section 2.1.3, the presence or absence of phosphate was first ascertained before any further tests or experiments were carried out. The same procedure was applied towards the oxalate group when dealing with products described in section 2.1.4.

Before analysis all the products were kept in a desiccator over calcium chloride for some time.

The following methods have been used for the determination of the constituent groups:

Ruthenium was determined gravimetrically by ignition in hydrogen and weighed as ruthenium metal. Compounds containing only volatile components apart from ruthenium (such as ammonia, chloride and water), could be directly ignited, whilst those containing phosphate or oxalate were decomposed first to the hydroxide.

Samples of the compounds containing 0.1 - 0.2 g. of ruthenium were weighed into a small quartz or silica crucible fitted with a rose lid, and connected to a hydrogen cylinder through a long thin tube. The rate of flow of hydrogen was carefully controlled by means of a needle valve and the gas stream was passed through a wash bottle containing concentrated sulphuric acid, in order to estimate the flow rate. The hydrogen was
passed through the apparatus until all air was driven out before the flame
was lit. A stream of hydrogen was passed in and the crucible was heated
first gently with a Bunsen burner. The flame was gradually increased and
the ignition was continued for 15 - 20 minutes. After that time the burner
was removed and the crucible was cooled under a slow stream of hydrogen,
transferred to a dessicator and weighed.

Compounds containing phosphate or oxalate were decomposed first
by boiling with strong sodium hydroxide solution or concentrated solution
of sodium carbonate. The precipitated oxide was filtered through a
quantitative filter paper, washed thoroughly with hot water and transferred
into a weighed crucible. The crucible was ignited then in air until all
the carbon from the filter paper had been burned away and the ignition
with hydrogen was carried out as described above.

Chloride was determined gravimetrically as silver chloride. For the de-
termination of the total amount of chloride, decomposition of the complex
was necessary in most of the cases. The decomposition was carried out as
described above for the determination of ruthenium. After filtering off
the precipitated ruthenium hydroxide, an aliquot of the filtrate (contain-
ing 0.06 - 0.08 g. chloride) was acidified with nitric acid. A slight
excess of 0.1N silver nitrate solution was then added slowly while stirring
the solution. The suspension was then heated nearly to boiling and
kept at 90°C for an hour. It was then filtered through a weighed
sintered glass crucible, washed with dilute nitric acid and weighed to constant weight. All vessels and crucibles containing silver chloride were wrapped with black paper to prevent decomposition of the silver chloride by the light.

Ionised chloride was determined by precipitation with silver nitrate from cold solution, and the precipitate was filtered as soon as it settled. Alternatively solution of the compound was passed through a cation exchange resin, and the chloride was precipitated from the effluent by the ordinary method.

Ammonia was determined volumetrically after treating the complex with sodium hydroxide in the apparatus shown in Fig.1.

A known amount of the substance containing about 0.04 g. ammonia was introduced into flask (A) and sufficient water was added to ensure that the contents of (A) would not be reduced to a small bulk during the experiment. Several pieces of porous pots were also placed in (A) to prevent bumping during the distillation.

50 ml. of 0.1N standard hydrochloric acid was pipetted into the conical flask (B) and was filled up with water to reach the lower end of tube (F). Next, 100 ml. of 10 per cent sodium hydroxide was introduced into the distillation flask through the tap funnel (C), a small portion being left in the funnel to avoid loss of ammonia through the tap.

Flask (A) was now rapidly brought to boiling by heating it with a
FIG. 1.

NITROGEN DETERMINATION APPARATUS
Bunsen burner, and then the flame was adjusted so that boiling was continuous but not too rapid. The distillation was continued until about two thirds of the liquid was distilled over. The source of heat was then removed and the tap opened. The condenser and the tube (F) were washed with distilled water and the washings collected in the conical flask (B). The apparatus was disconnected, and the excess of acid in flask (B) was titrated with 0.1N standard sodium hydroxide using methyl red as indicator.

For compounds which also contained a nitrosyl group, two nitrogen determinations were carried out. The first one was performed exactly as above to estimate nitrogen in the sample present as ammonia. The nitrosyl group was then reduced to ammonia by the method described below, and the second nitrogen determination then carried out. This later determination thus gave the total nitrogen in the sample, and from the difference of the two determinations the amount of nitrogen present as nitrosyl was calculated.

The reduction was as follows: Devarda's alloy (1.2 g.) was placed in flask (A), and a weighed sample (about 0.7 g.) of the nitrosyl compound in a suitable amount of water was introduced into the flask. The procedure thereafter was similar to the previous one except that 20 per cent sodium hydroxide was used instead of 10 per cent, and the initial application of heat was very gentle to avoid vigorous effervescence.
Phosphate was determined gravimetrically as ammonium phosphomolybdate. There are many procedures for this determination, each differing only in detail but each producing slightly different results. In any of these procedures it is advised to perform a check using potassium dihydrogen phosphate as a standard, and thus to obtain an empirical factor.

An aliquot of the test solution, containing 0.1 - 0.2 millimoles of phosphate was transferred by means of a pipette to a 400 ml. beaker. 100 ml. solution, containing 10 g. ammonium nitrate and 5 ml. concentrated nitric acid was then added and the beaker was heated to 40°C. Then 50 ml. of 3 per cent ammonium molybdate solution (also heated to 40°C) was added slowly with gentle stirring. The precipitate was left overnight and filtered into a weighed sintered glass crucible. It was washed with 75 ml. of "phosphate washing solution", containing 50 g. ammonium nitrate and 40 ml. concentrated nitric acid per litre) following by a wash with 1 per cent nitric acid. After drying in an oven at 110°C for one hour, the crucible was cooled in a desiccator and weighed.

By calibration with a known weight of analar potassium dihydrogen phosphate, the ammonium phosphomolybdate precipitate was found to contain 5.005 per cent phosphate.

Oxalate was precipitated as calcium oxalate and determined volumetrically with potassium permanganate.

The complex was decomposed by the usual method and the sodium
oxalate which was formed after the decomposition was extracted with hot water. An aliquot of this solution, containing about 0.2 g. oxalate, was added to a hot acidified solution of calcium salt. The precipitation was completed by neutralising the solution by the dropwise addition of dilute ammonia (1:1) with continuous stirring. The precipitate was filtered, washed and dissolved in hot dilute sulphuric acid. The solution was diluted with water until the acid concentration was about 0.1 N, heated to 80°C and titrated while hot with 0.1 N standard potassium permanganate.

2.1.5. Properties of phosphate complexes

The nature of the phosphate complexes, whose preparations were described in section 2.1.2., was studied by various methods in an attempt to elucidate their structures; and the formulae assigned to them were given on the basis of the results of these experiments. The methods of the investigation, together with the results obtained, are given below.

(a) Systematic chemical analyses were carried out to determine the relative amount of the constituent groups. The methods of analysis are described in section 2.1.4. and the results are summarised in Table 1.

The five complexes containing phosphate are distinguished by the reference letters A to E in this and the following tables, e.g.:

\[ A = \left[ \text{Ru} (\text{NH}_3)_6 \right] \text{PO}_4 \cdot 2\text{H}_2\text{O}; \quad B = \left[ \text{Ru} (\text{NH}_3)_4 (\text{H}_2\text{O})_2 \right] \text{PO}_4; \quad C = \left[ \text{Ru} (\text{NH}_3)_4 \text{PO}_4 \right] 2\text{H}_2\text{O}; \]

\[ D = \left[ \text{Ru} (\text{NH}_3)_4 \text{NO}_3 \right] \text{HPO}_4 \cdot \text{H}_2\text{O}; \quad E = \left[ \text{Ru} (\text{NH}_3)_5 \text{OH} \right] \text{HPO}_4 \cdot \text{H}_2\text{O}. \]
<table>
<thead>
<tr>
<th>Compound</th>
<th>Analysis of typical samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Ru</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_6$]PO$_4$ requires</td>
<td>30.30</td>
</tr>
<tr>
<td>Compound A : found</td>
<td>30.20</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_4$(H$_2$O)$_2$]PO$_4$ requires</td>
<td>33.80</td>
</tr>
<tr>
<td>Compound B : found</td>
<td>33.60</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_4$PO$_4$]2H$_2$O requires</td>
<td>33.80</td>
</tr>
<tr>
<td>Compound C : found</td>
<td>33.65</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_4$NO(OH)]HPO$_4$H$_2$O requires</td>
<td>30.60</td>
</tr>
<tr>
<td>Compound D : found</td>
<td>30.75</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_5$OH]HPO$_4$H$_2$O requires</td>
<td>31.85</td>
</tr>
<tr>
<td>Compound E : found</td>
<td>31.92</td>
</tr>
</tbody>
</table>
(b) Ion exchange methods have been used to ascertain whether the phosphate group is ionized or is acting as a ligand.

A sparingly soluble compound, when shaken with an excess of chloride form resin, will react with the resin, e.g. the phosphate will be exchanged with the chloride of the resin. On the other hand, complexes containing the phosphate group as a stable ligand group do not react with the resin under the same conditions.

In the present work insoluble ruthenium (IIl) ammine phosphates could be converted to the corresponding soluble chlorides by this treatment, whilst phosphato ruthenium (III) ammines remained unchanged.

The technique used was the following. A small quantity of the compound (0.5 g.) was suspended in water (150 ml.) and placed in a 200 ml. conical flask fitted with a rubber bung. Chloride form resin (1.2 g.) was then introduced and the conical flask and its contents were shaken for a few hours. In cases when the insoluble compound dissolved the resin was filtered off, the solution concentrated and the resulting ruthenium (III) ammine chloride could be recovered from the filtrate. When no dissolution occurred after a few hours of shaking, it was concluded that the compound was non-ionic.

The results of these experiments showed that compounds A, B, D and E all contain ionic phosphate and only compound C is non-ionic.

(c) Conductivity measurements were used to indicate the number of ions present. All the phosphate complexes are practically insoluble in water.
and therefore solutions containing them in a wide range of concentration could not be prepared. The most concentrated solutions were about 0.002 M and these were used in the following experiments. Conductivity water, prepared by the passage of distilled water through a column of mixed bed ion exchange resins, was used to prepare these solutions.

The conductance of the solutions was measured at 25°C using a Wheatstone Bridge. The cell used, which was of a glass construction with special stoppers to fit the two parallel platinum electrodes (Fig. 2), was held in a water thermostat bath at 25°C throughout the experiment. Measurements were taken at intervals until readings were constant, indicating that the temperature of the solution had reached that of the thermostat bath. Freshly prepared solutions were used in every case in order to minimize changes due to hydrolysis. The conductivity \( k \) of the solution at the particular concentration was calculated, knowing the constant of the cell \( 1/a \) and measuring the conductance \( 1/\eta \), from the formula:

\[
k = \frac{1}{a \eta} \]

from which the molar conductance \( \Lambda \) values were obtained by the help of the equation

\[
\Lambda = \frac{1000}{k/c \text{ ohms}^{-1} \text{ cm}^2 \text{ g mole}^{-1}}
\]

Measurements were also made on solutions of ruthenium (III) ammine chlorides for purposes of comparison and the results obtained are summarised in Table 1. Measurements were also taken after certain periods of time and any change observed had been recorded. From changes of the molar conductance value conclusions can be reached about the nature of the reaction that had taken place in the solution.
FIG. 2.

CONDUCTIVITY CELL

PLATINUM ELECTRODES
### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar conductance $\text{ohm}^{-1} \text{cm}^2 \text{g.mole}^{-1}$</th>
<th>No. of ions indicated</th>
<th>Molar conductance after two weeks</th>
<th>No. of ions indicated</th>
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<tbody>
<tr>
<td>$\text{cis} \left[ \text{Ru}(\text{NH}_3)_6 \right] \text{PO}_4 \cdot 2\text{H}_2\text{O}$</td>
<td>248</td>
<td>2 - 3</td>
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<tr>
<td>$\text{cis} \left[ \text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2 \right] \text{PO}_4$</td>
<td>238</td>
<td>2 - 3</td>
<td></td>
<td></td>
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<tr>
<td>$\text{cis} \left[ \text{Ru}(\text{NH}_3)_4 \text{PO}_4 \right] \cdot 2\text{H}_2\text{O}$</td>
<td>67</td>
<td>0 - 2</td>
<td>228</td>
<td>2 - 3</td>
</tr>
<tr>
<td>$\text{cis} \left[ \text{Ru}(\text{NH}_3)_4 \text{NO(OH)} \right] \text{HPO}_4 \cdot \text{H}_2\text{O}$</td>
<td>227</td>
<td>2 - 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{cis} \left[ \text{Ru}(\text{NH}_3)_5 \text{OH} \right] \text{HPO}_4 \cdot \text{H}_2\text{O}$</td>
<td>235</td>
<td>2 - 3</td>
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<tr>
<td>$\text{cis} \left[ \text{Ru}(\text{NH}_3)_6 \right] \text{Cl}_3$</td>
<td>386</td>
<td>3 - 4</td>
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<td></td>
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<tr>
<td>$\text{cis} \left[ \text{Ru}(\text{NH}_3)_5 \text{Cl} \right] \text{Cl}_2$</td>
<td>292</td>
<td>2 - 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{cis} \left[ \text{Ru}(\text{NH}_3)_4 \text{Cl}_2 \right] \text{Cl}$</td>
<td>204</td>
<td>2 - 3</td>
<td>360</td>
<td>3 - 4</td>
</tr>
</tbody>
</table>

Data are essentially in agreement with formulae assigned to the compounds. The conclusion drawn for the results of the ion exchange experiments that the phosphate present in compound $C$ is present as a ligand group is confirmed. Evidently this compound and the dichloro tetrammine ruthenium (III) ion both undergo hydrolysis when their solutions are allowed to stand.

*It is not known whether compound $D$ has a cis or trans structure as it has been prepared from a compound (nitroso hydroxo tetrammine ruthenium (III) chloride) reported in the literature without specifying whether it had a cis or trans structure.*
(d) The loss of water of the compounds was studied in order to determine whether the water present was held as water of crystallisation or water of co-ordination.

A sample (~1 g.) of the air dried compound was introduced into a crucible which had been previously dried and weighed. The crucible was then placed in a dessicator over calcium chloride and the loss of weight recorded at intervals until no further change occurred. A bottle of concentrated sulphuric acid was then placed in the dessicator and any further loss of weight recorded.

The results of these experiments showed that compounds A and C lost the equivalent of two molecules of water, compounds E and D lost one molecule of water, whilst compound B lost none. The results are given in Table 1.

(e) Spectrophotometric measurements were carried out on compounds D and E, which were dissolved in nitric acid (Compounds A, B and C were insoluble in acids). The apparatus used was a commercial spectrophotometer from which the optical density values were read directly. Measurements were made on the range of wavelength from 3600-8000Å and the molar extension coefficients were calculated on the assumption that the molecular weight are those required by the formulae given in Table 1.

Compound D possessed a strong absorption peak in the region of 3950Å and resembled the absorption spectrum of \[ \text{[Ru(NH}_3\text{)}_4\text{Cl}_2]^{2+} \] compound E showed an absorption maximum in the range of 3600Å, similar absorption peak, however, was not found in the case of \[ \text{[Ru(NH}_3\text{)}_5\text{OH}]^{2+} \text{Cl}_2. \]
2.1.6. **Properties of the oxalate complexes**

The oxalate complexes, whose preparations are described in section 1.2.3, were studied by methods similar to those applied for the study of phosphates (section 2.1.5), and the compounds were formulated on the ground of the evidence concluded from these experiments.

The results of these experiments are given below.

(a) Results of the determination of the constituent groups are summarised in Table 3. (The methods of analysis are described in section 2.1.4.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analyses of typical samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Ru</td>
</tr>
<tr>
<td>[Ru(NH₃)₄Cl₂]₂[Ox]₂,2H₂O requires</td>
<td>33.66</td>
</tr>
<tr>
<td>Compound F : found</td>
<td>33.20</td>
</tr>
<tr>
<td>[Ru(NH₃)₄[Ox]₃][Ox]₂,2H₂O requires</td>
<td>28.03</td>
</tr>
<tr>
<td>Compound G : found</td>
<td>28.25</td>
</tr>
<tr>
<td>[Ru(NH₃)₄Cl(H₂O)]₄[Ox]₂₋ requires</td>
<td>32.65</td>
</tr>
<tr>
<td>Compound H : found</td>
<td>32.45</td>
</tr>
</tbody>
</table>
(b) Ion exchange experiments showed that in compound F the oxalate is ionized while the chloride is in the co-ordination sphere; in compound G half of the oxalate present is ionized and finally, in compound H neither the chloride nor the oxalate appear to be ionic.

(c) Conductivity measurements made on saturated aqueous solution of the complexes gave the following results (Table 4). The concentration of these solutions was of the order of $M/1000$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar conductance $\text{cm}^2\text{ohm}^{-1}\text{cm}^2\text{g mole}^{-1}$</th>
<th>Number of ions indicated</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>276</td>
<td>2 - 3</td>
</tr>
<tr>
<td>G</td>
<td>222</td>
<td>2 - 3</td>
</tr>
<tr>
<td>H</td>
<td>56</td>
<td>0 - 2</td>
</tr>
</tbody>
</table>

All measurements were taken at 22°C.

(d) Examination of the loss of water showed that:

Compound F lost the equivalent of two molecules of water over calcium chloride.

Compound G lost one molecule of water, while

Compound H lost none, not even by heating to 110°C. The water was given off only above 150°C.
TABULAR RESULTS

Phosphate complexes

TABLE 5

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Reagent used</th>
<th>Probable nature of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{cis} [\text{Ru(NH}_3)_4\text{Cl}_2] \text{Cl} )</td>
<td>( \text{Na}_2\text{HPO}_4 )</td>
<td>( \text{[Ru(NH}_3)_6\text{PO}_4\cdot2\text{H}_2\text{O]} ) (A)</td>
</tr>
<tr>
<td>( \text{cis} [\text{Ru(NH}_3)_4\text{Cl}_2] \text{Cl} )</td>
<td>( \text{Na}_2\text{HPO}_4 ) in cold solution</td>
<td>( \text{[Ru(NH}_3)_4\text{H}_2\text{O}_2\text{]} \text{PO}_4 ) (B)</td>
</tr>
<tr>
<td>( \text{cis} [\text{Ru(NH}_3)_4\text{Cl}_2] \text{Cl} )</td>
<td>( \text{Na}_2\text{HPO}_4 ) in hot solution</td>
<td>( \text{[Ru(NH}_3)_4\text{PO}_4\cdot2\text{H}_2\text{O]} ) (C)</td>
</tr>
<tr>
<td>( \text{Ru(NH}_3)_5\text{OH}^-\text{Cl}_2 )</td>
<td>( \text{Na}_2\text{HPO}_4 )</td>
<td>( \text{[Ru(NH}_3)_5\text{OH}^-\text{HPO}_4\cdot\text{H}_2\text{O][_E]} ) (E)</td>
</tr>
<tr>
<td>( \text{Ru(NH}_3)_4\text{NO(OH)}^-\text{Cl}_2 )</td>
<td>( \text{Na}_2\text{HPO}_4 )</td>
<td>( \text{[Ru(NH}_3)_4\text{NO(OH)}^-\text{HPO}_4\cdot\text{H}_2\text{O]} ) (G)</td>
</tr>
</tbody>
</table>

*Analytical data are given in Table 1.

TABLE 6

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of ions expected</th>
<th>State of phosphate</th>
<th>State of water present</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ru(NH}_3)_6\text{PO}_4\cdot2\text{H}_2\text{O}] \text{Cl}_3 ) (A)</td>
<td>2</td>
<td>2 - 3</td>
<td>ionic</td>
</tr>
<tr>
<td>( \text{cis} \text{Ru(NH}_3)_4\text{H}_2\text{O}_2\text{]} \text{Cl}_3 ) (B)</td>
<td>2</td>
<td>2 - 3</td>
<td>ionic</td>
</tr>
<tr>
<td>( \text{cis} \text{Ru(NH}_3)_4\text{H}_2\text{O}_2\text{]} \text{Cl}_3 ) (C)</td>
<td>0</td>
<td>0</td>
<td>non-ionic</td>
</tr>
<tr>
<td>( \text{Ru(NH}_3)_5\text{OH}^-\text{HPO}_4\cdot\text{H}_2\text{O][_E]} ) (E)</td>
<td>2</td>
<td>2 - 3</td>
<td>ionic</td>
</tr>
<tr>
<td>( \text{Ru(NH}_3)_4\text{NO(OH)}^-\text{HPO}_4\cdot\text{H}_2\text{O]} ) (G)</td>
<td>2</td>
<td>2 - 3</td>
<td>ionic</td>
</tr>
</tbody>
</table>

a Indicated by conductivity (Table 2)
b As indicated by ion exchange
c As indicated by results of dehydration over CaCl₂ and at 110°C.
Oxalate complexes

### TABLE 7

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Reagent used</th>
<th>Probable nature of product*</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(NH₃)₅OH]Cl₂</td>
<td>(HCOOH)₂</td>
<td>[Ru(NH₃)₄ox]Cl₂ trans⁷</td>
</tr>
<tr>
<td>[Ru(NH₃)₄Cl₂]Cl</td>
<td>(NH₄)₂C₂O₄</td>
<td>[Ru(NH₃)₄ox]₂ox.2H₂O (F)</td>
</tr>
<tr>
<td>[Ru(NH₃)₄ox]Cl</td>
<td>(NH₄)₂C₂O₄</td>
<td>[Ru(NH₃)₄ox]H₂ox.2H₂O (G)</td>
</tr>
<tr>
<td>Chloro- derivative of Ruthenium Red (See section 2.1.1.j.)</td>
<td>(HCOOH)₂</td>
<td>[Ru(NH₃)₄Cl₂H₂O ox] or [Ru(NH₃)₄ox]Cl₂H₂O (H)</td>
</tr>
</tbody>
</table>

* Analytical data are given in Table 3.

** It has been previously reported¹⁷.

### TABLE 8

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of ions expected indicated</th>
<th>State of oxalate</th>
<th>State of water present</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans [Ru(NH₃)₄Cl₂]₂ox.2H₂O (F)</td>
<td>3 2 - 3 ionic</td>
<td>half ionic</td>
<td>water of hydration</td>
</tr>
<tr>
<td>[Ru(NH₃)₄ox]H₂ox.2H₂O (G)</td>
<td>2 2 - 3 half ionic</td>
<td>half ionic</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>[Ru(NH₃)₄ox]Cl₂H₂O</td>
<td>2</td>
<td>non ionic</td>
<td>not known</td>
</tr>
<tr>
<td>or [Ru(NH₃)₄Cl₂H₂O ox] (H)</td>
<td>2</td>
<td>0 non ionic</td>
<td>not known</td>
</tr>
</tbody>
</table>

(a) Indicated by conductivity (Table 4).

(b) As indicated by ion exchange.

(c) As indicated by results of dehydration over CaCl₂ and at 110°C.
2.2. DISCUSSION AND CONCLUSIONS

The preparation and properties of the phosphate and oxalate complexes of ruthenium (III) ammines are described in section 2.1, and the results of the various attempts to introduce the phosphate and oxalate groups as ligands are summarised in Tables 5, 6 and Tables 7, 8, respectively.

It is known that both phosphate and oxalate ions have donor properties due to the lone pair of electrons on the oxygen atoms. It is theoretically possible that the phosphate group should occupy one, two or three co-ordination positions according to whether it is present as $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^-$ or $\text{PO}_4^{3-}$ ion; and the oxalate group could take up one or two co-ordination positions. It was found, however, by previous workers $^{30,31}$ and in the present study that attempts to prepare complexes containing a monodentate phosphate ligand were unsuccessful. Further, it is unlikely from stereochemical considerations that it would take up three co-ordination positions. It can be concluded, therefore, that the phosphato complexes are stable only when the phosphate group takes up two co-ordination positions. Thus, even when it is present as $\text{PO}_4^{3-}$ it acts as a bidentate group forming a four-membered ring with the metal ion in the following way:

\[
\begin{array}{c}
\text{M} \\
\text{P} \\
\text{O} \\
\text{O}
\end{array}
\]

In most of the stable oxalato complexes the oxalate group occupies
also two co-ordination positions acting as a chelate ligand; and the stability of these complexes must be due to the formation of a five-membered ring with the metal ion, i.e.,

\[
\begin{array}{c}
\text{O} \\
\text{M} \\
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

In the present work it was possible to compare the relative ease of formation of phosphato and oxalato complexes of ruthenium (III) ammines, and thus to obtain a qualitative comparison of the relative stabilities of the four-membered ring (phosphate) and the five-membered ring (oxalate) structures.

2.2.1. Phosphate complexes

It is evident from the consideration of the analytical results that in all the five ruthenium ammine complexes containing phosphate there is only one (ionic or co-ordinated) phosphate group present for each ruthenium (III) ammine ion. The same results were obtained whether theoretical amount or an excess of phosphate was added to the various ruthenium (III) ammine chloride solutions. Furthermore, it proved impossible to replace an ammine by a phosphate group in either of the ammine complexes, although such replacement occurs with other ligands such as chloride or oxalate.

In the case of hexammine ruthenium (III) chloride precipitation of the phosphate occurred in the cold whether dicalcium hydrogen phosphate or
phosphoric acid was used as a precipitant. (However, better yields were obtained with the former). Thus the addition of phosphate solution did not affect the basic structure of the hexammine ion but only resulted in the replacement of the ionised chloride by phosphate.

Attempts to introduce the phosphate group as ligand into the pentammine have failed. No pure product could be isolated from the reaction mixture of the chloropentammine ruthenium (III) ion and phosphate; the hydroxopentammine ion, however, reacted with phosphates with the formation of hydroxopentammine ruthenium (III) phosphate. The phosphate group was attached in the form of $\text{HPO}_4^-$ to the divalent hydroxopentammine cation. Thus here, too, the structure of the cation remained unchanged. The analytical figures found for this compound would allow its formulation either as hydroxopentammine phosphate ($[\text{Ru(NH}_3)_5\text{OH}][\text{HPO}_4\cdot\text{H}_2\text{O}]$) as suggested above or as aquopentammine ruthenium (III) phosphate ($[\text{Ru(NH}_3)_5\text{H}_2\text{O}][\text{PO}_4^2-]$) in which case the phosphate would be present as $\text{PO}_4^{3-}$. It is known, however, that aquopentammine ruthenium (III) ions only exist in strongly acidic solutions, and the fact that the compound is prepared from disodium hydrogen phosphate ($\text{pH} \sim 9$) makes this formulation improbable.

In the case of the nitroso hydroxo tetrammine ion the same results were obtained whether solution of sodium phosphate or phosphoric acid was added, i.e. in both cases precipitation of the corresponding phosphate occurred, leaving the nitroso hydroxo tetrammine ion unchanged. On the

*not known whether cis or trans form
ground of the analytical figures this compound, too, could be formulated in
two ways, i.e. nitroso hydroxo tetrammine phosphate, as suggested above,
or aquo nitroso tetrammine phosphate. The latter formulation is, however,
unlikely for the following reasons: the aquo nitroso tetrammine ion,
similarly to the aquo pentammine ion, exists only in strongly acidic
solutions and the compound was prepared at pH~9. Furthermore, the nitroso
hydroxo tetrammine ion is an extremely stable one and it can be boiled with
dilute hydrochloric acid without bringing about any change in the co-ordina-
tion sphere. Therefore it is not likely that the addition of sodium phos-
phate would convert the nitroso hydroxo tetrammine ion into the aquo nitroso
tetrammine ion.

However, two types of tetrammines containing phosphate have been
obtained, namely phosphato tetrammine ruthenium (III) (compound C) and
diaquo tetrammine ruthenium (III) phosphate (compound B).

The formation of phosphato tetrammine ruthenium (III) was also ex-
pected when phosphoric acid was acted upon the hydroxo pentammine ruthenium
(III) ion, a reaction similar to that taking place between the above ion
and oxalic acid and which results in the formation of oxalato tetrammine
ruthenium (III) ion. However, no pure product could be isolated from the
reaction mixture of the hydroxo pentammine and phosphoric acid.

The results of ion exchange experiments have demonstrated that only
compound C contains the phosphate group as a ligand and in compounds, A,B,D
and E the phosphate present is ionised. These conclusions are in accord with those obtained from conductivity measurements (Table 2).

The molar conductivity - at a dilution of 1024 g. mole \(^{-1}\) litre or one of the same order - of an electrolyte which dissociates into two ions is expected to be of the order 100 ohms \(\text{cm}^{-1}\); and one dissociating into three ions should have a conductivity of about 200 ohm \(\text{cm}^{-1}\). The results of the conductivity measurements (Table 2) have shown the presence of two or three ions in compounds A, B, D and E in agreement with the formulae assigned to them. The values found for compound C, however, were much lower than expected for a compound giving two ions; therefore it must be non-ionic. The low conductance values observed are probably due to a slight hydrolysis which converts compound C to compound B according to the equation:

\[
\text{Ru(NH}_3\text{)}_4\text{P}_4\text{O}_4^{-} \text{in } \text{H}_2\text{O} \xrightarrow{} \text{Ru(NH}_3\text{)}_4(\text{H}_2\text{O})_2\text{P}_4
\]

i.e. the conductance is due to the diaquo phosphate.

In the phosphato tetrammine ruthenium (III) no ion should be initially present and the conductivity of the solution should rise only slowly as hydrolysis to the aquo complex proceeds. Such reactions are expected to be slow in the absence of acid or alkali. All the experimental results are in agreement with the theoretical expectations, the conductivity of the solutions of phosphato tetrammine ruthenium increases slowly, achieving approximately the same value as found for compound B after 2 weeks (Table 2).
The formation of both compound B and compound C, from the same starting material (cis dichloro tetrammine ruthenium (III) chloride) and by the use of the same reagent (sodium phosphate) for the preparation, can be explained by the following way. When phosphate is added to the ruthenium ammine solution the following reactions might occur:

\[
\text{cis} \left[\text{Ru(NH}_3\text{)}_4\text{Cl}_2\right]^+ + \text{PO}_4^{3-} \rightarrow \left[\text{Ru(NH}_3\text{)}_4\text{PO}_4\right]^0 + 2\text{Cl}^-
\]

i.e. direct replacement of the chlorides by phosphate with the formation of a chelate ring;

or

\[
\text{cis} \left[\text{Ru(NH}_3\text{)}_4\text{Cl}_2\right]^+ + 2\text{H}_2\text{O} \rightarrow \left[\text{Ru(NH}_3\text{)}_4\text{(H}_2\text{O})_2\right]^3+ + 2\text{Cl}^-
\]

i.e. hydrolysis of the dichloro tetrammine into the diaquo tetrammine ion which then reacts with the phosphate according to the equation:

\[
\left[\text{Ru(NH}_3\text{)}_4\text{(H}_2\text{O})\right]^3+ + \text{PO}_4^{3-} \rightarrow \left[\text{Ru(NH}_3\text{)}_4\text{(H}_2\text{O})_2\right]^0 + \text{PO}_4^4
\]

It is seen thus that when a solution of phosphate is added in the cold precipitation of the insoluble phosphato tetrammine ruthenium occurs before the compound hydrolyzes (equation 1); whilst when the solution is heated the cis dichloro tetrammine ion is converted first to the diaquo tetrammine ion (equation (2(a))) in which the phosphate does not replace water from the co-ordination sphere but remains in the ionised state, precipitating the diaquo tetrammine ion in the form of phosphate (equation 2(b)).

It is known from conductivity data that solutions of cis dichloro tetrammine ruthenium (III) chloride hydrolyze by standing (Table 2) and when the solution is boiled obviously this reaction must occur more rapidly (2(a)).
The facts that compound C hydrolyzes to compound B in aqueous solutions (shown by the increase of conductivity), and that it can be converted to compound B by boiling a suspension of it, demonstrate that amongst the two tetrammine phosphate complexes compound B is the more stable one. It is probable that the relative instability of compound C is caused by the steric strain of the four-membered phosphate-metal ring, and thus the formation of compound B, which is not associated with any steric strain, is thermodynamically favoured.

With the cobalt ammine phosphate complexes, too, the diaquo tetrammine phosphate appears to be more stable than the corresponding phosphate tetrammine, probably for the same (i.e. steric) reasons. Nevertheless the formation of phosphato tetrammine complexes of both metals and the absence of phosphato pentamamine complexes in each system indicates that the four-membered ring is stabilized by the usual chelate effect although not to the same extent as the five- and six-membered rings.

Studies of dehydration together with the analytical results have shown that all the phosphate complexes crystallise as hydrates. It was found that the water was lost at room temperature over calcium chloride from all the compounds except compound B. There are two alternative ways of explaining the role of water in these compounds:

(a) It is not chemically combined with the compounds but occupies voids in the lattice structure, which would be in accord with the ease of
removal of water from these compounds, and

(b) the water is linked by hydrogen bridges to the oxygen atoms of
the phosphate group. Hydrogen bonds are comparatively weak, their
energies being of the order of 5 kcal per mole. They are, therefore,
easily destroyed. It seems unlikely, however, that these bonds would be
destroyed without the application of heat and therefore the first alterna­
tive seems to be more likely. There is the additional point, however,
that the compounds are very sparingly soluble, which might indicate that
the crystal is held together by forces strong enough to resist the action
of a strongly polar solvent - hence the electrostatic forces may be
reinforced by those of hydrogen bonding.

Whilst many ruthenium (III) ammine chlorides may be dried at 110°C
without any change occurring in the structure, all the complexes containing
phosphate, except compound A, proved to be unstable at temperatures above
100°C. Therefore the preparation of phosphate complexes from the corres­
ponding hydroxo- or aquo-ammine phosphates was not possible by this method.

In this respect, too, the behaviour of the ruthenium ammine phosphate
complexes is similar to that of the corresponding cobalt compounds 31, where
also decomposition of the complex occurred before complete dehydration had
been achieved.

2.2.2. Oxalate complexes

When oxalate is added to a solution of hexammine ruthenium (III)
chloride precipitation occurs, but a pure product could not be isolated from the precipitate. The formation of an insoluble compound when the hexammine ruthenium (III) ion is treated with oxalate was also reported by Glen; however, no formula was given for the compound. No pentammine containing the oxalate as ligand could be prepared. When the hydroxo pentammine ruthenium (III) ion is treated with oxalic acid ammonia is lost with the formation of the oxalato tetrammine ion (also reported previously). This reaction demonstrates the relative stability of the five-membered chelate ring compared to that of the four-membered phosphate ring, as no phosphato tetrammine could be obtained under the same conditions. Further action of oxalate on the oxalato tetrammine ion resulted in the formation of oxalato tetrammine ruthenium (III) oxalate (Comp. Table 3), where the ionised oxalate must be present as a monobasic group, i.e. C_2O_4H.

Addition of oxalate to the trans dichloro tetrammine ruthenium (III) ion results in the precipitation of the corresponding oxalate (Comp. F Table 3) without changing the basic structure of the cation. The cis dichloro tetrammine ruthenium (III) ion on addition of oxalate, however, forms oxalato tetrammine ion (the same that is obtained from the hydroxopentammine) under the same conditions.

The results of ion exchange experiments have shown that in Compound F the oxalate is ionised and the chloride is co-ordinately linked, whilst in Compound G half of the oxalate appears to be ionic and half is in the
co-ordination sphere.

Conductivity data also support the formulae assigned to these complexes, showing the probable presence of 3 ions in Compound F and 2 in Compound G. No change of conductivity was observed with these compounds showing that they - unlike the similar phosphate complexes - do not undergo hydrolysis. This fact, too, demonstrates that the oxalata tetrammine ruthenium (III) ion is more stable than the phosphato tetrammine ruthenium (III).

Studies of heat and dehydration showed that both Compound F and G lost water readily over calcium chloride confirming that the water is held as water of hydration. Furthermore, these compounds proved to be stable to heat, heating to 100°C only resulted in the removal of water without decomposing them.

As it was pointed out in the Introduction of the present work, the structure of the "Ruthenium Red" (formulated previously as \(\text{Ru(NH}_3)_4\text{Cl(OH)}\text{Cl} \)) had been much debated since the above formula was assigned to it by Morgan and Burstall in 193618,19,20; and the correct formula has not been found yet.

Some derivatives of it have been prepared and studied in the present work in an attempt to acquire some information about the parent compound by studying these derivatives. The Ruthenium Red itself is very unstable in solutions; therefore methods used for the study of the other compounds
could not be applied in this case.

When the chloro derivative of Ruthenium Red (section 2.1.1.j) was treated with oxalic acid a precipitate was obtained which corresponded to the empirical formula \( \text{Ru}_4\text{NH}_3\text{ox.} \text{Cl.N}_2\text{H}_2\text{O} \) (Comp. H, Table 3). It could be thus described either as \( [\text{Ru(NH}_3)_4\text{ox}] \text{Cl.N}_2\text{H}_2\text{O} \) (a), or as \( [\text{Ru(NH}_3)_4\text{(H}_2\text{O})\text{Cl}] \text{ox} \) (b). The first formula should contain ionised chloride and the second should contain ionised oxalate; however, the presence of neither of them was observed. Furthermore, formula (a) is unlikely, as the compound is not identical with the previously discussed oxalato tetrammine ruthenium (III) chloride prepared by ether methods. The absence of any ionised group thus makes either of the above formulation improbable. If both oxalate and chloride were in the co-ordination sphere, the co-ordination number of the ruthenium atom would be more than six, which is not in agreement with the known stereochemistry of the ruthenium (III) ammine complexes. The low conductivity value observed suggests that the compound is not ionic. It appears, therefore, that the compound has a very complex structure which needs to be further investigated.
SECTION 3.

CHLORIDES OF RUTHENIUM (III)
3.1. EXPERIMENTAL

Three types of ruthenium (III) chlorides have been studied in the present work, e.g. (a) "commercial" ruthenium chloride, (b) hydrated (soluble) ruthenium chloride, and (c) anhydrous (insoluble) ruthenium chloride.

The commercial ruthenium chloride was used as starting material for these investigations. The latter two compounds have been prepared in the present work from a mixture of ruthenium (III) and ruthenium (IV) chlorides supplied by the Mond Nickel Company.

3.1.1. Preparation of the Compounds

(a) Commercial ruthenium chloride

It is understood that this is prepared from ruthenium metal - obtained from the platinum ore concentrates - by the following method. The metal is fused with a mixture of sodium-hydroxide and peroxide which treatment converts it into sodium ruthenate. Chlorine gas is passed into the solution of the ruthenate and the resulting ruthenium tetroxide is distilled over into 6N hydrochloric acid. The acid solution is evaporated nearly to dryness, and finally concentrated nitric acid is added to remove any traces of osmium. (Nitric acid oxidizes osmium to the tetroxide which is boiled off, but does not oxidize ruthenium). The solution is then evaporated to dryness to give a dark brown hygroscopic powder, which is very soluble in water and alcohol.
(b) **Hydrated (soluble) ruthenium chloride**

This was prepared from a mixture of ruthenium (III) and ruthenium (IV) chlorides by heating it to 120°C for a few days. By this treatment it was possible to remove the excess of chlorine and most of the water. It is a dark brown powder soluble in water but not as readily as the parent compound.

The preparation of the starting material is the following. Pure ruthenium metal, which has been obtained from ammonium nitroso chloro-ruthenite or commercial ruthenium chloride by reduction, is treated the same way as described for the preparation of commercial ruthenium chloride above, except that the treatment with nitric acid is omitted. It is a dark brown hygroscopic powder readily soluble in water and alcohol; however it is not a stoichiometric compound but probably a mixture of hydrated $\text{RuCl}_3$ and $\text{RuCl}_4$.*

(c) **Anhydrous ruthenium chloride**

This was prepared by the chlorination of the mixture of ruthenium (III) and ruthenium (IV) chlorides at about 500°C. As ruthenium (IV) chloride is not stable at this temperature, ruthenium (III) chloride is the only product. Furthermore, the high temperature assures the complete removal of water and hydroxyl group which might be present in the starting material.

The technique used is the following. Small silica boats were used.

---

* In the present work the anhydrous soluble ruthenium (III) chloride was not obtained by high temperature chlorination as was reported by Hill and Beamish.
filled with the soluble chloride (3 - 5 g. each) and placed in a long silica tube which was situated in a furnace and connected to a chlorine cylinder. A stream of chlorine was passed through it and the furnace was heated up to 500°C. The furnace was kept at this temperature for about an hour and then heating was stopped. A stream of chlorine was maintained in the tube during the heating process and also while it was cooling. The product is a shiny black crystalline compound.

This procedure is a slightly modified version of one described in the literature\textsuperscript{193} for the preparation of anhydrous ruthenium chloride.

3.1.2. Analytical methods

\textbf{Ruthenium} was determined gravimetrically as ruthenium metal. A direct ignition was possible whenever the solid substance could be used for the determination, as all these compounds only contain volatile components. When solutions, used for the ion exchange experiments, were analysed the ruthenium was precipitated first as the hydroxide and ignited as such. The procedure used was exactly the same as the one described in section 2.1.4 for the determination of ruthenium.

\textbf{Chloride} was determined gravimetrically as silver chloride. The insoluble chloride was decomposed first by fusing it with sodium carbonate and the chloride was determined from the water-soluble extract which had been acidified. In the case of the commercial and soluble ruthenium chlorides the total amount of chloride was determined from a nitric acid solution of the
substances, whilst the ionized chloride was determined by precipitation from cold aqueous solution. The results of the latter estimation only gave approximate values as the silver chloride could not be obtained in a pure form without the presence of acid. The procedure here, too, was the same as the one described in section 2.1.4.

Nitrosyl group in the commercial ruthenium chloride was determined by reducing it with Devarda's alloy, and the liberated ammonia was distilled over into a known amount of standard 0.1N hydrochloric acid. The excess of acid was back titrated with standard sodium hydroxide. The apparatus used was the same as that described for the determination of ammonia, section 2.1.4., Fig.1

**TABLE 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Ru</th>
<th>% total chloride</th>
<th>% ionized chloride</th>
<th>% NO</th>
<th>% H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Commercial ruthenium chloride found</td>
<td>40.55</td>
<td>41.80</td>
<td>36.5</td>
<td>6.06</td>
<td>11.65</td>
</tr>
<tr>
<td>[RuCl(H₂O)₃][Ru(NO)Cl₄] requires</td>
<td>40.53</td>
<td>42.50</td>
<td></td>
<td>6.13</td>
<td></td>
</tr>
<tr>
<td>(b) Hydrated ruthenium chloride found</td>
<td>48.15</td>
<td>50.10</td>
<td>34.8</td>
<td></td>
<td>1.75</td>
</tr>
<tr>
<td>RuCl₃ requires</td>
<td>48.87</td>
<td>51.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Anhydrous ruthenium chloride found</td>
<td>49.17</td>
<td>50.72</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.1.3. Properties of the chlorides

The properties of the three compounds whose preparation is described in the previous section were studied in the solid state and mainly in solution in an attempt to elucidate their structures. From a study of the species present in solution it was hoped that some conclusions as to the nature of the solid substances might be reached. The study of the anhydrous chloride proved to be a problem of great difficulty because of its insolubility in acids and in organic solvents.

The methods of investigation with the results obtained are given below:

(a) **Systematic chemical analyses** were carried out with methods described in section 3.1.2. and the results of the analyses are given in Table 1.

(b) **Effect of heat and drying agents**

It was found that the commercial ruthenium chloride lost very little (less than one per cent) or no water over calcium chloride. No loss of weight occurred under 100°C and when it was heated above that temperature the loss of chlorine occurred simultaneously with the loss of water. From the mixture of ruthenium (III) and ruthenium (IV) chlorides part of the water was removed over calcium chloride. Loss of water simultaneously with chlorine occurred at temperatures above 70°C and the process was completed at 120°C, e.g., it was heated at this temperature...
until constant weight was reached. When it was heated above 120°C part of the chloride was converted into the oxide. The dehydration curve is given in Fig.3.

The anhydrous chloride was stable to heat up to 120°C and began to decompose at higher temperatures.

(c) Ion exchange studies

Preliminary experiments have shown that positively and negatively charged species containing ruthenium are sorbed from solutions of commercial ruthenium chloride and hydrated ruthenium (III) chloride. The column method was used to separate and identify these species.

The technique used was the following.

(i) Cation exchange experiments

Solution of the compound about M/50 was prepared and aliquots of this solution (50 - 100 ml.) were passed through a column of Zeokarb 225 resin in the hydrogen form. Resins with varying degrees of cross-linking were tried and the resin used for the final experiment had a water regain of ~1. The sorbed species were eluted with 6M nitric acid and the column then washed with water.

Both the original solution after its passage through the column and the eluate were made up to 250 ml. in a graduated flask; aliquots of these were analysed and the results are given below.
FIG. 3

DEHYDRATION CURVE OF RUTHENIUM CHLORIDE

PERCENTAGE OF RUTHENIUM AND CHLORIDE

TEMPERATURE °C.

Ru = O
Cl = △
Commercial ruthenium chloride

The results are calculated in terms of atomic ratios and are summarised in the following table:

**TABLE 2**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Resin</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_{Ru}$</td>
<td>$N_{Cl}$</td>
</tr>
<tr>
<td>1</td>
<td>1.000</td>
<td>0.996</td>
</tr>
<tr>
<td>2</td>
<td>1.000</td>
<td>0.998</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>1.006</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
<td>1.009</td>
</tr>
<tr>
<td>Mean value</td>
<td>1.000</td>
<td>1.002</td>
</tr>
</tbody>
</table>

Furthermore $N_{Ru}$ resin : $N_{Ru}$ soln. $\sim 1 : 1$ and $N_{Cl}$ resin : $N_{Cl}$ soln. $\sim 1 : 5$

Hydrated ruthenium chloride

The results of these experiments also calculated in terms of atomic ratios are given in Table 3.

**TABLE 3**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Resin</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_{Ru}$</td>
<td>$N_{Cl}$</td>
</tr>
<tr>
<td>1</td>
<td>1.000</td>
<td>2.004</td>
</tr>
<tr>
<td>2</td>
<td>1.000</td>
<td>1.988</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>1.990</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
<td>1.972</td>
</tr>
<tr>
<td>Mean value</td>
<td>1.000</td>
<td>1.988</td>
</tr>
</tbody>
</table>

Furthermore $N_{Ru}$ resin : $N_{Ru}$ soln. $\sim 1 : 1$ and hence $N_{Cl}$ resin : $N_{Cl}$ soln. $\sim 1 : 2$. 
Anion exchange experiments

The column method was applied also here. The exchanger used was the strongly basic DeAcidite EF resin in the chloride form (water regain 1.25). In the case of commercial ruthenium chloride the use of resin with a higher water regain was necessary (1.75). Aliquots of the solution, which was in each case the same as that used for the cation exchange experiments, were passed through a column of resin; and the sorbed species were eluted again with dilute nitric acid. The large amount of chloride already present on the resin made impossible the estimation of chloride which might be sorbed. Ruthenium was, however, determined in the resin end in solution. These experiments only confirmed the results obtained from cation exchange experiments.

The solutions used for these experiments were always freshly prepared to avoid any change due to hydrolysis.

Commercial ruthenium chloride

The results of the experiments carried out with this compound have shown that

\[ \frac{N_{\text{Ru resin}}}{N_{\text{Ru soln.}}} \sim 1 : 1 \]

The presence of nitrosyl group could not be detected in solutions after passage through the anion exchange column. These findings are consistent with those of the cation exchange experiments.
Hydrated ruthenium chloride

These results, too, are in agreement with those of the above described cation exchange experiments, showing that

\[ \frac{N_{\text{Ru resin}}}{N_{\text{Ru soln.}}} \sim 1:1 \]

(d) X-ray examination, carried out at the Research Laboratories of the Mond Nickel Company, have shown that the anhydrous ruthenium chloride has a well defined crystalline structure, while the commercial and hydrated chlorides appear to be amorphous powders.
3.2. DISCUSSION AND CONCLUSIONS

(a) Commercial ruthenium chloride

Results of both cation and anion exchange experiments have demonstrated that the nitrosyl group present in the compound is part of the anion. On the basis of these observations the positively and negatively charged species existing in solution can be formulated as \([\text{RuCl}_aq]^+\) and \([\text{Ru(NO)Cl}_5]^-\) respectively. The fact that water is not removed in a desiccator over calcium chloride suggests that the water molecules are co-ordinately linked to the ruthenium cation and are not present as water of hydration. Furthermore, analysis of the solid itself corresponds to the formula \(\text{Ru}_2\text{Cl}_6\text{NO}_3\text{H}_2\text{O}\). (Table 1).

On the ground of this evidence it is suggested, therefore, that the commercial ruthenium chloride has the following structure

\[
\left[\text{RuCl}(\text{H}_2\text{O})_3\right] \left[\text{Ru(NO)Cl}_5\right].
\]

The difference found between the amount of ionized and total amount of chloride (Table 1) can be explained by assuming that the chloride present in the anion is precipitated, whilst the chloride in the cation is not affected by the addition of silver nitrate. It is known that from a neutral solution of potassium nitrosochlororuthenate most of the chloride is precipitated by the addition of silver nitrate.

The pentachloronitrosyl ion is present in many other stable compounds of ruthenium (III). Potassium, sodium and ammonium salts of the
The commercial ruthenium chloride has been known and used for a long time. Studies about its structure, however, have not been previously reported. The presence of nitrosyl group in the compound was observed only recently when its Infrar Red spectrum was taken (at the Laboratories of University College). The nitrosyl group is introduced, no doubt, when at the final stage of purification the chloride is treated with concentrated nitric acid.

(b) Hydrated ruthenium chloride

As the previously described experiments show, complete dehydration of this substance is not possible and the anhydrous form can only be prepared by high temperature chlorination. Furthermore, the anhydrous form is always insoluble and thus the small amount of water present in the hydrated compound must be responsible for its solubility.

(Previous attempts to prepare this compound (hydrated ruthenium chloride) from a mixture of ruthenium (III) and ruthenium (IV) chlorides have failed. Various reducing agents, such as potassium iodide, stannous
and ferrous ions, have been used but no satisfactory results have been obtained because of the difficulty of isolating the pure ruthenium (III) chloride from the reaction mixture. Purification by recrystallisation was not possible owing to the lack of a suitable solvent).

The positively and negatively charged species, present in solution, whose existence was shown by ion exchange experiments can be formulated as (RuCl₄)²⁺ and [RuCl₄]⁻ respectively. A very simple description of the solid would thus be a dimer having the structure Ru₂Cl₆:

![Diagram of Ru₂Cl₆]

similar to the halides of other trivalent metals, such as Fe₂Cl₆, Au₂Cl₆, Al₂Cl₆, etc. When the substance is dissolved in water the chlorine bridges are split which results in the formation of (RuCl₂)⁺ and (RuCl₄)⁻ ions. The (RuCl₂)⁺ ion probably exists in a hydrated form, i.e., [RuCl₂(H₂O)₂]⁺ or [RuCl₂(H₂O)₄]⁺, and it is possible that in solutions the ion [RuCl₄]⁻, too, acquires two molecules of water forming [RuCl₄(H₂O)₂]⁻ ion. The presence of the ion (RuCl₂)⁺ in solutions containing ruthenium (III) and chloride was proposed also by previous workers¹²,¹³, and salts of the ion [RuCl₄]⁻ have also been reported in the literature³⁴.

The above description of the solid as a dimer, however, ignores the presence of water in the solid; and a more complex structure is
thus needed to account for the presence of this water. For example, it might have a polymeric structure similar to the anhydrous chloride given below, which could be formulated as:

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Ru} & \quad \text{Ru} & \quad \text{Ru} \\
\text{Cl} & \quad \text{OH}_2 & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Ru} & \quad \text{Ru} & \quad \text{Ru} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

Fig. I

i.e. the water is bonded to the ruthenium atoms by a co-ordinate link. It requires only one molecule of water for every four or five ruthenium atoms to change the uniform cross-linked structure (see anhydrous ruthenium chloride, Fig. II) into a relatively open one where the attack of the water molecules can occur more easily throughout the structure. This would explain why the small amount of water leads to such a large difference in the properties of the dried soluble form compared with the anhydrous ruthenium chloride. The experimental results can thus be explained by
assuming that part of the water which is easily removed is present as water of hydration, whilst the small amount of water which cannot be removed under the same conditions must be an integral part of the structure. It appears that the removal of this water would convert the soluble form (Fig.I) into the insoluble one (Fig. III).

(c) Anhydrous ruthenium chloride

The remarkable inertness of this compound suggests that it exists in a polymeric form, which by analogy with the (also inert) anhydrous palladium (II) chloride $[\text{PdCl}_2]_{\infty}$ could be formulated as $[\text{RuCl}_3]_{\infty}$. The fact that acids have no effect on it but it is attacked by ammonia and various organic amines also supports the structure proposed above as amines are well known for their power of splitting halogen bridges in polynuclear compounds. Thus, ammonia with anhydrous palladium (II) chloride gives discrete molecules of dichloropalladium diammine $\text{Pd(NH}_3)_2\text{Cl}_2$.

The $[\text{RuCl}_3]_{\infty}$ could exist either as an infinite chain lattice (Fig.I) or as a layer lattice (Fig.II).

the bridges between the octahedron in the first case (Fig.II)
being formed in such a way that the three chlorine groups occupy the faces of two octahedron. That is, if the Ru atoms are at the centres of the octahedron, then these octahedron are placed face to face and, indeed, share a face.

or

\[
\begin{array}{c}
\text{Cl} \\
\text{Ru} \\
\text{Cl} \\
\text{Ru} \\
\text{Cl} \\
\text{Ru} \\
\text{Cl} \\
\text{Ru}
\end{array}
\]

Fig. III

In the second case (Fig. IV), the cross-linked form, each octahedron shares two edges and two corners. In both cases the individual groups of RuCl₃ are joined by chlorine bridges, so that the formal charge on each ruthenium atom is three, whilst the coordination number is six.

X-ray studies of the anhydrous and dried soluble chloride support the formulae put forward above. Both the linear chain and cross-linked network (Fig. II and III) are highly ordered arrangements and would thus lead to a stable crystalline state, in agreement with the experimental results. On the other hand the soluble form could have its water molecules present in a quite random way, leading to a much less ordered structure; this might explain the amorphous nature of the compound.
SECTION 4.

PHOSPHATE COMPLEXES OF RUTHENIUM (III)
4.1. EXPERIMENTAL

4.1.1. Attempts to prepare ruthenium phosphate

It was pointed out in the Introduction of this thesis (section 1.2) that no ruthenium (III) phosphate has been reported. It was decided, therefore, to prepare the compound with methods similar to those used for the preparation of other tervalent metal phosphates, such as iron (III), aluminium (III), and indium (III).

The method used was the following: An excess of phosphoric acid was added to a solution of ruthenium (III) chloride followed by the addition of sodium hydroxide. (The use of ammonium hydroxide – to neutralise the excess of acid – was avoided because of the possible formation of an ammine complex). A faint precipitate was first obtained, which partly dissolved by heating. Analysis of the product, after washing and drying, has shown that it consisted only partly of ruthenium phosphate, and was presumably a mixture of ruthenium-phosphate and -hydroxide. Furthermore, the ratio of ruthenium to phosphate was not constant in the various preparations.

It seemed appropriate, therefore, to study the formation of ruthenium phosphate complexes in solutions by means of ion exchange. The methods used were similar to those applied for the study of phosphate complexes of other tervalent metals, i.e. iron (III)\(^{37}\), aluminium (III)\(^{38}\), chromium (III)\(^{39}\), and indium (III)\(^{40}\).
4.1.2. Preparation of solutions

(a) Ruthenium phosphate solution was prepared by dissolving ruthenium hydroxide in phosphoric acid. The ruthenium hydroxide was prepared by adding a solution of sodium hydroxide to a solution of ruthenium (III) chloride and subsequently boiling the solution. The precipitated hydroxide was washed by decantation; each fresh batch of wash water was thoroughly mixed with the suspended hydroxide by stirring before it was allowed to settle. When the washings were free of chloride, the hydroxide was filtered off, washed and air dried. The product appeared to be free of both chloride and sodium ions.

(b) Ruthenium chloride solution (0.1 M) used in the experiments was prepared by dissolving the correct amount of hydrated ruthenium chloride (preparation described in section 3.1.1.) in water, and the pH of the solution was adjusted by the addition of perchloric acid.

(c) Phosphoric acid was prepared by dilution of analar syrupy phosphoric acid. The solution so prepared was standardised by determination of phosphate content by precipitation as ammonium phosphomolybdate.

4.1.3. Preparation of resins

(a) Cation exchange resin

The cation exchange resin used in all the experiments was ZeoKarb 225, a strongly acid resin, in the hydrogen form. The resin as received (from the Permutit Company Ltd.) was washed successively several times with
hydrochloric acid and water in order to remove the iron impurity that is always present in these resins. The washed resin was then air dried and sieved; the 20 - 40 mesh fraction was used. The washing of the resin was always carried out with freshly deionised water. The water was deionised by passing distilled water through a column of mixed bed ion exchange resin.

The capacity of the resin was determined by passing 0.5 N sodium chloride solution (circa 250 ml.) through a column of resin (0.5000 g.) in the hydrogen form, and determining the acid liberated in the effluent by titration with 0.1 N sodium hydroxide with phenolphthalein indicator.

(b) Anion exchange resin

The anion exchanger used was the Deacidite FF strongly basic resin. The resin as received (also from the Permutit Company Ltd.) was washed several times with 2N hydrochloric acid followed by water and finally air dried. The dried resin was sieved and the 20 - 40 mesh fraction used. Chloride form resin was prepared by treatment with 2N hydrochloric acid as described above.

Phosphate form resin was prepared from the chloride form by passing through it a solution of 2 N sodium dihydrogen phosphate until the effluent was free from chloride. The resin was then washed with water until the washings were neutral to methyl orange (pH~ 5) and air dried.

The capacity of the exchanger was determined in the following way: 500 ml. 2 - 3 N nitric acid was passed through a column containing 1,000 of the chloride form resin,
and the chloride content of the effluent was determined. In the case of the phosphate form resin, 1,000 g. of the exchanger (weighed in the phosphate form) was converted to the chloride form and the determination was carried out as described above.

The capacity of each batch of resin was determined before use and the results of the experiments are recorded as gram moles of sorbed material per equivalent of resin.

4.1.4. Batch Experiments

The procedure in these studies is to examine the sorption of metal together with the anion (phosphate and chloride in this case) both on cation and anion exchangers. Solutions of the metal phosphate and mixed solutions of the metal salt with phosphoric acid are used in the experiments.

The technique of these experiments is the following: To portions of solution under examination, kept in conical flasks fitted with rubber bungs, 0.5 g. of cation exchanger or 1.0 g. of anion exchanger were added. At least two weeks with frequent shaking were allowed for solution and resin to come to equilibrium. After this period the solution was separated from the resin by filtration through a dry ion-exchange column. The filtrate was retained and aliquot portions of it used for analysis and pH measurements. The measurements are the equilibrium pH values quoted in the table of results. The materials sorbed on the resin were eluted after washing with 2 - 3 M nitric acid and subsequently determined. Analysis of the eluate provides
a check on the analysis of the filtrate; and thus made it possible to account quantitatively for the ions initially present in the solution and on the resin.

4.1.5. Determination of ruthenium, phosphate and chloride

In the analysis of the solutions aliquots were taken from which ruthenium, phosphate and chloride - when present - were determined. All the estimations were carried out gravimetrically; ruthenium was determined as ruthenium metal, phosphate as ammonium phosphomolybdate and chloride as silver chloride. The procedures in each case were the same as those described in section 2.1.3.

4.1.6. Cation Exchange Experiments

Sorption experiments were carried out using ZeoKarb 225 cation exchange resin with ruthenium chloride solution in the presence of phosphoric acid. These experiments indicated the presence of phospho ruthenium positively charged species and no chloride was sorbed by the exchanger. The results of the experiments are summarised in Table 1 and plotted in Fig.4. The results, however, could not be treated by the method - described by Salmon - and used for the studies of sorption of other metal phosphates. The above method is based on the assumption that one complex phosphate ion is sorbed together with the metal ion, which, however, is not the case with ruthenium, as ruthenium is sorbed together with chloride and not as the free cation only from solutions of ruthenium chloride. The
conclusions reached from these experiments, therefore, provide only qualitative information about the nature of the phosphato ruthenium ions present in solutions.

Qualitative tests have indicated that ruthenium together with phosphate was sorbed also from solutions of ruthenium phosphate by cation exchange resin. Experiments with ruthenium phosphate were, therefore, carried out and the results are given in Table 2, Fig. 5.

4.1.7. Anion Exchange Experiments.

(a) Ruthenium phosphate solutions were prepared by dissolving ruthenium hydroxide in phosphoric acid with the proportions as indicated in Table 4. Portions (1.0 g.) of the anion exchange resin DeAcidite FF in the phosphate form were then added to 50 ml. samples of the ruthenium phosphate solutions. Blank experiments were carried out with phosphoric acid alone in order to determine the average charge of the phosphate sorbed on the resin in the absence of ruthenium.

After allowing the solution and resin to reach equilibrium the resin was separated and washed with carbon dioxide free water until the washings were neutral to methyl orange. The quantities of ruthenium and phosphate sorbed on the resin were then determined and the results are summarised in Table 4.

A method, described by Salmon, has been used as a basis for the treatment of the results obtained from these experiments.
In the case of the sorption of \(1:n\) complex \(M\text{H}_q\text{A}_m\)
formed between a tervalent metal cation \(M^{3+}\) and an anion derived from a
tribasic acid \(\text{H}_3\text{A}\), if the quantity of \(M\) sorbed (as the complex) per
equivalent of exchanger is \(N_m\), and the total quantity of \(A\) sorbed (as
complexed and free \(A\) ions) is \(N_A\) and if, under identical conditions, but
in the absence of \(M\), \(A\) is sorbed as \(\text{H}_b\text{A}^{(3-b)-}\) ions, then

\[
\text{moles complex sorbed} = N_m
\]

\[
\text{moles free } \text{H}_b\text{A}^{(3-b)-} \text{ sorbed} = N_A - N_m (3 - q)
\]

\[
\text{equivalents of complex sorbed} = N_m (3N - 3 - q)
\]

\[
\text{equivalents of } A \text{ sorbed} = (3 - b)(N_A - nN_m)
\]

\[
\text{total equivalents sorbed} = 1 = N_m(nb - q - 3) + N_A (3 - b)
\]

whence

\[
q = nb - 3 - \frac{1 - N_A (3 - b)}{N_m}
\]

The quantity \((3 - b)\) was determined from blank experiments carried
out in the absence of the metal. From the results values of \(q\) have been
calculated for \(n = 1, 2\) and 3; these are included in the table.

(b) Experiments carried out with mixed solutions of ruthenium chloride
have shown the presence of anionic phosphate complexes in these solutions.
The results of these studies are summarised in Table 3 (Fig.6).
TABLE 2

Sorption of ruthenium and phosphate by ZeoKarb 225 H form resin from solutions containing ruthenium chloride and phosphoric acid.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Resin</th>
<th>% Ru ** accounted for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>pH</td>
<td>Moles sorbed/equiv. resin Ru&lt;sup&gt;3+&lt;/sup&gt;</td>
</tr>
<tr>
<td>0</td>
<td>1.30</td>
<td>0.405*</td>
</tr>
<tr>
<td>0.33</td>
<td>1.23</td>
<td>0.435</td>
</tr>
<tr>
<td>0.48</td>
<td>0.98</td>
<td>0.446</td>
</tr>
<tr>
<td>0.76</td>
<td>1.14</td>
<td>0.474</td>
</tr>
<tr>
<td>0.98</td>
<td>1.10</td>
<td>0.494</td>
</tr>
<tr>
<td>1.26</td>
<td>1.10</td>
<td>0.508</td>
</tr>
<tr>
<td>1.68</td>
<td>1.04</td>
<td>0.498</td>
</tr>
<tr>
<td>2.92</td>
<td>1.06</td>
<td>0.463</td>
</tr>
<tr>
<td>4.62</td>
<td>1.10</td>
<td>0.432</td>
</tr>
<tr>
<td>6.25</td>
<td>1.16</td>
<td>0.410</td>
</tr>
</tbody>
</table>

Ruthenium chloride solution pH 1.30 0.3 M
Phosphoric acid 0.3 M
Weight of resin 0.5 g.

*Ruthenium is sorbed with chloride, when phosphate is present only trace of chloride is sorbed.

** The sum of ruthenium on the resin and in solution in equilibrium with the resin expressed as percentage of ruthenium originally present in the solution.
FIG. 4.

Sorption of Ruthenium and Phosphate by ZeoKarb 225 resin from solutions containing Ruthenium Chloride and Phosphoric acid.
**TABLE 2**

Sorption of ruthenium and phosphate by ZeoKarb 225 H form resin from solutions of ruthenium phosphate.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{PO_4}{Ru}$</td>
<td>pH</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>8.60</td>
<td>1.52</td>
</tr>
<tr>
<td>6.48</td>
<td>1.40</td>
</tr>
<tr>
<td>5.24</td>
<td>1.24</td>
</tr>
<tr>
<td>4.51</td>
<td>1.12</td>
</tr>
<tr>
<td>3.42</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Weight of resin 1.0 g.

Volume of solution 100 ml.
FIG. 5.

Sorption of Ruthenium and Phosphate by Zeo Karb 225 resin from solutions of Ruthenium Phosphate.

MOLS. SORBED PER EQUIVALENT OF RESIN

<table>
<thead>
<tr>
<th>pH</th>
<th>1.0</th>
<th>1.1</th>
<th>1.2</th>
<th>1.3</th>
<th>1.4</th>
<th>1.5</th>
<th>1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>PO₄</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3
Sorption of ruthenium, phosphate and chloride by DeAcidite FF - FeO₄ from solutions of ruthenium chloride and phosphoric acid.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ru</th>
<th>P0₄</th>
<th>Cl</th>
<th>% Ru* accounted for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/P0₄</td>
<td>pH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.76</td>
<td>1.14</td>
<td>0.082</td>
<td>0.060</td>
<td>0.502</td>
</tr>
<tr>
<td>1.40</td>
<td>1.16</td>
<td>0.086</td>
<td>0.066</td>
<td>0.488</td>
</tr>
<tr>
<td>2.24</td>
<td>1.20</td>
<td>0.093</td>
<td>0.090</td>
<td>0.480</td>
</tr>
<tr>
<td>3.42</td>
<td>1.24</td>
<td>0.104</td>
<td>0.106</td>
<td>0.462</td>
</tr>
<tr>
<td>5.24</td>
<td>1.28</td>
<td>0.110</td>
<td>0.122</td>
<td>0.446</td>
</tr>
<tr>
<td>6.48</td>
<td>1.34</td>
<td>0.116</td>
<td>0.136</td>
<td>0.436</td>
</tr>
</tbody>
</table>

Ruthenium chloride solution pH 1.32 0.1 M
Phosphoric acid 0.3 M
Weight of resin 0.5 g.

* The sum of ruthenium on the resin and in solution in equilibrium with the resin expressed as percentage of ruthenium originally present in solution.
FIG. 6.

Sorption of Ruthenium Phosphate and Chloride by DeAcidit FF resin from solutions of Ruthenium Chloride and Phosphoric acid

\[
\frac{[PO_4]}{[Ru]} \text{ IN SOLUTION}
\]

Mols. sorbed per equivalent of resin

- Cl = ●
- Ru = ○
- PO₄ = ●
TABLE 4.

Sorption of ruthenium and phosphate by DeAcidite FF resin from solutions of ruthenium phosphate

<table>
<thead>
<tr>
<th>Solution</th>
<th>Resin</th>
<th>( q_{n=1} )</th>
<th>( q_{n=2} )</th>
<th>( q_{n=3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{P_{0_4}}{Ru} )</td>
<td>pH</td>
<td>( N_{Ru} )</td>
<td>( N_{P_0_4} )</td>
<td>( N_{P_0_4} )</td>
</tr>
<tr>
<td>6.48</td>
<td>1.40</td>
<td>0.012</td>
<td>0.605</td>
<td>-2.65</td>
</tr>
<tr>
<td>5.24</td>
<td>1.24</td>
<td>0.019</td>
<td>0.586</td>
<td>-3.56</td>
</tr>
<tr>
<td>4.51</td>
<td>1.12</td>
<td>0.030</td>
<td>0.602</td>
<td>-1.54</td>
</tr>
<tr>
<td>3.42</td>
<td>1.01</td>
<td>0.039</td>
<td>0.622</td>
<td>-1.38</td>
</tr>
</tbody>
</table>

Weight of DeAcidite FF-\( P_{0_4} \) form resin 1.0 g.

Volume of solution 50 ml.
4.2. DISCUSSION AND CONCLUSIONS

4.2.1. Cation exchange experiments

The experiments carried out with various amounts of ruthenium chloride and phosphoric acid have shown that the sorption of ruthenium by the exchanger achieves a maximum when the mole ratio of $[\text{PO}_4^{3-}] / [\text{Ru}^2+]$ by the exchanger achieves a maximum when the mole ratio of $[\text{PO}_4^{3-}] / [\text{Ru}^2+]$ is $\sim 1.5$; the sorption of phosphate also goes through a maximum at the same mole ratio. (Table 1, Fig. 4). It was found that ruthenium was sorbed together with chloride in the absence of phosphate, whilst in the presence of phosphate only traces of chloride were detected on the resin. The sorption of ruthenium is enhanced in the presence of phosphate indicating that the phosphato complex is more readily sorbed than the chloro complex.

The positively charged species in solution - assuming they are mononuclear - might be either of the following: $[\text{RuHPO}_4^-]^+ (A)$, $[\text{RuH}_2\text{PO}_4^+]^{2+} (B)$ and $[\text{Ru(H}_2\text{PO}_4)_2]^+ (C)$. It is difficult to account quantitatively for the various species present; it seems logical, however, that if (A) and (B) would be the only species sorbed the sorption of ruthenium and phosphate would occur in equimolecular amounts, whilst the sorption of (C) would require two moles of phosphate for each mole of ruthenium. As the sorption of ruthenium was found to be appreciably higher than that of the phosphate, the sorption of C is unlikely. To account for this higher sorption of ruthenium we have to assume that in addition to the sorption of A and B
some binuclear species must be also sorbed, such as $[\text{Ru}_2(\text{PO}_4)(\text{OH})_2]^{2+}$.

Experiments carried out with ruthenium phosphate solution have shown that the sorption of ruthenium is very small and falls with the decrease of pH (Table 2). The sorption of phosphate follows the same pattern showing very slight sorption; thus the concentration of $[\text{RuHPO}_4^+]$ or $[\text{Ru}_2\text{H}_2\text{PO}_4]^{4+}$ in these solutions must be appreciably smaller than in solutions of ruthenium chloride and phosphoric acid.

4.2.2. Anion Exchange Experiments

Experiments carried out with solutions of ruthenium chloride and phosphoric acid have shown that ruthenium together with phosphate and chloride is sorbed by the DeAcidite FF-P0 4 form resin, but the amounts of ruthenium and phosphate sorbed are much smaller than that of chloride. Nevertheless the amounts of ruthenium and phosphate sorbed increase steadily with increase of the mole ratio of phosphate to ruthenium in the solution, and in the same time the amount of chloride sorbed falls gradually (Table 3, Fig.6). Furthermore the phosphate and ruthenium are sorbed by the exchanger in approximately equimolecular amounts. It seems likely therefore that the sorbed species are either

$$[\text{Ru(PO}_4)_2]^{3-} \quad \text{or} \quad [\text{RuCl}_4]^-$$

In both cases the complex ions would be sorbed together with free chloride.

The sorption of ruthenium and phosphate on samples of anion exchange
resin in the phosphate form from solutions of ruthenium phosphate demonstrates the presence in solution of anionic ruthenium complexes (Table 4). The quantities of ruthenium sorbed were small, however, and thus it is not possible, from a consideration of the q values obtained, to deduce the precise nature of the ruthenium phosphate species present.

Ruthenium (III) thus seems to differ from the other tervalent metals studied in that cationic and anionic complexes are found in both chloride-phosphoric acid and in phosphoric acid solutions. Iron, aluminium, and indium, apparently form cationic complexes only in chloride-phosphoric acid solutions\(^37;38;40\), and anionic complexes only in phosphate media. It is noteworthy, however, that with ruthenium (III) the complexes appear to be predominantly cationic in chloride-phosphoric acid solutions and predominantly neutral or anionic in phosphoric acid solution. The behaviour of ruthenium (III) in forming cationic phosphate complexes in phosphoric acid solution would suggest a resemblance to that of chromium (III) which also forms cationic phosphate complexes under similar conditions\(^39\).
**FINAL CONCLUSIONS**

In all the ruthenium ammine compounds containing phosphate or oxalate, the oxy-acid group was present in the ionised form except in the case of the tetrammines where both phosphate and oxalate were introduced into the co-ordination sphere forming a chelate ring with the ruthenium atom. The five-membered (oxalate) ring was more readily formed and more stable - as expected from steric reasons - than the four-membered (phosphate) ring.

In all the complexes prepared there were six ligands co-ordinated to the central atom in accord with the previous information on the stereochemistry of ruthenium (III). On the basis that no oxidising or reducing conditions were involved in the preparation of the phosphato and oxalato complexes, the assumption was made that the tervalent ruthenium, present in the various ammine complexes used as starting materials, remained unchanged. This assumption was supported by the analytical data of these complexes which corresponded to the presence of tervalent ruthenium.

The failure of the attempts to introduce phosphate into the pent-ammine is in agreement with known properties of the phosphate group as ligand showing that it appears to form a stable ligand group in ammine complexes only when it acts as a bidentate group. In the present case the oxalate group, too, tended to take up two co-ordination positions which was de-
monstrated by the formation of oxalato tetrammine ion - rather than oxalato pentammine ion - by the action of oxalic acid on the hydroxopentammine ion.

Studies of the chloro derivative of Ruthenium Red (formulated by Morgan and Burstill as $[\text{Ru(NH}_3)_4\text{Cl}_2]\text{Cl}$) and the oxalate compounds obtained from it provide additional support for the conclusions of K. Gleu and J.M. Fletcher, namely, that the properties of the compound are not in accord with the structure assigned to it by Morgan and Burstill; and that to account for these properties a polynuclear structure must be assumed. No evidence was found, however, for the existence of a trinuclear structure as suggested by Fletcher.

Studies of the commercial ruthenium chloride and hydrated ruthenium chloride have shown the presence of positively and negatively charged species in aqueous solutions of these compounds. All the ions found were known previously to exist in various ruthenium compounds. It has not been suggested, however, that these species - namely $[\text{RuCl}_4]$ and $[\text{Ru(NO)}\text{Cl}_5]^-$, $[\text{RuCl}_2\text{aq}]^+$ and $[\text{RuCl}_4\text{aq}]^-$ are present in solutions of the "commercial" ruthenium chloride and hydrated ruthenium chloride respectively. Furthermore, it was found that the "commercial" ruthenium chloride is a stoichiometric compound which can be formulated as $[\text{RuCl(H}_2\text{O)}_3][\text{Ru(NO)}\text{Cl}_5]$. The ion exchange studies carried out with the solutions of the "commercial" ruthenium chloride and hydrated ruthenium chloride have provided useful preliminary information, and have indicated that to gain a fuller understanding about
the structure of these compounds a more extensive investigation in the solid state is required.

All attempts to dissolve the anhydrous ruthenium chloride have failed and therefore the methods used for the study of the other two chloro-compounds could not be applied in this case. In the present work the formation of insoluble and soluble ruthenium (III) chloride did not occur simultaneously as reported by previous workers. It should be noted, however, that the conditions of the preparation employed in this work were not identical with those before. High temperature chlorination has always resulted in the formation of insoluble chloride only, whilst the soluble chloride has been obtained by another method (section 3.1.1.). Attempts to dehydrate the soluble (hydrated) chloride have shown that the compound started to lose chlorine before complete dehydration was achieved; thus the hydrated form could not be converted into the anhydrous form by this method. Experiments carried out with a number of preparations - obtained by chlorination at various temperatures - have indicated that the more closely the compound approaches the composition of anhydrous ruthenium chloride the more insoluble it is. In this case, too, an investigation in the solid state would be necessary in order to account, (a) for the great inertness of the compound, and (b) for the large differences between the properties of the hydrated and anhydrous form. However, it seems very probable that the two forms of ruthenium (III) chloride, and also
the commercial ruthenium chloride, have the polymeric structures which are proposed in the present work.

The results of ion exchange studies have demonstrated the presence of both positively and negatively charged ruthenium phosphate complexes in solutions containing ruthenium (III) and phosphoric acid. Evidence was found for the formation of mixed chloro phosphate complexes and these are the only known mixed chloro-ortho phosphato complexes so detected. Similar mixed sulphato-phosphato complexes of iron (III) are, however, known but not chloro phosphatoiron (III) complexes.
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