

CHEMISTRY OF RHENIUM

A Thesis submitted by
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CONTENTS

<u>Chapter.</u>	<u>Page.</u>
1. The Simple Chemistry of Rhenium	1
2. The Complex Chemistry of Rhenium	11
3. Carboxylic Acid Complexes	20
3a. Complexes derived from the reaction between rhenium trichloride and carboxylic acids in absence of air.	21
3b. Complexes derived from the reaction between rhenium trichloride and carboxylic acids in presence of air.	37
3c. Complex derived from the reaction between acetic acid and rhenium pentachloride	45
3d. The infra-red spectra of carboxylic acid complexes	47
Nitrogen ligands	58
Infra-red spectra of Nitrogen ligand complexes	63
4. Experimental	65
References	84

ABSTRACT

Complex compounds of Re(III) of the type $[\text{Re}(\text{RCOO})_2\text{Cl}]_2$ ($\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2, (\text{CH}_3)_2\text{CH}$ and $\text{CH}_3(\text{CH}_2)_6$) have been prepared. They are believed to have structures similar to copper and chromium acetates. The thiocyanate derivative $[\text{Re}(\text{CH}_3\text{CH}_2\text{CH}_2\text{COO})_2\text{SCN}]_2$ is described as well as the sulphate $[\text{Re}_2(\text{CH}_3\text{CH}_2\text{CH}_2\text{COO})_4 \cdot 2\text{H}_2\text{O}] \text{SO}_4$. A five-co-ordinate Re(III) complex $\text{ReCl}_3 \cdot (\text{RCOOH})_2$ ($\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2$) is also described.

A series of Re(IV) complex compounds $[\text{ReO}(\text{RCOO})\text{Cl}]_2$ and $[\text{ReOH}(\text{RCOO})\text{Cl}_2]_2$ have been prepared.

The Re(V) complexes $[\text{ReO}_2(\text{RCOO})]_2$ and $\text{ReCl}_3 \cdot (\text{CH}_3\text{COO})_2$ have also been made.

Compounds of rhenium with nitrogen ligands $\text{ReO}(\text{OH})\text{py}_2\text{Cl}_2$, $\text{ReO}(\text{OH})\text{dipyCl}_2$, $[\text{ReO}_2\text{py}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$, $[\text{ReO}_2\text{py}_4]\text{Ph}_4\text{B}$ are also described. The infra-red spectra, magnetic properties and supposed structures of the compounds are described and discussed.

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1. THE SIMPLE CHEMISTRY OF RHENIUM

Rhenium is characteristic of its position in the table of elements, being in the long period between tungsten and osmium. It is highly refractory with a melting point of 3180° -second to tungsten among metals, and has a density of 21.04. The natural element consists of two isotopes ^{187}Re and ^{185}Re , but nine other isotopes are known. It crystallises in a close-packed hexagonal structure similar to technetium, ruthenium and osmium. It is the rarest of the naturally occurring elements. Its average concentration in the earth's crust (0.001 part per million) is of the same order of magnitude as that of some of the platinum metals but it does not occur as the element, or as a distinct mineral species. Although its existence as dvi-manganese was predicted by Mendeleev, it was only detected in 1925 by X-ray spectrum.

Preparation of the metal.

Rhenium is now recovered as a byproduct in the manufacture of molybdenum; the flue dusts obtained from molybdenum concentrates are enriched in rhenium because of the volatility of rhenium heptoxide. The rhenium contained in these dusts can be extracted with water containing an oxidising agent;

alternatively, the rhenium in these dusts can be solubilised by heating them with lime at 600° .

Calcium perrhenate is readily leached out with water from the insoluble calcium molybdate. The rhenium in solution can be recovered as the sparingly soluble salt $KReO_4$ by addition of potassium chloride.

Originally the metal was produced by reducing this salt with hydrogen at 1000° but the product was always contaminated with potassium. Impure rhenium can be purified by conversion into pentachloride with chlorine, hydrolysing the pentachloride to rhenium dioxide, and then reducing the last⁽¹⁾. Rhenium is best obtained by hydrogen reduction of ammonium perrhenate⁽²⁾.

Rhenium and technetium resemble one another much more than they do manganese; their compounds are often iso-structural and are frequently similar in appearance and in physical and chemical properties, also each exhibits multiplicity of valency. The significant difference between rhenium and manganese is the great stability of the latter's bivalent state. Even in the quadrivalent state in which the two elements show the greatest resemblance, the tendency for Mn^{+4} to behave as an oxidising agent is very marked. When rhenium is compared with group VIII

metals, a greater resemblance is seen between the chemistry of rhenium and ruthenium than that of the neighbouring osmium. Thus ruthenium forms a stable tribromide and trichloride but with osmium the tetrahalides are more stable. The dioxide of rhenium is more stable than that of osmium. There is greater similarity between rhenium and molybdenum than between rhenium and tungsten.

Oxidation State VII

Simple derivatives such as the heptoxide and sulphide are known as well as mixed halides involving partial replacement of oxygen, for example Re_2O_7 , ReO_3F , ReOF_5 and ReO_2F_3 ; the last two compounds are formed when dry rhenium dioxide or potassium perrhenate is heated with fluorine⁽³⁾. It was found that potassium permanganate and manganese dioxide react with fluorine to give MnF_3 contaminated with a little difluoride, and no oxyfluoride of manganese is produced in these reactions⁽³⁾.

The only Re(VII) oxychloride is perrhenyl chloride ReO_3Cl ; the bromide ReO_3Br is also known. It is only recently that rhenium heptafluoride has been prepared⁽⁴⁾ by passing fluorine at 250 mm. pressure over rhenium heated to $300-400^\circ$. Rhenium heptoxide dissolves in water to give perrhenic acid.

This acid can also be prepared by dissolving the metal powder in hydrogen peroxide; perrhenic acid is a strong acid and like pertechnetic acid it can be titrated by using indicators such as methyl red. All compounds of Re(VII), Tc(VII) and Mn(VII) are diamagnetic as expected for a d^0 configuration.

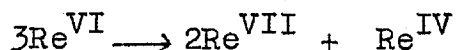
Oxidation State VI

Rhenium trioxide is a red paramagnetic solid which can be obtained by reducing the heptoxide with rhenium at 250° ⁽⁵⁾ or with rhenium dioxide at 300° ⁽⁶⁾. It can also be prepared by heating the heptoxide with carbon monoxide or sulphur dioxide⁽⁷⁾. This trioxide can be reduced with hydrogen to the dioxide then finally to the metal. Several workers tried to prepare the technetium analogue by reacting the metal with heptoxide⁽⁸⁾ but none has been completely successful.

The hexafluoride was originally made from fluorine and rhenium at 125° ⁽⁹⁾ and chlorine trifluoride has also been used as a fluorinating agent. The Raman and infra-red spectra of the compound have been studied⁽¹⁰⁾. According to Ruff and Kwasnik it attacks silica at room temperature. Other workers maintain that it is stable and reacts with silica above 300° ^{*}. There are reports in the early literature

* As will be discussed on page 8.

of a volatile, deep green chloride of rhenium which was thought to be the heptachloride or the hexachloride but it was never characterised^(11,12). This green product was observed when the workers used rhenium prepared from the reduction of ammonium perrhenate with hydrogen. Later on rhenium was produced commercially and this gives rhenium pentachloride when heated with oxygen-free chlorine. Very recently Colton prepared technetium hexachloride⁽¹³⁾ as a volatile green compound by interaction of oxygen-free chlorine with the metal. Later he prepared rhenium hexachloride⁽¹⁴⁾ using rhenium prepared by reduction of ammonium perrhenate with hydrogen, and oxygen-free chlorine at 600°. The hexachloride is dichroic, appearing red-brown by transmitted light and dark green by reflected light; it is thermally stable in both chlorine and nitrogen in contrast to technetium hexachloride which gives the red tetrachloride on thermal decomposition. On hydrolysis it gives the dioxide and the perrhenate ion according to the usual disproportionation reactions of rhenium (VI) and technetium (VI) compounds:-



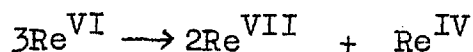
The affinity of rhenium for oxygen is great, especially in its higher oxidation states. The following oxyfluorides are known: ReO_2F_2 , ReOF_4 . These are

obtained⁽¹⁵⁾ when a mixture of fluorine and oxygen is passed over rhenium at 125-300°; rhenium hexafluoride⁰ was also among the reaction products which were separated by fractional distillation. Robinson and his Co-workers reported that the last reaction gives only ReOF_5 and ReO_2F_3 ⁽³⁾. ReOF_4 is now prepared by the reduction of rhenium hexafluoride with rhenium carbonyl⁽¹⁷⁾.

Rhenium oxytetrachloride ReOCl_4 is obtained together with ReO_3Cl by oxidising a mixture of tri- and pentachloride of rhenium using oxygen or Re_2O_7 ⁽¹⁶⁾.

Rhenium dioxy dibromide ReO_2Br_2 is obtained by the action of bromine on rhenium heptoxide; this remained the only oxybromide of Re(VI) until Colton prepared ReOBr_4 ⁽¹⁸⁾. He reported that this is the main product of the reactions of rhenium dioxide, rhenium heptoxide or rhenium trioxide with bromine vapour; it can also be obtained in very small amounts by the action of oxygen on rhenium pentabromide⁽¹⁸⁾, rhenium tetrabromide⁽¹⁹⁾ or potassium hexabromorhenate(VI). It is best prepared by passing bromine vapour over ReO_2 .

This compound sublimes with little decomposition on gentle heating in a stream of bromine, but strong heating causes decomposition to rhenium tribromide⁽¹⁸⁾. It is stable in dry air but immediately hydrolysed by water to rhenium dioxide and perrhenic acid.



Oxidation State V

Rhenium appears to be the only element of the triad, Re, Tc, and Mn which gives rise to simple pentavalent compounds, the pentafluoride, pentachloride and pentabromide being known. The pentafluoride can be obtained by reducing the hexafluoride using tungsten carbonyl and excess of tungsten hexafluoride⁽¹⁷⁾. This pentafluoride disproportionates in vacuo above 180° to the tetra- and hexa-fluorides.

The pentachloride is obtained by heating rhenium metal (made by reducing potassium perrhenate) in a stream of chlorine and purified by sublimation under vacuum; it is also prepared by heating Ag_2ReCl_6 ⁽²⁰⁾ which gives in addition to silver chloride, rhenium trichloride and rhenium pentachloride; rhenium pentachloride is the more volatile of the two. It is prepared similarly by heating at 400° under pressure the heptoxide with carbon tetrachloride⁽²¹⁾. Very recently Colton prepared the pentabromide⁽¹⁸⁾ of rhenium from the metal and bromine at 650° and described it as a bluish green solid melting readily to a similarly coloured liquid. Its vapour is deep blue and the compound distills with little decomposition on heating in a stream of bromine vapour. Moderate

heating or an attempt to distil it in a vacuum or in a nitrogen stream leads by rapid decomposition to the tribromide. It fumes in moist air and water causes instant hydrolysis which proceeds with the usual disproportionation of Re(V) compounds to rhenium (IV) and Re(VII). This worker was unable to obtain a solution of the compound in any of several organic solvents, bromine being always liberated.

Oxidation State IV

This is one of the better known oxidation states of rhenium and technetium, the dioxides of rhenium and technetium closely resemble each other and both have the molybdenum dioxide structure⁽²²⁾. The disulphides of the two metals also resemble each other and both are prepared by heating the heptasulphide with sulphur and the excess of sulphur being sublimed away in vacuum. Ruff and Kwasnik made a tetrafluoride by reducing the hexafluoride with either hydrogen at 200° or sulphur trioxide at 400. However, Hargreaves et al. believed that the compound prepared in this way is a mixture of tetra- and penta-fluoride. Ruff and Kwasnik claimed that rhenium hexafluoride reacts with silica at laboratory temperature to give rhenium oxytetrafluoride. Aynsley, Peacock and Robinson⁽³⁾ reported that no reaction was observed at room tempera-

ture, and that only above 300° does rhenium hexafluoride react with quartz yielding minute quantities of dark green-blue solid agreeing with the description given by Ruff and Kwasnik for rhenium tetrafluoride and reported that the quantities were too small for confirmatory analysis.

The existence of rhenium tetrachloride has been disputed although the isolation of tetrabromide⁽¹⁹⁾ and tetraiodide⁽²³⁾ indicates that the tetrachloride may exist. The tetrachloride is known in case of technetium and it can be made by the action of chlorine on the metal⁽¹³⁾ and it can be sublimed unchanged in the chlorine stream. It was first prepared, however, by the action of carbon tetrachloride on technetium heptoxide at 400° in a bomb⁽²¹⁾.

Oxidation State III

Rhenium trichloride results when the pentachloride is heated in an inert gas⁽²⁴⁾. It is also formed by thermal dissociation of silver hexachlororhenate (IV) or from sulphuryl chloride and rhenium⁽²⁵⁾. Hagan and Sieverts⁽²⁶⁾ in 1933 found that passing bromine vapour over heated rhenium gave a green material which they described as the tribromide and which they said sublimed easily in vacuum. They also noted that when

oxygen was present a blue solid was obtained to which they assigned formula ReO_2Br_2 . Colton⁽¹⁸⁾ in 1962 proved this was wrong and that the compound formed was the pentabromide which gives the tribromide as dark brown crystals, stable in air and giving stable red solutions in acetone alcohol or ether, and hydrolysed more quickly than the trichloride. He has also shown that the compound thought to be ReO_2Br_2 is in fact ReOBr_4 . Rhenium tri-iodide is a black crystalline solid obtained by heating rhenium tetraiodide in a sealed tube to 350° ⁽²³⁾. Alternatively, ammonium iodorhenate $(\text{NH}_4)_2\text{ReI}_6$ is decomposed in a vacuum at 325° , and the solid residue heated with excess of iodine in a sealed tube at 200° . In both instances the iodine is dissolved in carbon tetrachloride, which leaves the insoluble rhenium tri-iodide. The tri-iodide is only slightly soluble in water and dilute acids, it is nearly insoluble in alcohol, acetone and ether. Like the tetraiodide, it loses iodine slowly in a vacuum, especially when heated.

Oxidation State II

Only few complex compounds are known in this oxidation state, and the only simple compound ReO ⁽²⁴⁾ has remained uninvestigated since its preparation in 1937.

Oxidation State I

Apart from the compounds $\text{ReI}^{(17)}$ and $\text{Re}_2\text{O}^{(27)}$ no simple derivatives of the univalent metals are known.

2. THE COMPLEX CHEMISTRY OF RHENIUM

Until recently little work has been done on the complexes of rhenium in low-valency states. However, the increased interest shown in recent years in the complex chemistry of the transition metals has led to the preparation of a number of stable low valent rhenium compounds. Much use has been made of strong field cyanide and tertiary phosphine, arsine and carbonyl ligands as these are well known to stabilise lower valency states.

This thesis deals with the preparation of new complexes of three -, four -, and five valent rhenium, but for completeness a review of the complex chemistry of this element in its six lowest valency states will be given.

Rhenium (0)

Six co-ordinate $\text{Re}(0)$ occurs in the dimeric carbonyl $\text{Re}_2(\text{CO})_{10}$ ⁽²⁸⁾ which contains a metal-metal bond.

Rhenium (I)

The complex cyanide $\text{K}_5[\text{Re}(\text{CN})_6]$ ⁽²⁹⁾ was made by reducing a mixture of hexachlororhenate(IV) $\text{K}_2[\text{ReCl}_6]$, and potassium cyanide in water with potassium amalgam.

Isocyanide complexes of the type $[\text{Re}(\text{CH}_3\text{C}_6\text{H}_4\cdot\text{NC})_6]^+$ ⁽³⁰⁾ are also known. Hieber and Schuster ⁽³¹⁾ have reported

that rhenium penta carbonyl halide reacts with potassium cyanide to give potassium dicyanotetra carbonyl rhenium (I) $K[Re(CO)_4(CN)_2]$. Other carbonyl complexes of rhenium in this valency state are the carbonyl halides $Re(CO)_5X$ ^(32,33,34) $[Re(CO)_4X]_2$ and $py_2Re(CO)_3I$ ⁽³⁵⁾. The carbonyls and carbonyl halides react with hot methanolic caustic potash to give the salt $K[Re_2(CO)_8O_2H]$ ⁽³⁶⁾ which is believed to contain bridging oxygen and hydroxyl groups. The salt $[Re(CO)_6] AlCl_4$ is also known ⁽³⁷⁾. Fischer and Öfele ⁽³⁸⁾ prepared Re(I) tetracarbonyl diethylene cation $[Re(CO)_4(C_2H_4)_2]^+$. Rhenium I also forms a number of Sandwich Complex ions of the type $(Re^I Ar)^+$ (Ar = benzene or mesitylene) ⁽³⁹⁾ which give precipitates with large anions.

Rhenium (II)

The only complexes in which this valency has been established with certainty are derived from O-phenylene bisdimethylarsine (L) and are of formula $[ReL_2X_2]$ (X = Cl, Br or I) ⁽⁴⁰⁾. Russian workers ⁽⁴¹⁾ claim to have made K_2ReCl_4 ; $ReCl_2 \cdot 4H_2O$; $H_2ReCl_4 \cdot 2H_2O$; $H_2[Re(OH)_3Cl]$; $H_2[Re(OH)_4]$; $(py-H) H[ReCl_4]$, $ReCl_2 \cdot (CH_3COOH)_x$ (x=4, 2 or 1), and $ReCl_2 \cdot (CH_3COOH)_x py$, but give no magnetic data. Earlier these workers ⁽⁴²⁾ claimed to have isolated $(NH_4)_2 \cdot ReCl_4$ and cis and trans isomers of $ReCl_2 \cdot 2py$ but again no magnetic

evidence was presented. Indian workers have made $\text{Na}_3 [\text{Re}(\text{CN})_5\text{H}_2\text{O}]$ and salts of the anion $[\text{Re}(\text{CN})_5(\text{CO})]^{3-}$ and have confirmed the valency of the rhenium in them analytically (43, 44). Freni and Valenti (45) claimed to have prepared $[\text{ReCl}_2(\text{PPh}_3)_2]$ from the interaction of rhenium heptoxide, the tertiary phosphine and hydrazinium chloride in ethanol. An investigation of this substance has shown that this compound was wrongly formulated and that the compound was in fact $[\text{Re}^{\text{V}}\text{O}(\text{OEt})\text{X}_2(\text{PPh}_3)_2]$ (46) and that a compound of the formula $[\text{ReCl}_2(\text{PPh}_3)_2]$ can only be prepared using sodium perrhenate hydrazinium chloride and triphenyl phosphine in hydrogen chloride under anhydrous conditions. Bistriphenylphosphine rhenium di-iodide was prepared from the chloride by reaction with sodium iodide; the compound $[\text{ReCl}_2\{\text{C}_2\text{H}_5(\text{PPh}_2)_2\}_2]$ was also prepared.

Rhenium (III)

Trivalent rhenium is known in the compounds $\text{K}_3[\text{Re}(\text{CN})_6]$ (47), $[\text{Re}(\text{diarsine})_2\text{Cl}_2]^+\text{ClO}_4^-$ (40) and in complex halides of the type $(\text{ReCl}_4)^-$ (48). Rhenium trichloride in acetone reacts with sodium and potassium salts of dimethyl-, diethyl-, dibutyl-, and pentamethylenedithiocarbamic acids to give compounds of the general formula $\text{ReCl}_2(\text{NR}_2\text{CS}_2)$ (49). Acetylacetone reacts with rhenium dioxide or rhenium sesquioxide to give rhenium

(trisacetylacetonate)⁽⁵⁰⁾. Rhenium trichloride triphenyl phosphine was prepared by interaction of the tertiary phosphine with rhenium trichloride in ethanol or acetone^(18,26). Interaction of $\text{ReCl}_3 \cdot \text{PPh}_3$ in acetone with chlorine in presence of an excess of the phosphine gave a product which at first was thought to be $[\text{ReCl}_3 \cdot (\text{PPh}_3)_2]$ ⁽⁵¹⁾ but later shown to be a phosphine oxide complex $[\text{ReCl}_3 \cdot (\text{OPPh}_3)_2]$ ⁽⁵²⁾. It was observed that rhenium trichloride and rhenium tribromide when dissolved in liquid ammonia formed compounds which were thought to be ammoniates with formulae such as $\text{ReCl}_3 \cdot 6\text{NH}_3$ ⁽⁵³⁾. MyaoTsin-Shen and V.G. Tronev claimed to have prepared $\text{ReCl}_3 \cdot 4\text{am}$ (am = NH_3 , $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, and $\text{C}_5\text{H}_5\text{N}$) and suggested that all three chlorine atoms are equivalent and not co-ordinated, i.e. the amine has the structure $[\text{Re am}_4]\text{Cl}_3$ ⁽⁵⁴⁾, but none of these compounds has been confirmed. Compounds having the general formula $\text{Re}_2\text{Cl}_6\text{L}$ (L=2-6 lutidine, α -vinyl pyridine, and trimethylamine), $\text{Re}_2\text{Cl}_6\text{L}_2$ (L= α -picoline) are known⁽⁵¹⁾. Jozowska-Trzebiatowska prepared the oxobromorhenate ion $[\text{ReOBr}_5]^{4-}$ by the reduction of potassium perhenate in hydrochloric acid with sulphur dioxide⁽⁵⁵⁾.

When solutions of perhenates in aqueous ethylene diamine are reduced with metallic potassium or barium they give compounds which were at first thought

to be rhenides⁽⁵⁶⁾ containing rhenium of negative valency. However, nuclear magnetic resonance⁽⁵⁷⁾ and infra-red spectroscopy showed the presence of metal-hydrogen bonds. Floss and Grosse having reinvestigated their product, assign to it the formula $M\{Re^{III}H_4\}2-4H_2O$ ⁽⁵⁸⁾. Subsequent work has not lessened the confusion and Ginsberg et al. have reformulated the compound as K_2ReH_8 ⁽⁵⁹⁾. Further work is clearly needed.

The product of the reaction between sodium cyclopentadienide and rhenium pentachloride which was originally thought to be $Re(C_5H_5)_2$ is now known to be a hydride $(\eta-C_5H_5)_2ReH$ ⁽⁶⁰⁾ in which the rhenium can be considered to be trivalent. This hydride reacts with carbon monoxide to give a compound which was thought to be $(C_5H_5)_2ReH(CO)_2$ ⁽⁶¹⁾ and later shown to be $(C_{10}H_{11})Re(CO)_2$ ⁽⁶²⁾. Treatment of dihalobistriphenyl phosphine rhenium(II) compounds with sodium borohydride in ethanol yielded red crystals of $ReH_3(PPh_3)_2 \cdot 2C_2H_5OH$ ⁽⁶³⁾. Recrystallisation of this compound from benzene gives $ReH_3 \cdot (PPh_3)_2$. When the same reaction is performed with excess of triphenyl phosphine, a seven-co-ordinate compound $ReH_3(PPh_3)_4$ is obtained.

Rhenium (IV)

In this valency rhenium forms a number of stable halide complexes in which the element is six-

co-ordinate. These include the simple halide complexes $M_2[ReX_6]$ (M =univalent metal, $X=Cl, Br, I$ ^(64,65), or F ⁽⁶⁶⁾). Organic bases such as pyridine, quinoline, p-toluidine⁽⁶⁷⁾, brucine, acridine, nitron, tetron⁽⁶⁸⁾, dipyridyl, bisdipyridyl, tripyridyl⁽⁶⁹⁾ form salts with the anion $[ReCl_6]^{2-}$. Hydroxy pentachlororhenates $M_2[Re(OH)Cl_5]$ ⁽⁴⁵⁾ and the oxygen-bridged dimer $M_4[Re_2OCl_{10}]$ ⁽⁷⁰⁾ are also known as well as an iodine complex py_2ReI_4 ⁽⁵¹⁾. Eight-co-ordinate rhenium (IV) occurs in the $[Re(CN)_7NO]^{3-}$ ⁽⁴⁷⁾ ion which was isolated as the silver salt from a solution of $K_3[Re^V(CN)_8]$ which had been boiled with dilute nitric acid.

Indian workers⁽⁷²⁾ claimed to have prepared $H[(OH)_3ReC_2O_4 \cdot 2H_2O]$ which changes slowly in aqueous solution to the dibasic form $H_2[(OH)_4ReC_2O_4]$. These acids were made by refluxing freshly prepared rhenium dioxide in oxalic acid. They also claimed to have prepared alkali and alkaline-earth salts of these acids. The same workers also prepared $[Re(C_6H_2O_2-OHCOO)_2] \cdot 6H_2O$ by the action of gallic acid on pure crystalline potassium rhenichloride⁽⁷³⁾. Jazowska-Trezebiatowska and co-workers prepared⁽⁷⁴⁾ what seem to be salts of the same compounds and showed them to be dimeric and suggested that they are bridged through oxygen. They reformulate the compounds as $K_4[Re_2(OH)_6(C_2O_4)_2O]$ and

$K_4 [Re_2(OH)_2(C_2O_4)_4O]$. When the first of these is dissolved in 2M- acetic acid and alcohol is added to the solution the complex acid $H_4 [Re_2(OH)_2(C_2O_4)_4O]$ precipitates.

A compound of formula $K_3 [ReO(CN)_4OH]$ was claimed⁽⁷⁵⁾ to have been obtained by the action of potassium cyanide solution on rhenium dioxide but this has never been confirmed. Treatment of $ReH_3(PPh_3)_2$ with hydrochloric, or hydrobromic acid yielded the complex halide $ReX_4(PPh_3)_2$ ⁽⁶³⁾.

Rhenium (V)

The reaction between $K_2Re^{IV}I_6$ and potassium cyanide in hot methanol gives $K_3 [Re(CN)_3]$ ⁽⁴⁷⁾ which is a stable compound containing eight-co-ordinate rhenium (V). An earlier claim⁽⁷⁶⁾ to have made the compound $K_3 [ReO(CN)_4]$ was in error and the compound was in fact $K_3 [ReO_2(CN)_4]$ ^(77,69). Other oxo and hydroxy complexes of rhenium (V) such as $[ReO_2en_2]Cl$, $[Re(OH)_2en_2]Cl_3$, $[ReO(OH)en_2]Cl_2$ ⁽⁷⁸⁾, and $[ReO_2py_4]Cl$ ⁽⁷⁹⁾ (en = ethylene diamine, py = pyridine) are well known. Biguanidine⁽⁸⁰⁾ (Big-H) forms complexes $[ReO(OH)(Big H)_2] (OH)_2$ and $[ReO_2(Big H)_2]^+$ and diphenylcarbazone⁽⁸¹⁾ gives $(DpCH) [Re(OH)_2Cl_2DpC]$. Recently some similar thiocyanato complexes $K_3 [ReO_2(SCN)_4]$ have been reported⁽⁸²⁾. Other complex thiocyanates $[Re^VO(SCN)_3(PPh_3)_2]$ and $[ReO(SCN)_3(PEt_2Ph)_2]$ ⁽⁴⁶⁾ are also known.

Earlier claims by Freni and Valenti to have prepared phosphine halide complexes of rhenium (II) were in error and the compounds are in fact oxo and alkoxo⁽⁴⁶⁾ complexes of the types $[\text{ReOCl}_3(\text{PR}_3)_2]$ and $[\text{ReOX}_2(\text{PR}_3)_2]$ ($X = \text{Cl}, \text{Br}, \text{I}$).

On varying the iodide concentration and the temperature of the reaction between potassium perrhenate, hydrochloric and hydroiodic acids, $\text{K}_2[\text{ReOCl}_5]$ ⁽⁸³⁾ was one of the reaction products. The O-phenylene-dimethyl arsine complexes $[\text{ReD}_2\text{Cl}_4]\text{ClO}_4$, $[\text{ReD}_2\text{Br}_4][\text{Br}_3^-]$ and $[(\text{ReD}_2\text{Cl}_2)_2\text{O}][\text{ClO}_4]_4$ are known⁽⁸⁴⁾. Rhenium(V) is also known in the alkali salts of the ion $[\text{ReF}_6]^-$ ⁽⁸⁵⁾.

3. CARBOXYLIC ACID COMPLEXES

Strong-field ligands, for example cyanide, carbonyl, triphenylphosphine and arsine have been extensively applied as ligands in the study of the complex chemistry of rhenium. In the present work relatively weak ligands (e.g. monocarboxylic acids) were used. Thus the reaction between acetic and other low carboxylic acids and rhenium trichloride has been studied both in the presence and in the absence of air. Four different types of compound (two in each case) with rhenium in three different oxidation states namely: rhenium (III), rhenium (IV) and rhenium (V) have been obtained. Their infra-red spectra and magnetic susceptibilities are presented.

3.a. Complexes derived from the reaction between rhenium trichloride and carboxylic acids in absence of air:-

In this reaction two types of compound were formed: orange crystals having the composition $\left[\text{Re}(\text{RCOO})_2 \text{Cl} \right]_2$, ($\text{R}=\text{CH}_3$, CH_3CH_2 , $\text{CH}_3\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}$ or $\text{CH}_3(\text{CH}_2)_6$); and black compounds having the composition $\text{ReCl}_3 \cdot (\text{RCOOH})_2$.

These were separated by the difference in their solubilities.

3.b. Complexes derived from the reaction between rhenium trichloride and carboxylic acids in air:

Two types of compound are again formed: purple crystals having the composition $[\text{ReO}(\text{RCOO})\text{Cl}]_2$ ($\text{R}=\text{CH}_3\text{CH}_2\text{CH}$, $\text{CH}_3\text{CH}_2\text{CH}_2$, or $\text{CH}_3(\text{CH}_2)_6$) and orange crystals having the composition $[\text{ReO}_2(\text{RCOO})]_2$. These could be separated by their different solubilities either in alcohol or the carboxyl acid itself, the first type being soluble in alcohol and insoluble in the carboxylic acid whereas the second type is soluble in the carboxylic acid (hot) and insoluble in alcohol.

3.a. Complexes derived from rhenium trichloride in absence of air.

On refluxing Re(III) chloride with carboxylic acids under nitrogen, orange needle-like crystals slowly deposit from the very dark brown solutions. These have the composition $(\text{RCOO})_2\text{ReCl}$ (where $\text{R}=\text{CH}_3$, CH_3CH_2 , $\text{CH}_3\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}$, or $\text{CH}_3(\text{CH}_2)_6$) and appear to be dimers judging by the molecular weight determined by the ebullioscopic method in chlorobenzene, their very low solubilities in alcohol, acetone benzene, chloroform and similar solvents, and their high melting points. The solubilities increase, and melting points decrease, with increase of the length of the alkyl chain; the acetate was heated up to 328°C without melting or decomposing and is practically insoluble in all solvents tried (e.g. benzene, acetone, alcohol and chloroform), the propionate decomposes at 245°C and is slightly soluble in acetone but is insoluble in most of the other common organic solvents (e.g. benzene,

chloroform and dichloromethane). The isobutyrate is soluble in alcohol, acetone, chloroform, dichloromethane and tetrahydrofuran and is slightly soluble in cold benzene and chlorobenzene and is soluble in the last two solvents on boiling; it is insoluble in carbon tetrachloride, ether and petroleum spirit and melts at 221°C. The n-butyrate has solubilities similar to its isomer and melts at 215°. The octoate is freely soluble in acetone alcohol, chloroform, dichloromethane, soluble in benzene, chlorobenzene, tetrahydrofuran and is insoluble in carbon tetrachloride and petroleum spirit and melts at 196°C. All these compounds are very stable, being unaffected by water or cold dilute mineral acids and can be left exposed to the air for several months without appreciable decomposition. They are, however, decomposed to rhenium dioxide on boiling with strong bases.

Such a gradation in properties has been observed by Chatt et al.⁽⁸⁶⁾ in binuclear platinum chloride complexes of the type L_2PtCl_4 (where L=olefins, amines, tertiary organic phosphines, arsine and stibines and dialkyl sulphides, selenides and tellurides). Solubility increases rapidly as the homologous ascended from the sparingly soluble methyl to conveniently

soluble propyl derivatives; then more slowly as the homologous series is ascended further. Solubility also increases on ascending the eutropic series from phosphine to stibine complexes. Stability falls rapidly in the same series: the phosphine complexes are very stable, the arsine complexes decompose very slowly in boiling ethanolic solution and the stibine complexes decompose spontaneously in any warm solvent. The stabilities of stibine complexes also decrease rapidly on ascending the homologous series from trimethyl to tri-n-propyl complex. The dialkyl series of complexes is the most insoluble. The dimethyl and diethyl sulphide complexes are practically insoluble in all solvents tried, but the dipropyl sulphide complex is slightly soluble in some boiling solvents such as chloroform and ethyl methyl ketone. Solubility increases as the homologous series is ascended.

Structure of the complexes.

As the usual method of rupturing halogen bridges is to allow the compound to react with amine in a solvent such as benzene, it appears unlikely that the structure of these compounds involves halogen bridges (as in fig (1)), for when their solutions in benzene are refluxed (under nitrogen) with p-toluidine, triphenyl-

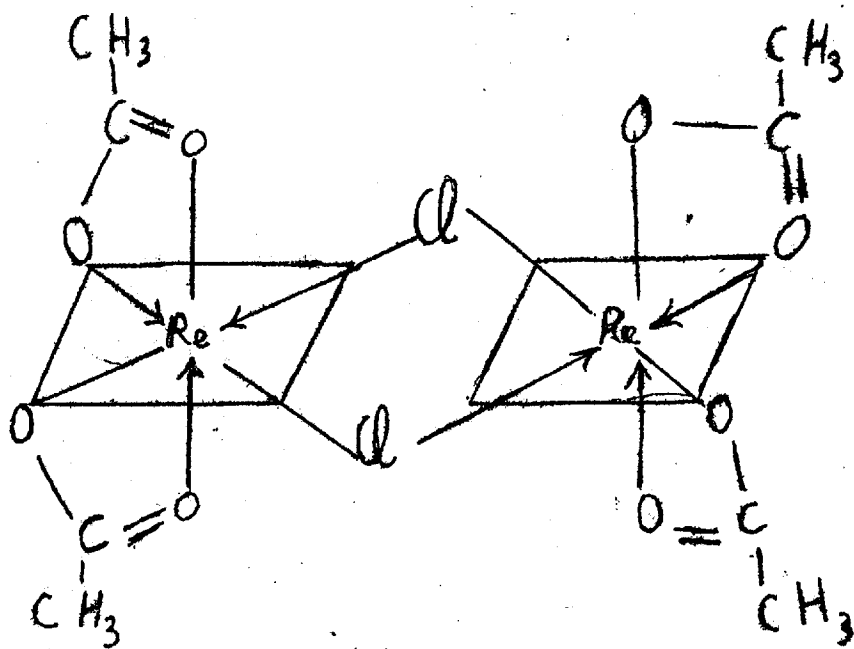


fig (1)

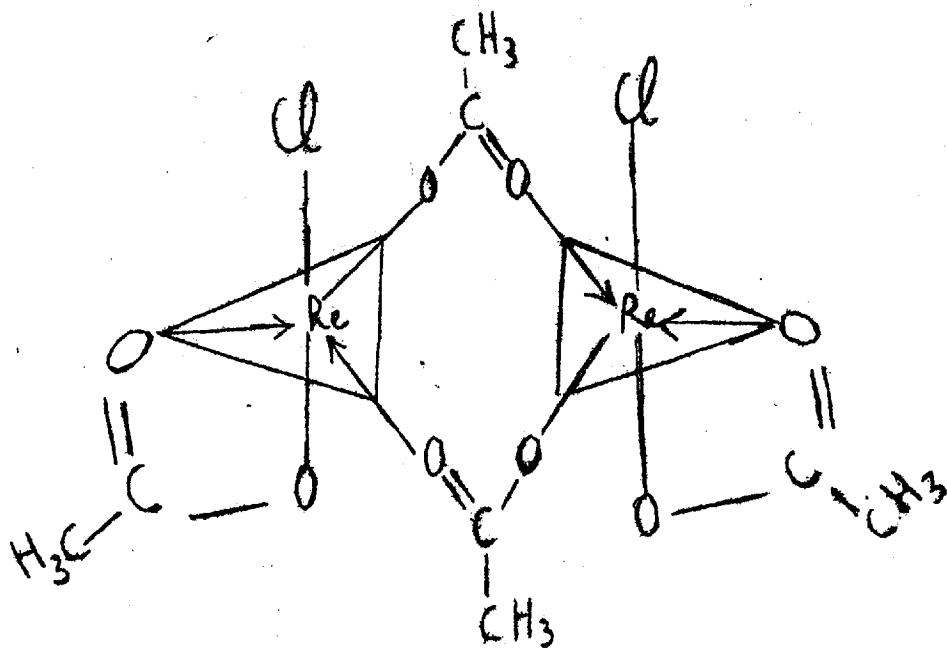


fig (2)

phosphine or dry pyridine no reaction occurs. The work of Abel, Bennett and Wilkinson⁽⁸⁷⁾ on the halogen-bridged polymers of norbornadiene with ruthenium, that of Irving on ruthenium carbonyl iodide⁽⁸⁸⁾, and that of Chatt et al. on halogen bridged platinum (II)⁽⁸⁹⁾ and on rhodium (I)⁽⁹⁰⁾ complexes has shown that in these circumstances halogen bridges would be cleaved to give compounds of the type $LRe(RCOO)_2Cl$ (where L=p-toluidine, triphenyl phosphine, or pyridine).

The structure indicated in fig. (2) (involving trigonal bipyramidal- d^3sp hybridized-rhenium) can be rejected on the grounds that it contains two kinds of carboxylate groups: bridging and nonbridging. This is unlikely for if this were the case the infra-red spectrum should show absorption bands corresponding to two different carboxylate groups (in the region from ~ 1620 - 1200 cm^{-1}) but in fact only one is ever observed. The fact that these compounds are unaffected by cold dilute mineral acids eliminated the structure in which only one oxygen atom of each carboxylate group is involved in the bond to metal fig. (3). Acids would be expected to dissolve such complexes with monofunctional carboxylate groups through protonation of the unco-ordinated oxygen atom. Furthermore, in such a structure the infra-red spectrum would have a band characteristic of CO group

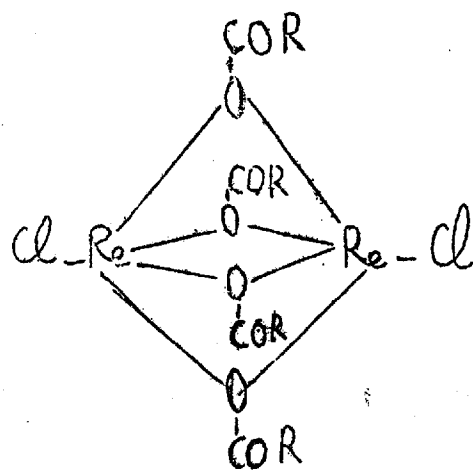


Fig (3)

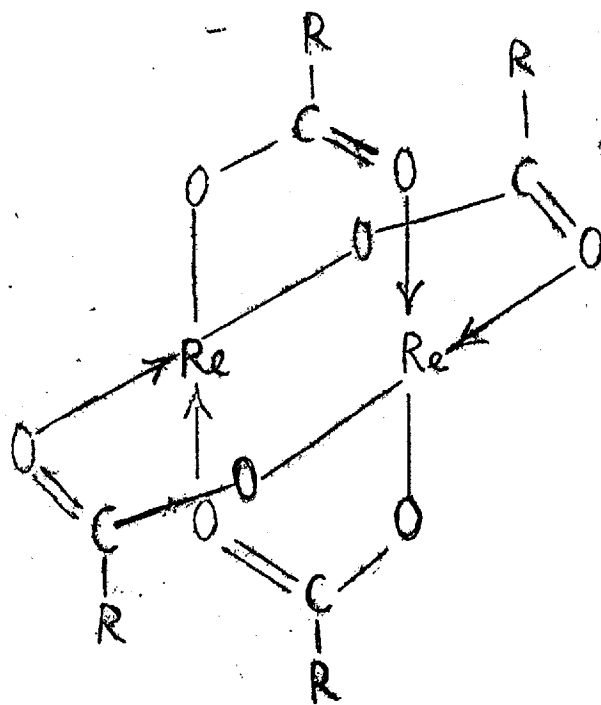


Fig (4)

in esters (at about 1720 cm^{-1}) which is not the case. The most likely structure for the complexes seems to be one with four bridging carboxylate groups and a direct rhenium to rhenium bond as in fig. (4).

The existence of bridging acetate groups has been previously demonstrated by Werner (1910) on chemical grounds and by X-ray methods in basic zinc⁽⁹¹⁾ and beryllium acetates. In none of these cases was there any evidence of metal to metal bonding. Bridging acetate groups also occur in the polymeric molybdenum diacetate⁽⁹²⁾ which is prepared by the reaction between molybdenum carbonyl and acetic acid in presence of acetic anhydride and also in a heavier transition metal compound for when the dimeric 1:5 cyclooctadiene rhodium chloride is treated with potassium acetate in acetone solution the compound $[(C_8H_{12})_2Rh_2(CH_3COO)_2]$ is obtained⁽⁹⁰⁾. X-ray work on the hydrated acetates of copper and chromium⁽⁹⁴⁾ and very recently on the hydrated acetate of rhodium⁽⁹⁵⁾ and on the compound $[Cu_2(CH_3COO)_4(C_5H_5N)_2]$ ⁽⁹⁶⁾ has shown that they have structures containing bridging acetate groups in an arrangement identical with that in the proposed structures of the rhenium complexes.

Confirmation of the presence of a direct Re-Re bond, or at any rate considerable Re-Re interaction, is provided by the observed diamagnetism of the compounds,

both in the solid state determined by the Gouy method on the acetate and in solution by n.m.r. method on the octoate. In these compounds the Re(III) has a d^4 configuration and is thus strictly analogous to Cr(II) whose hydrated acetate is also diamagnetic. This diamagnetism of chromium acetate at first led to its being assigned a tetrahedral configuration⁽⁹⁷⁾, but X-ray studies⁽⁹⁴⁾ showed that the molecule was dimeric with the two chromium atoms locked by the carboxylate groups at a distance of 2.64 \AA apart. Geometrical considerations show that the length of the M-O bond has little effect upon the M-M distance in compounds of the type shown in fig. (4), so that it can be presumed that the Re-Re distance in $\text{Re}_2(\text{RCOO})_4\text{Cl}_2$ will also be about the same as in the chromium compound. The exact nature of the interaction between the two chromium atoms is still somewhat doubtful, although it has been suggested by Figgiset al.⁽⁹⁸⁾ that it involves a mixture of one σ -, two π - and one δ -bonds utilizing the 3d orbitals of the chromium atoms. Calculations of overlap integrals have suggested that the bond is rather weak but there is sufficient exchange to effectively pair the spins of the electrons occupying the 3d levels in each chromous acetate molecule and thus produce the observed diamagnetism. However, it appears probable that the

molecule is really held together by the bridging acetate groups.

A rather similar situation exists in the dimeric copper acetate⁽⁹⁸⁾ molecule except that the bond in this case appears to be considerably weaker so that the compound still exhibits some paramagnetism, although not as much as would be expected if there were no Cu-Cu interaction at all. Recently the view has been put forward that the Cu-Cu bond is almost wholly- σ -⁽⁹⁹⁾ but the question is still not settled.

The greater size of rhenium together with the fact that the two rhenium atoms can be expected to be fixed at about the same separation as the chromium atoms will result in greater, electronic interaction between the rhenium atoms so that the bond will probably be considerably stronger. It is not possible to obtain an assessment of this effect from magnetic measurements, however, as the chromium compound is already diamagnetic, but it is likely that the Re-Re bond plays a significant part in holding the two halves of the molecule together.

A magnetic study of the homologues of copper acetate (propionate, butyrate, etc.,) has shown that these also have anomalously low magnetic moments and presumably similar structures to the acetate⁽¹⁰⁰⁾. The

length of the fatty acid chain should not affect the shape of the COO part of the molecule and Catalin molecular models showed that the paraffinic part of the molecule could easily be accommodated around the edge of the central grouping. The same argument can also be applied to the rhenium carboxylates which are all diamagnetic and which presumably have the same structures as the acetate. Other compounds which contain Re-
Re bond are the dioxide⁽²²⁾ and the carbonyl⁽²⁸⁾.

In an attempt to demonstrate conclusively that the compounds do not contain bridging halogen groups certain replacement reactions were performed. The compounds react with silver thiocyanate in boiling benzene to give a brown-black compound $[\text{Re}(\text{RCOO})_2\text{SCN}]_2$. This compound gives a non-conducting solution in acetone, is soluble in water and is soluble in benzene to give a dark brown solution.

The infra-red spectrum of this compound shows a very strong peak at 2033 cm^{-1} , this can be due only to the thiocyanate groups. It has been found that potassium thiocyanate absorbs at $\sim 2063 \text{ cm}^{-1}$,⁽¹⁰¹⁾ terminal thiocyanate groups in platinum (II) and palladium (II) complexes in the range $2100 - 2120 \text{ cm}^{-1}$ and bridging thiocyanate groups in the range $2150 - 2182 \text{ cm}^{-1}$ ⁽¹⁰²⁾. It has also been found that the

compound $[\text{Pt}(\text{C}_{10}\text{H}_{12})(\text{SCN})_2]_n$ (in which $\text{C}_{10}\text{H}_{12}$ is the diolefin dicyclopentadiene) has very strong absorption bands at 2159 and 2055 cm^{-1} (103), indicating the presence of both bridging and nonbridging or free SCN^- groups, and consequently it was assigned the structure $[\text{C}_{10}\text{H}_{12}\text{Pt}(\text{SNC})_2\text{PtC}_{10}\text{H}_{12}](\text{SCN})_2$. From these results it appears fairly certain that the peak at 2033 cm^{-1} in the rhenium complex arises from nonbridging SCN groups and that the compound must have the structure shown in fig. (5). The formation of such complexes confirms that halogen bridges were not involved in the original compounds. As discussed by Lindqvist and Stanberg⁽¹⁰⁴⁾ the transition metals may be classified into two groups according to whether they are bonded to the thiocyanate group through the nitrogen or sulphur atom. Thus metals in the first transition series appear to form isothiocyanate complexes (N-bond) whereas elements in the second half of the second and third transition series tend to form thiocyanate (S-bonded). It is significant that

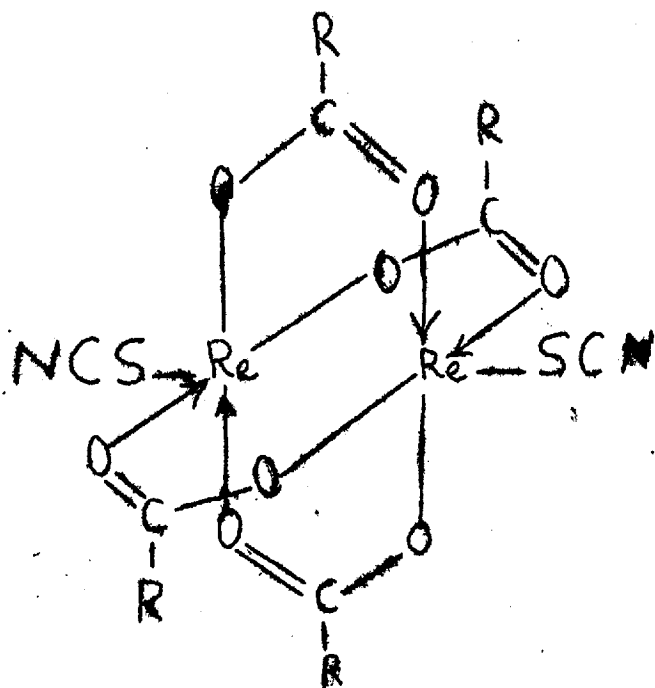
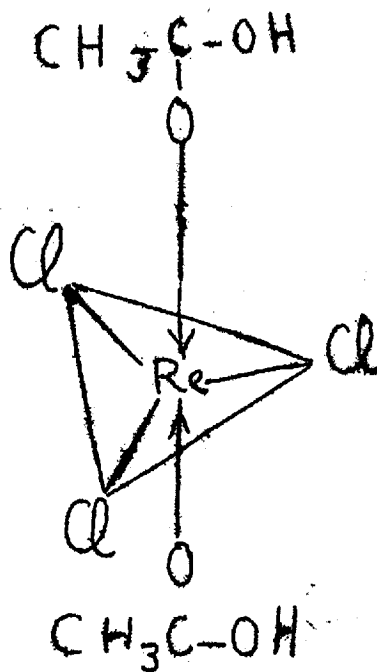


Fig (5)



Fig(6)

this behaviour closely parallels the division into class (a) and class (b) acceptors proposed recently by Ahrland et al.⁽¹⁰⁵⁾ for the co-ordination of metal ions with an extensive series of ligands. This (a)-(b) division is based upon the stability constants of ions in solution, i.e. the free energies of replacement of one ligand by another. For class (a) metals the order of strength of attachment in water is $F^- > Cl^- > Br^- > I^-$, and for class (b) metals the order is reversed. The fact that the bonding extremes are $M - N = C = S$ and $M - S - C \equiv N$ on conventional formulation suggested that it should be possible to distinguish between the two forms by studying the CN and CS frequencies in the infra-red spectrum. Lewis, Nyholm and Smith⁽¹⁰⁶⁾ found that the feature most characteristic of metal sulphur bonding is a lower C - S stretching frequencies $\sim 700 \text{ cm}^{-1}$ to be compared with $\sim 800 \text{ cm}^{-1}$ when the bonding is through nitrogen. In the present case it was found difficult to differentiate between the two different bonding (N-bonding or S-bonding) since in this region of the spectrum there are other bonds due to the butyrate group ($CH_3(CH_2)_2COO$). Recently Schäffer⁽¹⁰⁷⁾ has suggested that it is possible to distinguish between an isothiocyanate and thiocyanate structure on the basis of the position of the ligand in the spectrochemical series. The

thiocyanate groups is considered to be approximately in the same position as chloride in the series, whilst isothiocyanate falls between water and ammonia, i.e. $\text{Cl} \approx \text{-SCN} < \text{F} < \text{-NCS} < \text{NH}_3 < \text{CN}$. In the present case visible spectra for both $[\text{Re}(\text{CH}_3(\text{CH}_2)_2\text{COO})_2\text{SCN}]_2$ and $[\text{Re}(\text{CH}_3(\text{CH}_2)_2\text{COO})_2\text{Cl}]_2$ was measured to make possible such a comparison.

Unfortunately the result was not conclusive.

These compounds $[\text{Re}(\text{RCOO})_2\text{Cl}]_2$ in acetone also react with the stoichiometric amount of silver sulphate in water; silver chloride is precipitated and the mother liquor on evaporation gives a greenish blue solid which analyses for the compound $[\text{Re}_2(\text{RCOO})_4 \cdot 2\text{H}_2\text{O}] \text{SO}_4$.

After removal of the orange crystals from the dark solution obtained by refluxing rhenium trichloride with carboxylic acids under nitrogen, other compounds which have the stoichiometry $\text{ReCl}_3 \cdot (\text{RCOOH})_2$ (where $\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2$) can be obtained from the mother liquor. Addition compounds of this type have been found before, for example, $\text{CH}_3\text{COOH-SbCl}_5, \text{CH}_3\text{COOH} - \text{SbCl}_4, \text{CH}_3\text{COOH} - \text{SbCl}_3$ and H.COOH-SbCl_5 (108). In the last case no solid compounds were separated and the infra-red spectra of these compounds were measured on a mixture of the acid and the metal chloride in a

definite proportion, and the observed negative shift of the carbonyl stretching frequency was taken as proof that the oxygen of the carbonyl group was co-ordinated to the metal. In the present case, however, only very small shift has been observed.

The compounds are monomeric as shown by their molecular weights determined by the standard isopiestic method⁽¹⁰⁹⁾ in acetone using azobenzene as reference. They are very soluble in many common organic solvents e.g. alcohol, acetone, ether, chloroform, dichloromethane, but are however insoluble in benzene, carbon tetrachloride, petrol and water. They give non-conducting solutions in nitrobenzene. The presence of hydroxyl groups is confirmed by their infra-red spectra. The fact that these compounds are diamagnetic implies that they have trigonal bipyramidal structures d^3sp fig. (6) rather than square pyramidal, since ligand field⁽¹¹⁰⁾ considerations for the two cases indicate that only the bipyramidal form would lead to a diamagnetic $Re(III) (d^4)$ complex. These compounds provide an early example of five co-ordinate $Re(III)$ complexes: the only other examples known so far are the compound prepared from the reaction of rhenium trichloride triphenyl phosphine ($ReCl_3 \cdot PPh_3$) with chlorine which was at first thought to be $ReCl_3 \cdot (PPh_3)_2$ ⁽⁵¹⁾, but later

proved to be a phosphine oxide complex $\text{ReCl}_3 \cdot (\text{OPPh}_3)_2$ (52); and the hydride $\text{ReH}_3(\text{PPh}_3)_2$ (53).

Attempted Reactions

In an attempt to prepare the ester analogues of the last type of compound discussed, rhenium trichloride was mixed with ethyl and methyl acetates. Although purple solutions were obtained, removal of the solvent under vacuum always resulted in the production of oils which repeated washing with light petroleum failed to solidify. The analytical figures obtained for the oils were unsatisfactory.

Attempts to make the compounds $[\text{Re}(\text{RCOO})_2\text{Cl}]_2$ from rhenium trichloride, sodium acetate or butyrate and the corresponding acid anhydride led to pale yellow solids. When these were washed with water (to remove NaCl expected to be formed in the reaction) they decomposed to black solids (probably ReO_2) indicating that they could not be mixtures of NaCl and $[\text{Re}(\text{RCOO})_2\text{Cl}]_2$ since these compounds are stable to water.

3.b. Complexes derived from the reaction between carboxylic acids and Re_2Cl_6 in air

When the reaction between $\text{Re}(\text{III})$ chloride and butyric, isobutyric or octoic acid is performed in the presence of air, purple needle-like crystals slowly deposit from the hot orange solution. The purple crystals were filtered off (the orange solutions will be discussed later on) and found to have the stoichiometry $\text{ReO}(\text{RCOO})\text{Cl}$, and appeared to be dimeric judging by their molecular weight and by their low solubilities in acetone, chloroform and dichloromethane. These compounds again show a gradation in properties as the carboxylic acid series is ascended. The butyrate and isobutyrate are soluble in alcohol, slightly soluble in acetone, chloroform and dichloromethane, and are insoluble in benzene, carbon tetrachloride and petroleum; the octoate is very soluble in alcohol, acetone, dichloromethane, chloroform, benzene and chlorobenzene, but decomposes in the last two solvents on boiling. The isobutyrate melts at 304° , the butyrate at 210° and the octoate melts at 154° . The butyrate and isobutyrate are very stable compounds and can be left exposed to air without appreciable decomposition taking place, while the octoate turns oily on exposure to the air for several days. They are all insoluble in water and

boiling water decomposes them to rhenium dioxide. They give non-conducting solutions in acetone.

In the infra-red spectra of these compounds the carbonyl bands occur in nearly the same region as in $[\text{Re}(\text{RCOO})_2\text{Cl}]_2$, and it seems likely that the compounds contain two carboxylic groups linked to two rhenium atoms as in fig. (7). Furthermore no sharp band could be seen in the region $850 - 1000 \text{ cm}^{-1}$ which could be assigned to $\text{Re} = \text{O}$ stretching frequency⁽¹¹¹⁾; also by comparison between the spectra of these compounds with those of $[\text{Re}(\text{RCOO})_2\text{Cl}]_2$ there was no extra band in this region ($850 - 1000 \text{ cm}^{-1}$). These compounds did not react with halogen bridge cleaving reagents such as p-toluidine under nitrogen. It seems likely therefore that the compounds have the structure shown in fig. (7).

The fact that they are diamagnetic implies that there is rhenium-rhenium interaction, as a $\text{Re}(\text{IV}) d^3$ complex would have been expected to be paramagnetic. This interaction could take place in either of two ways. Firstly interaction through oxygen as in the case of $[\text{Re}_2\text{OCl}_{10}]^{4-}$ ⁽⁷¹⁾; or secondly a direct type is the most likely since once again the two rhenium atoms are held in proximity by the bridging carboxylate groups.

When these compounds are treated with air-free mineral acids they turn blue and dissolve somewhat;

the same blue colour can be imparted to strong acids by shaking them with solutions of the purple crystals of the compounds in organic solvents. It seems likely that this behaviour is due to protonation of one or both of the oxygen atoms. Indeed with hydrochloric acid a compound having the formula $[\text{ReOH}(\text{RCOO})\text{Cl}_2]_2$ was formed, thus confirming this suggestion and showing that protonation of both oxygen atoms has taken place. These new compounds are soluble in acetone, chloroform, dichloromethane very slightly soluble in benzene and insoluble in water; and give non-conducting solutions in nitrobenzene which implies that the two chlorine atoms are co-ordinated to the two rhenium atoms and that the compound has the structure shown in fig. (8).

The compounds are diamagnetic (as shown by the n.m.r.⁽¹¹²⁾ method) suggesting that metal to metal interaction still exists in them; the presence of such interaction implies that the compounds are early examples of seven-co-ordinate Re(IV); the only other example of seven-co-ordinate Re(IV) known so far is $\text{ReH}_4 \cdot (\text{PPh}_3)_3$ ⁽¹¹³⁾ reported by Malatesta et al. and prepared by interaction of $\text{ReH}_3 (\text{PPh}_3)_4$ with sodium borohydride. After refluxing for four days no more purple crystals formed in the hot Re_2Cl_6 -acid solutions. After the purple crystals were removed as described in the preceding section the orange

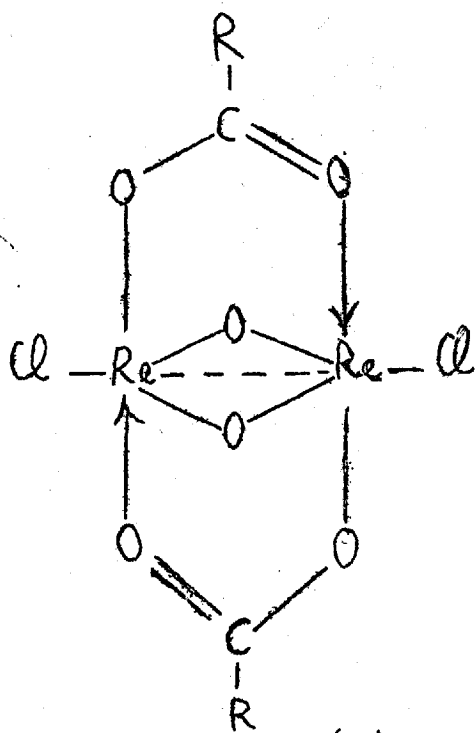


Fig (7)

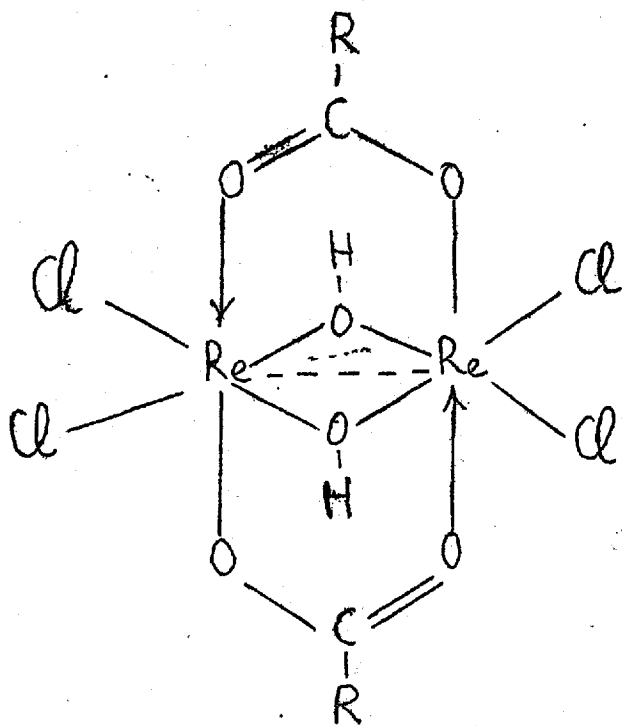


Fig (8)

acid solutions were left to cool when orange crystals were deposited. These crystals have the composition $\text{ReO}_2(\text{RCOO})$ (where $\text{R} = \text{CH}_3\text{CH}_2\text{CH}$ or $\text{CH}_3\text{CH}_2\text{CH}_2$), although in the case of octoic acid the yield was too small to give enough pure sample for analysis. The compounds appear to be dimeric judging from their molecular weights, their high melting points and low solubilities in chloroform, dichloromethane, benzene and chlorobenzene. They are insoluble in cold water and boiling water decomposes them to rhenium dioxide, acetone also causes their decomposition.

They are derivatives of Re(V) and the oxidation of Re(III) has been accomplished by the oxygen since these compounds were never obtained when the reaction was performed under nitrogen, and it seems likely that the carboxylate groups enhanced this oxidation. They are diamagnetic as shown by the Gouy method⁽¹¹⁴⁾ on the solid, and give non-conducting solutions in nitrobenzene which eliminates the possibility of their being ionic compounds similar to $[\text{UO}_2(\text{OAC})_3]^-$ ⁽¹¹⁵⁾ ion.

In the infra-red spectra the carboxylate stretching frequency occurs in nearly the same region as that for the previous types of compounds and only one strong band in the $\text{Re} = \text{O}$ region (932 cm^{-1}) is observed although there is another strong band (825 cm^{-1}) but

this can be attributed to any part of the alkyl chain. It seems likely that the compounds have the structure shown in fig. (9) (although the structure in fig. (10) could not be eliminated conclusively).

The fact that these compounds are diamagnetic does not imply that there is necessarily any Re-Re interaction for there is no reason to believe that five-co-ordinate Re(V) should be paramagnetic, and although rhenium pentachloride was found to be paramagnetic⁽¹¹⁶⁾ with μ_{eff} varying from 2.2 to 2.3 B.M., nothing is known of its stereochemistry. It is however likely that Re-Re interaction exists in this type of complex since again the two rhenium atoms are held close together by the carboxylate group. It appears that when the reaction between acetic and propionic acids (in presence of their respective anhydrides) and rhenium trichloride is carried out in air the same type of complex (as in the case of n-butyric isobutyric and octoic acids) is formed since orange crystals could be seen mixed with purple-black solid; however these were so insoluble as to render their separation into analytically pure samples impossible.

As discussed by Nyholm, Coffey and Lewis⁽¹¹⁷⁾, metal to metal bonds in inorganic compounds are more common than is often supposed. These workers classi-

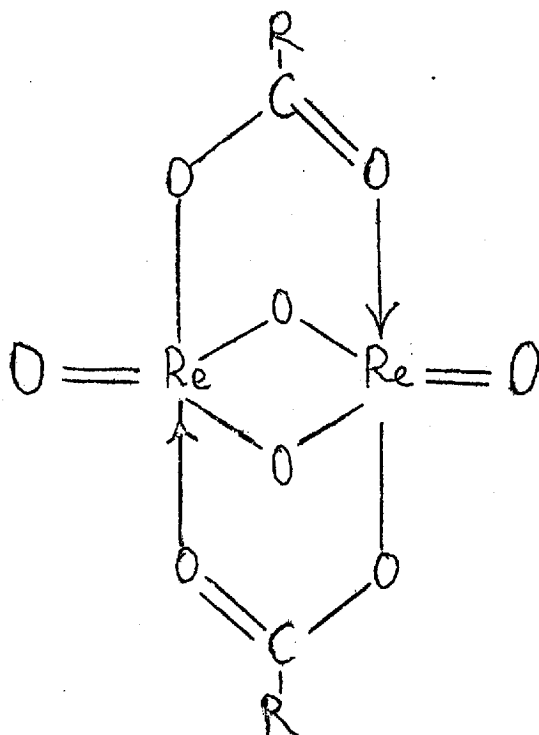
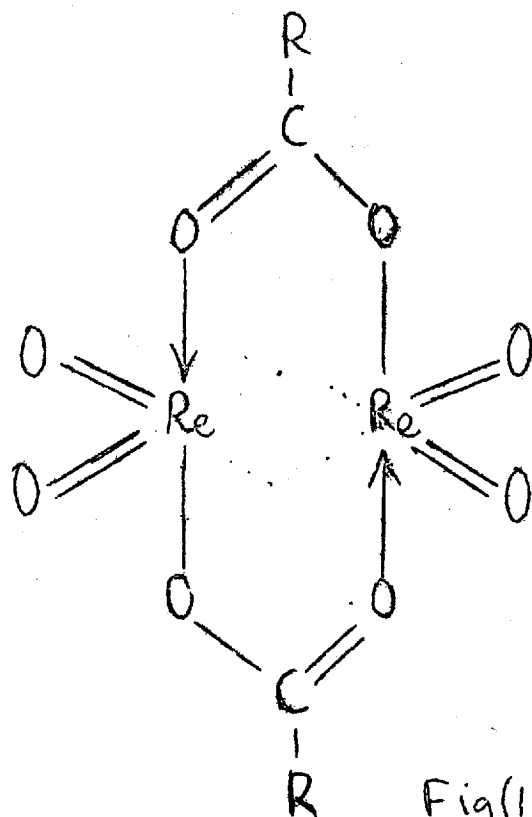


Fig (9)



Fig(10)

fied them into two main groups (a) the multicentre type such as occurs in metals and the concentrated metal halides (e.g. NbI_4 , MoI_3 , MoCl_2 etc.); (b) the covalent type involving a simple covalent bond such as occurs in mercury (I) halides and in dimanganese decacarbonyl.

They reported that an examination of the known examples of metal-metal bonds reveals that they occur most readily when (1) the metal atom has a spin-paired configuration with an odd number of electrons i.e. d^5 , d^7 , d^9 and d^{10} ; (2) the metal atom is in a low oxidation state. In the present work metal to metal interaction appears to exist in the dimeric Re(III) complexes $[\text{Re}(\text{RCOO})_2\text{Cl}]_2$ (where $\text{R}=\text{CH}_3$, CH_3CH_2 , $\text{CH}_3\text{CH}_2\text{CH}$, $\text{CH}_3\text{CH}_2\text{CH}_2$ or $\text{CH}_3(\text{CH}_2)_6$), Re(IV) complexes $[\text{ReO}(\text{RCOO})\text{Cl}]_2$ ($\text{R}=\text{CH}_3\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}$ or $\text{CH}_3(\text{CH}_2)_6$), $[\text{ReOH}(\text{RCOO})\text{Cl}_2]_2$ ($\text{R}=\text{CH}_3\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}$) and probably in the Re(V) complex $[\text{ReO}_2(\text{RCOO})]_2$ ($\text{R}=\text{CH}_3\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}$).

3.c. Complexes derived from rhenium pentachloride

Rhenium pentachloride reacts with acetic acid under nitrogen in presence of acetic anhydride to give a black compound having the composition $\text{ReCl}_3(\text{CH}_3\text{COO})_2$. This compound seems to be polymeric since it is insoluble in most common organic solvents, for example acetone, benzene and dichloromethane and it is only slightly soluble in chloroform and nitrobenzene (giving a non-conducting solution in the last solvent). It did not melt when heated up to 298°C . It is unaffected by cold dilute mineral acids and decomposed by bases to rhenium dioxide. The structure of this compound is possibly as shown in fig. (11) and involves seven-co-ordinate Re(V) . The only other seven-co-ordinate Re(V) compounds known so far are the complex hydride $\text{ReH}_5(\text{PPh}_3)_2$ reported by Malatesta et al.⁽¹¹³⁾ and the compound prepared lately by Mawby and Venanzi⁽¹¹⁸⁾ namely $[\text{ReOX}_3(\text{TAS})]$ ($\text{X}=\text{Cl}$ or Br and $\text{TAS}=\text{bis}$ (O-diphenyl arsino phenyl arsine) by interaction of rhenium trihalide and the triarsine. These authors reported that oxidation from Re(III) to Re(V) took place during the reaction, and that they are not certain whether these complexes are six or seven-co-ordinate. Also Ferguson, Kirkham and Nyholm⁽¹¹⁹⁾ reported that a seven-co-ordinate paramagnetic pentavalent rhenium

complex $[(\text{ReD}_2\text{Cl}_2)_2\text{O}]_2(\text{ClO}_4)_4$ ⁽⁸⁴⁾ was formed on oxidising the trivalent chlorine complex $[\text{ReD}_2\text{Cl}_2]\text{ClO}_4$ with 15-N nitric acid (D=o-phenylenebis-dimethyl arsine). In the present case the compound is diamagnetic.

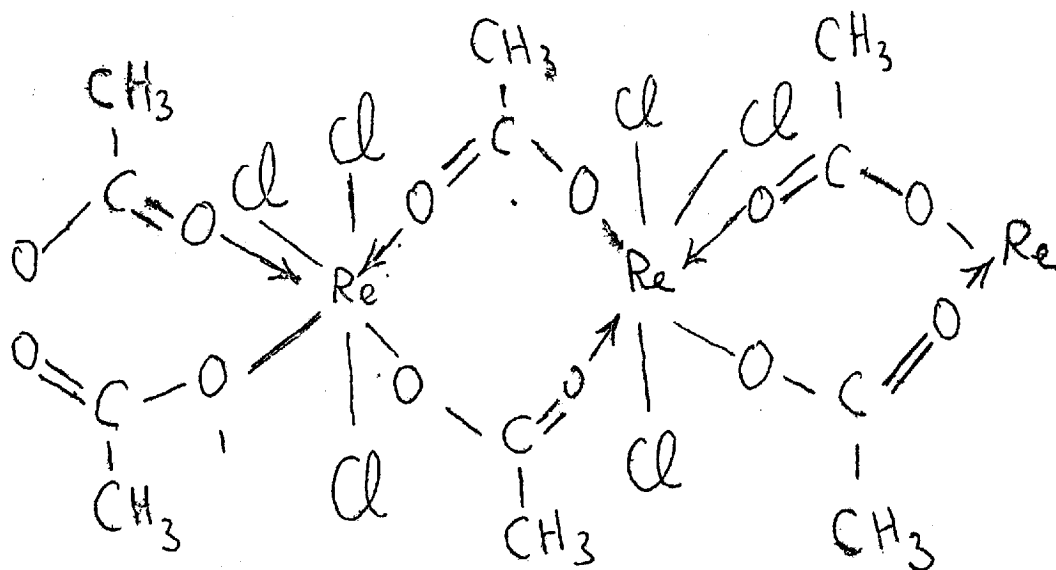


Fig (11)

3.d. The infra-red spectra of carboxylic acid complexes

Not many data are available concerning the infra-red of metal carboxylate complexes. French workers (1943) have studied the infra-red spectra of some metal acetates, propionates, butyrates, isobutyrate, oxalates and some other aromatic complexes⁽¹²⁰⁾. Their study was confined to the region 600-1600 cm^{-1} which rendered their assignments somewhat incorrect since some carboxylate compounds are known to have C-O stretching frequency higher than this region.

Recently Okawara et al.⁽¹²⁾ compared the infra-red spectra of organotin acetates which show carbonyl stretching frequencies at about 1580 and 1440 cm^{-1} with that of acetoxytrimethylsilane which shows a carbonyl stretching frequency at 1725 cm^{-1} and a C-O-(Si) stretch at 1267 cm^{-1} and concluded that the former compounds contain carboxylate anions. Later Beattie and Gilson⁽¹²²⁾ discussed their results and reported that the main problem in this case is a stereochemical one (not one of degree of ionic character) and that one should not expect to find great differences between the spectra of ionic acetate and chelate or bridging acetate groups. They also reported that there would be considerable difference between the free

carbonyl group in an ester and CO_2 acting as a chelate or bridging group. They supported their conclusion by some results of Duncanson et al.⁽¹²³⁾ who have shown that the carbonyl frequencies in tetra-acetyl diborate occur at 1718 and 1605 cm^{-1} . These are interpreted in terms of two free carbonyl groups and two bridging carbonyl groups respectively, since boron has a maximum covalency of four. The value of 1605 cm^{-1} for the bridging group is close to that found in ionic acetates where the C-O stretching frequencies occur in the region 1580 cm^{-1} . The same workers observed the spectra of basic acetates of zinc and beryllium, which would conventionally be regarded as covalent and where the crystal structures are known, and compared them with certain organotin acetates; their results are shown in tables (1) and (2)

Table (1) C-O Stretching Frequencies in cm^{-1}

NaOAc	Me_3SnOAc	$\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$
1408	1428	1418
1578	1576	1603

Table (2) C-O Stretching Frequencies in cm^{-1}

$\text{Be}_4\text{O}(\text{OAc})_6$	$\text{Zn}_4\text{O}(\text{OAc})_6$	$(\text{OAcMe}_2\text{Sn})_2\text{O}$
1481	1443	1410
1623	1598	1580

From this comparison they have demonstrated that there is no simple way of distinguishing between a discrete acetate ion and a bridging acetate group.

Other results which could be stated in support of their view are the infra-red spectra of hydrated and anhydrous chromium acetate⁽¹²⁴⁾. The carbonyl stretching frequencies of these are shown in table (3).

Table (3) C-O Stretching Frequencies in cm^{-1}

$\text{Cr}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$	$\text{Cr}_2(\text{OAc})_4$	$\text{Cu}_2(\text{OAc})_4$
1423	1422	~1420
1586	1571	1591

Japanese workers⁽¹²⁵⁾ compared the infra-red spectrum of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in which the acetate group is known to be unidentate from X-ray studies⁽¹²⁶⁾ with that of bidentate cupric acetate and claimed that

the two Cu-O bondings in the latter are responsible for higher frequency shift of the asymmetric C-O stretching mode (1603 cm^{-1} in the case of the copper complex compared to 1530 cm^{-1} in the case of the nickel one). It appears, however, that this is not always the case since in the infra-red spectrum of molybdenum diacetate⁽¹²⁷⁾, which is believed to contain the polymeric structure in fig (II), the asymmetric C-O stretching frequency occurs even at a lower region (1512 cm^{-1}) compared to that of nickel diacetate (1530 cm^{-1}). Furthermore the dimeric 1:5 cyclooctadiene rhodium acetate⁽⁹⁰⁾ which is believed to have the structure in fig (III) whows asymmetric C-O stretching frequency at 1530 cm^{-1} (asymmetric and symmetric C-O stretching frequencies for the last two compounds are shown in table (4)).

Table (4) C-O Stretching Frequencies in cm^{-1}

$[\text{Mo}(\text{OAc})_2]_n$	$[\text{diene}_2\text{Rh}_2(\text{OAc})_2]$
1410	1419
1512	1530

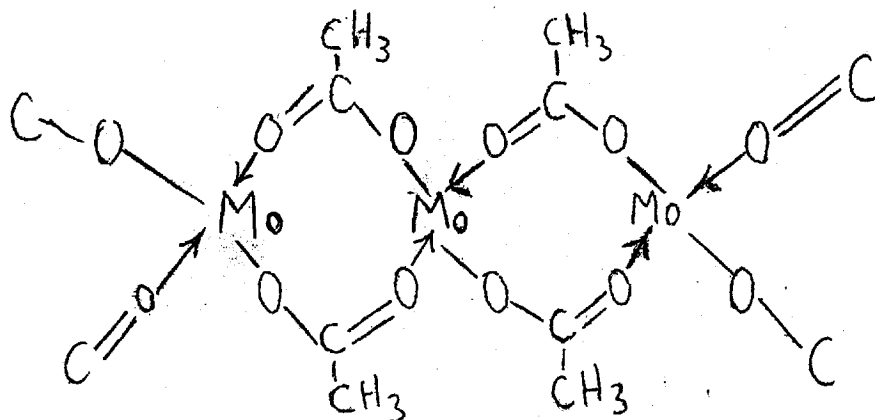
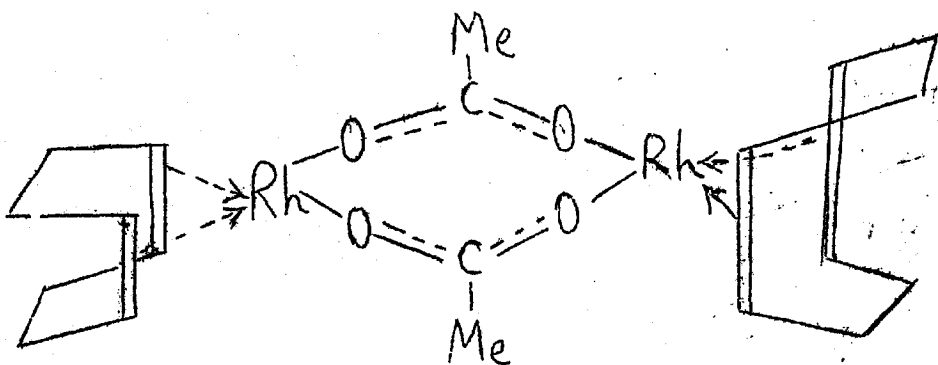


Fig (II)



Fig(III)

The fact that these workers relied on few compounds to draw this conclusion rendered it incorrect.

The infra-red spectra of the rhenium complexes described in this work are given in tables (5-20).

Table (5)

The infra-red spectrum of $[\text{Re}(\text{CH}_3\text{COO})_2\text{Cl}]_2$ in cm^{-1}

2924	m) CH	1040	s } rock-
1456	v.s C-O	1020	s } ing
1425	sh def. CH_3	945	w C-C
1385	v.s C-O	680	v.s def.
1345	s def. CH_3		$\begin{array}{c} \text{O} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{O} \end{array}$

Table (6)

The infra-red spectrum of $[\text{Re}(\text{CH}_3\text{CH}_2\text{COO})_2\text{Cl}]_2$ in cm^{-1}

2990	s	1304	v.s	885	w
2940	s	1085	s	850	s
2890	s	1015	m	800	s
1470	v.s	975	w	686	s
1438	v.s	935	s	650	s
1375	s				

Table (7)

The infra-red spectrum of $[\text{Re}(\text{CH}_3\text{CH}_2\text{CH}_2\text{COO})_2\text{Cl}]_2$ in cm^{-1}

3000	s	1375	v.s	933	m
2955	s	1305	v.s	887	s
2885	s	1267	s	861	s
1470	v.s	1200	s	797	v.s
1450	sh	1195	s	765	m
1437	v.s	1037	w	723	s
1400	sh	955	sh	650	v.s

Table (8)

The infra-red spectrum of $[\text{Re}((\text{CH}_3)_2\text{CHCOO})_2\text{Cl}]_2$ in cm^{-1}

2980	s	1377	v.s	963	m
2930	s	1300	s	928	s
1470	v.s	2185	sh	845	s
1440	sh	1164	m	755	s
1430	v.s	1981	s	672	s

Table (9)

The infra-red spectrum of $[\text{Re}(\text{CH}_3\text{CH}_2\text{CH}_2\text{COO})_2\text{SCN}]_2$ in cm^{-1}

2980	v.s	1480	v.s	1085	s
2940	sh	1430	v.s	890	m
2880	sh	1375	v.s	820	w
2033	v.s	1310	s	790	sh
1581	s	1260	s	760	s
1521	s	1205	m	650	s

Table (10)

The infra-red spectrum of $\text{ReCl}_3(\text{CH}_3\text{COOH})_2$ in cm^{-1}

3360	b	1385	s	920	s
2924	s	1350	m	845	s
1708	s	1080	m	775	s
1476	s	1040	s	685	s
1445	v.s	920	s		

Table (11)

The infra-red spectrum of $[\text{ReO}\{(\text{CH}_3)_2\text{CHCOO}\}\text{Cl}]_2$ in cm^{-1}

2970	m	1383	m	960	sh
2950	m	1365	m	940	s
1480	v.s	1300	s	887	s
1463	sh	1170	m	835	s
1430	v.s	1080	s	670	b

Table (12)

The infra-red spectrum of $[\text{ReO}\{\text{CH}_3(\text{CH}_2)_2\text{COO}\}\text{Cl}]_2$ in cm^{-1}

2924	m	1260	s	938	s
2950	m	1205	m	913	s
1470	v.s	1195	b	858	s
1430	v.s	1099	m	793	m
1400	sh	1073	sh	748	sh
1330	m	1045	w	723	s
1305	m	978	m	650	s

Table (13)

The infra-red spectrum of $[\text{Re}(\text{OH})(\text{CH}_3)_2\text{CHCOO}\text{Cl}_2]_2$

* 3380	s	1377	s	1080	v.s
2980	m	1367	sh	925	s
2930	m	1300	s	840	m
1475	v.s	1285	sh	760	m
1451	v.s	1165	w	675	m
1431	v.s				

Table (14)

The infra-red spectrum of $[\text{ReO}_2(\text{CH}_3)_2\text{CHCOO}]_2$

2970	s	1335	w	976	s
2930	sh	1312	s	935	v.s
2875	s	1270	s	815	v.s
1462	v.s	1167	m	755	s
1440	sh	1095	s	680	s
1415	v.s				

Table (15)

The infra-red spectrum of $[\text{ReO}_2\{\text{CH}_2(\text{CH}_2)_2\text{COO}\}]_2$ in cm^{-1}

2970	m	1290	s	980	s
1465	v.s	1267	v.s	932	v.s
1440	sh	1220	s	825	v.s
1420	v.s	1205	sh	755	s
1385	s	1092	s	670	s
1310	v.s	1080	sh		

Table (16)

The infra-red spectrum of $[\text{Re}(\text{CH}_3((\text{CH}_2)_6\text{COO})_2\text{Cl})_2]$
in the region $4000-1200 \text{ cm}^{-1}$

2950	sh	1400	s
2910	v.s	1365	m
2850	sh	1340	m
1468	v.s	1320	m
1440	sh	1295	m
1420	v.s	1245	m

Table (17)

The infra-red spectrum of $\text{ReCl}_3(\text{CH}_3\text{COO})_2$ in cm^{-1}

2940	s	1025	m
1560	s	1010	m
1455	v.s	930	w
1425	v.s	720	s
1396	v.s	650	s

Table (18)

The infra-red spectrum of $[\text{ReOH}\{\text{CH}_2(\text{CH}_2)_2\text{COO}\}\text{Cl}_2]_2$

3370	s	1430	v.s	1090	v.s
2980	m	1365	v.s	960	w
2910	m	1296	v.s	920	m
1470	v.s	1275	sh	840	m
1450	v.s	1158	m	744	m
				665	m

Table (19)

The infra-red spectrum of $[\text{Re}\{(\text{CH}_3)_2\text{CHCOO}\}_2\text{SCN}]_2$ in cm^{-1}

2980	s	1375	v.s	840	m
2940	sh	1300	v.s	770	sh
2880	sh	1165	m	750	m
2030	v.s	1090	v.s	715	m
1475	v.s	960	w	680	m
1425	v.s	920	m		

Table (20)

The infra-red spectrum of $\text{ReCl}_3 \cdot \left\{ \text{CH}_3(\text{CH}_2)_2\text{COOH} \right\}_2$

3370	b	1415	v.s	1030	m
2970	s	1385	v.s	975	w
2930	s	1317	v.s	946	s
2870	s	1262	s	840	s
1710	s	1200	m	790	s
1462	v.s	1090	s	660	s

Table (20a)

The infra-red spectrum of $\left[\text{Re}_2(\text{CH}_3\text{CH}_2\text{CH}_2\text{COO})_4 \cdot 2\text{H}_2\text{O} \right] \text{SO}_4$
in cm^{-1}

3400	b	1385	sh	1025	s
2960	s	1315	v.s	940	m
2900	sh	1270	s	895	s
1625	m	1210	s	795	s
1470	v.s	1175	s	720	m
1440	v.s	1080	s	650	s

Nitrogen ligandsPyridine complexes

Rhenium pentachloride dissolved in acetone (G.P.R. grade) reacted with pyridine to give a green compound which precipitates rapidly and the solution turned orange; this green precipitate was filtered off (the orange acetone pyridine solution was left to settle as will be discussed below) and recrystallised from chloroform. It was found to have the composition $\text{ReO}(\text{OH})\text{py}_2\text{Cl}_2$ and possibly has the structure in fig. (12). The fact that an α - α dipyridyl analogue

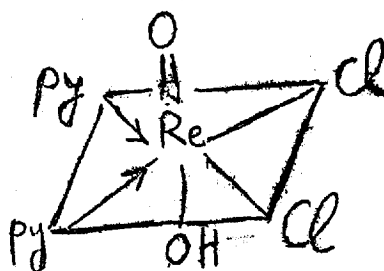


Fig (12)

is known (as will be described later on) implies that the two pyridine molecules in this complex must be in the cis position. This compound is sparingly soluble in pyridine and acetone, and is insoluble in benzene, alcohol, tetrahydrofuran, carbon tetrachloride, water (cold or hot) and ether. It gives

a non-conducting solution in nitrobenzene. The infra-red spectrum of this compound shows a band corresponding to an O-H stretching frequency at 3300 cm^{-1} and two bands in the region corresponding to $\text{Re}=\text{O}$ (978S , 912S cm^{-1}), one of these could be due to a crystal effect and as the compound is not sufficiently soluble to make an infra-red spectrum in solution it was not possible to eliminate this effect.

The compound is diamagnetic which is common among six-co-ordinate Re(V) compounds. It is unaffected by cold concentrated mineral acids e.g. hydrochloric acid.

After settling, the orange pyridine-acetone solution (left after removal of the green compound discussed above) deposited orange crystals which had the composition $[\text{ReO}_2\text{py}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$. These are soluble in water and give precipitates with large anions, for example the tetraphenylborate anion.

It was impossible to remove the water of crystallisation of this complex salt, even by maintaining it for 48 hours at 100°C in a vacuum. This compound was also prepared by addition of pyridine to a solution of $(\text{PPh}_3)_2\text{ReOCl}_3$ in alcohol⁽²⁸⁾. It is interesting to point out that the compound $[\text{ReO}_2\text{py}_4]\text{Cl}$ was reported by Russian workers⁽¹²⁹⁾.

who prepared it by the reaction of potassium oxochlororhenate (V) $K_2 [ReOCl_5]$ with aqueous pyridine. Also in a note by Indian workers⁽¹³⁰⁾ the compound ReO_2py_4Cl was reported among other products of the reaction between a concentrated aqueous solution of potassium hexachlororhenate (IV) $K_2 [ReCl_6]$ and pyridine, however, it was not pointed out that this compound is ionic or that it is soluble in water.

In the present work the complex $[ReO_2py_4]Cl \cdot 2H_2O$ shows no band in the infra-red spectrum in the region $850 - 1000 \text{ cm}^{-1}$ (the region in which $Re=O$ stretching frequency is considered to occur) which at first suggested that the compound possibly has the formula $[Re(OH)_4py_4]Cl$. But the fact that the tetraphenylborate complex has no band in the infra-red spectrum corresponding to O-H stretching frequency (around 3200 cm^{-1}) and the oxygen content of this complex was always half that expected for the composition $[Re(OH)_4py_4] BPh_4$ excluded this possibility and suggested that the original compound $[ReO_2py_4]Cl \cdot 2H_2O$ contained two mols of water of crystallisation which was removed in the formation of the tetraphenylborate complex. Furthermore the tetraphenylborate salt shows no band in the region $850 - 1000 \text{ cm}^{-1}$.

It was suggested later that the band at 820 cm^{-1} which cannot be attributed to the pyridine ligand⁽¹³¹⁾ and should be assigned to $\text{Re} = \text{O}$ stretching frequency displaced from the normal $\text{M} = \text{O}$ region because of the trans arrangement of the $\text{O} = \text{Re} = \text{O}$ bonds. This lowering of the single stretching frequency expected in trans dioxo grouping was first commented on by Johnson et al.⁽¹³²⁾.

The compound is soluble in pyridine, slightly soluble in acetone, alcohol and chloroform; it is soluble in water and decomposes to rhenium dioxide on boiling in the last solvent. It is insoluble in benzene, carbon tetrachloride and nitrobenzene. That the compound is a uni-univalent electrolyte was confirmed by the conductivity measurement.

The compound is diamagnetic which is usual among the measured six-co-ordinate Re(V) compounds. Indeed the only paramagnetic six-co-ordinate Re(V) known so far is the ion $[\text{ReF}_6]^-$ ⁽⁸⁵⁾; the magnetic properties of several of the alkali salts of this ion have been determined⁽⁶⁾ and μ_{eff} values vary from 1.53 to 2.05 B.M. at 300°K .

This orange rhenium complex reacts with concentrated mineral acids to give red-coloured solutions, but attempts to separate a red solid product failed

since the reaction is reversible and the original compound was always obtained. However, if the reactants were boiled a green solid precipitated which is practically insoluble in all solvents tried and which analyses for the composition $\text{ReOpy}_2\text{Cl}_3 \cdot \text{H}_2\text{O}$.

α - α dipyridyl complex:

Rhenium pentachloride dissolved in acetone reacts with α - α dipyridyl to give several products among which was a green product having the composition ReO(OH)dipy Cl_2 . This compound is soluble in acetone and chloroform and it is insoluble in benzene, carbon tetrachloride and alcohol. The compound is diamagnetic similar to its pyridine analogue.

In the infrared spectrum of this compound a band was observed in the region corresponding to O-H stretching frequency (3360 cm^{-1}) in addition to two bands observed in the region where Re=O stretching frequency is known to occur (930 and 880 cm^{-1}). The band at 930 cm^{-1} is strong while that at 880 cm^{-1} is a weak band; this could be a splitting due to crystal effects and the compound was not sufficiently soluble to allow an infrared spectrum in solution to be taken.

Attempted Reaction.

In an attempt to prepare an ortho phenanthroline complex similar to the dipyridyl complex described above

rhenium pentachloride was dissolved in acetone, and to this solution an acetone solution of orthopenanthroline was added. A difficulty soluble mixture was formed for which the analysis was always unsatisfactory.

Attempted triphenyl phosphine oxide reaction.

A mixture of rhenium trichloride and triphenyl phosphine oxide was refluxed in acetone for four hours; purple crystals were obtained, but were insoluble in all solvents tried and could not be recrystallised. Their carbon and hydrogen analyses were always lower than the calculated value if the compound had the formula $(\text{ReCl}_3 \cdot \text{Ph}_3\text{PO})$.

Table (21)

The infra-red spectrum of $\text{ReO}(\text{OH})\text{Cl}_2\text{py}_2$ in cm^{-1}

3300	w	1453	v.s	1015	s
3076	v.w	1380	v.w	978	s
1630	w	1245	m	912	s
1612	v.s	1220	s	870	s
1570	w	1155	s	817	m
1558	w	1067	v.s	766	v.s
1535	s	1050	s	690	v.s
1492	s				

Table (22)

The infra-red spectrum of $[\text{ReO}_2\text{py}_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ in cm^{-1} .

3400	m	1351	m	820	v.s
3086	s	1212	s	780	s
3025	s	1160	sh	766	sh
1625	sh	1146	m	745	sh
1609	s	1060	s	700	v.s
1563	m	1010	m	690	v.s
1478	m	955	v.w		
1450	v.s	880	w		

Table (23)

The infra-red spectrum of $\text{ReO}(\text{OH})\text{dipy}\text{Cl}_2$ in cm^{-1} .

3360	b	1260	w	930	s
3060	s	1220	s	880	w
3000	s	1190	sh	860	w
2920	w	1160	s	830	v.s
1635	m	1080	v.s	785	v.s
1565	v.s	1060	s	760	v.s
1459	v.s	1050	s	750	v.s
1429	v.s	1008	s	720	v.s
1315	w	970	w	710	v.s

4. EXPERIMENTAL

Infra-red spectra were recorded using a Perkin-Elmer Model 21 double beam Infra-red spectrometer.

Samples were studied in "nujol" and "hexachlorobutadiene" mulls using sodium chloride and calcium fluoride optics.

Nuclear magnetic spectra were measured on a Varian Associates Model 4300 B spectrometer. Magnetic measurements on solids were made using the Gouy method⁽¹¹⁴⁾ and on solutions by the method of D.F. Evans⁽¹¹²⁾.

4.1. Analytical methods.

Carbon, hydrogen, nitrogen, oxygen some halogen and some molecular weight determinations were performed by the Imperial College Microanalytical Laboratory. Rhenium was determined either gravimetrically or colourimetrically. The gravimetric method was carried out using nitron⁽¹³³⁾. The samples were oxidised to perrhenate using sodium peroxide and sodium hydroxide and the solution was neutralised with sulphuric acid. The neutral solution of potassium perrhenate (which should contain at most 0.1 gm of rhenium); was diluted with hot water (about 20 ml), 0.5 ml 2-N sulphuric acid were added and the solution was heated to 80°C. The rhenium was precipitated as nitron perrhenate by addition of 5% nitron solution (0.8 gm commercial nitron dissolved in 1 ml. glacial

acetic acid, then diluted to 16 ml. and filtered using a fine crucible). The mixture was cooled to room temperature, left for two hours in ice water with occasional stirring, filtered through a fine sintered crucible and washed with the mother liquor diluted 13_ fold with ice cold water. Excess nitron was removed by washing with a saturated solution of nitron ~~perhenate~~ in ice cold water. The precipitate was then dried for 2-3 hours at 110°C and weighed. The colourimetical ⁽¹³⁴⁾ method was carried out using α -furyl dioxime. The complexes were oxidised to ~~perhenate~~ by fusion with a mixture of sodium hydroxide and sodium peroxide. (Nitric acid cannot be used for this oxidation as it interferes with the colourimetric measurements). The mass was extracted with water and diluted accurately to 250 ml. An aliquot (usually 2-5 ml.) was taken and transferred to a 50 ml. graduated flask. Five ml. concentrated hydrochloric acid and 5 ml. of stannous chloride solution (10 gms/100 ml.) were added and then 13 ml. of an acetone solution of α -furyl dioxime. The solution was diluted to the mark and left to stand for about 40 minutes to allow the colour to develop. The optical density of the solution was measured at 532 m μ . Two standard samples were always analysed at the same time to allow a Beer's law Plot to be made. The method is useful

for rhenium concentrations between 25 and 200 p.p.m.

Rhenium pentachloride

Rhenium pentachloride was prepared by chlorinating rhenium metal⁽²¹⁾. It was found necessary to perform the reaction at a temperature not higher than about 550°C. as very pure rhenium metal gave the hexachloride at about 600°C. This has since been used as a method for the preparation of rhenium hexachloride⁽¹³⁾. The pentachloride forms fine dark brown or black crystals and it can be easily sublimed along the tube in which the preparation is performed to prevent a blockage. When all the rhenium is changed into pentachloride (shown by the disappearance of all brown fumes in the neighbourhood of the boat) the black crystalline product is sublimed in a current of chlorine into the next section of the tube. The tube is then sealed off, the tap at its end is closed and the tube is supported in a vertical position, and by gentle tapping all of the crude ReCl_5 is collected at the end of the first section. The tap is then connected to an oil pump and the system is evacuated. The tube is clamped at 45° to the vertical and the product is slowly heated to 160°C by means of a small electric furnace. A small amount of oxychloride which distills over at 50°C and condenses

on the cooler portion of the tube is expelled by warming gently with a small flame. When a temperature of 160° has been reached the first constriction is emptied and the tube is sealed off at the second constriction.

Rhenium trichloride.

Rhenium trichloride was prepared by the thermal decomposition of the pentachloride in a stream of nitrogen. To obtain a purer product the tube was sealed off at the first constriction, after all of the pentachloride had been decomposed. The product was shaken into the first section, the tube inclined at an angle of 45° to the horizontal and the chloride was sublimed under reduced pressure at a temperature of 450°C . The product was sublimed twice, allowed to cool to room temperature and the tube was broken at points just above and below the place where the trichloride had formed. In this way the product is a brick-red colour rather than the usual dark purple of the less pure material.

4.2. Carboxylic acid compounds.

Chlororhenium (III)- μ -tetra-acetate - chlororhenium (III).

Rhenium trichloride (2.5 gm.) was refluxed with acetic acid (25 ml.) in presence of acetic

anhydride (1 ml.) just at the boiling point of the acetic acid while passing a stream of nitrogen through the solution. The reaction was carried out for four days during which orange crystals separated from the very dark brown solution. These were decanted washed with acetone and then several times with petrol (30-40°) and dried in vacuum (0.1 mm.). The yield was 0.22 gm. (about 8%). The supernatant liquid was worked up as below. The compound is insoluble in most common organic solvents, for example acetone, chloroform, dichloromethane, benzene, carbon tetrachloride, alcohol and ether. It is unaffected by cold mineral acids (dilute or concentrated). It decomposes only on boiling in concentrated nitric acid giving colourless solution (probably forming perrhenic acid), also bases decompose it to rhenium dioxide [Found: C, 14.1; H, 1.7; O, 19.1; Cl, 10.4; Re, 55.9. Required for $[\text{ReC}_4\text{H}_6\text{O}_4\text{Cl}]_2$: C, 14.1; H, 1.8; O, 18.8; Cl, 10.4; Re, 54.9%]. Does not melt below 330°C.

Chlororhenium (III)- μ -tetrapropionato
chlororhenium (III)

The reaction was performed as for chlororhenium (III) μ -tetra acetato chlororhenium (III) using propionic acid (25 ml.) and propionic anhydride (1 ml.). The acid solution was left to cool and the

orange crystalline powder was decanted, washed with small amount of acetone (1 ml.) followed by several washings with petrol (30-40°) and dried under vacuum (0.1 mm.). This compound is sparingly soluble in acetone, and insoluble in benzene, chloroform, dichloromethane and ether. The yield was 0.4 gm. (about 13%).

[Found: C, 19.4; H, 2.1; O, 17.2%. Required for $[\text{ReCl}_6\text{H}_{10}\text{O}_4]_2$: C, 19.5; H, 2.7; O, 17.4%]. Decomposed at 245°C.

Chlororhenium (III)- μ -tetra-n-butyrate
chlororhenium (III).

The reaction was performed as for the previous compound using rhenium trichloride (2.5 gm.), n-butyric acid (25 ml.) and n-butyric anhydride (1 ml.). In this case orange crystals up to 1 cm. long were obtained; these were decanted and washed with Analar petroleum spirit (30-40°) and dried under vacuum. Sometimes the compound made in this way is impure and purification can be effected by recrystallisation from dichloromethane. Yield 1.08 gm. (about 34%) of orange crystals, soluble in acetone, chloroform, and tetrahydrofuran, sparingly soluble in benzene and chlorobenzene (very soluble in hot) and insoluble in carbon tetrachloride and ether. [Found: C, 24.4; H, 3.6; O, 16.7%. Required for $[\text{ReCl}_6\text{H}_{14}\text{O}_4]_2$: C, 24.3; H, 3.5; O, 16.2%]. M. p. 215°C.

Chlororhenium (III) μ -tetra-isobutyrate
chlororhenium (III).

Rhenium trichloride (2.5 gm.) was refluxed with isobutyric acid (25 ml.) for four days while passing a stream of nitrogen through the solution. The acid solution was left to cool and the orange crystals formed were crystallised from dichloromethane. This compound has solubilities similar to that of the n-butyrate complex. Yield is 1.07 gm. (about 34%). [Found: C, 24.8; H, 3.9; O, 16.6%. Required for $[\text{ReClC}_8\text{H}_{14}\text{O}_4]_2$; C, 24.3; H, 3.5; O, 16.2%]. M. p. 221°C.

Chlororhenium (III) μ -tetraoctoate
chlororhenium (III).

Rhenium trichloride (2.5 gm.) was refluxed with octoic acid (25 ml.) while passing a stream of nitrogen through the solution, The reaction was carried out for three days. After cooling glistening orange leaflets were precipitated. These were crystallised from dichloromethane and found to be soluble in most common organic solvents such as acetone, alcohol, chloroform, dichloromethane, tetrahydrofuran, benzene, chlorobenzene, but insoluble in carbon tetrachloride, petroleum spirit and ether. Yield is 1.05 gm. (about 25%). [Found: C, 38.0; H, 5.9; O, 12.7; Cl, 7.4% mol. wt. 1100 \pm 100. Required for $[\text{ReClC}_{16}\text{H}_{30}\text{O}_4]_2$: C, 37.8; H, 5.9; O, 12.6; Cl, 7.0% mol. wt., 1016]. M. p. 196°C.

Aquorhenium (III) μ -tetra-n-butyrate-
aquorhreneium (III) sulphate.

Equimolecular quantities of chlororhenium (III) μ -tetra-n-butyrate chlororhenium (III) (0.4702 gm.) in acetone (6 ml.) and silver sulphate (0.1851 gm. = 0.594×10^{-3} moles) in distilled water (30 ml) were mixed under nitrogen. The orange solution of the butyrate complex turned blue and silver chloride precipitated quickly and was filtered off under nitrogen. On removing the solvent on the vacuum pump a greenish blue powder separated and was centrifuged off and dried at 100°C under vacuum overnight. [Found: C, 22.2; H, 3.8; O, 25.7%; Required for $[\text{Re}_2\text{C}_{16}\text{H}_{32}\text{O}_{14}\text{S}]$: C, 22.5; H, 3.8; O, 26.3%].

Thiocyanatorhenium (III) μ -tetra-n-
butyrate thiocyanato rhenium (III)

Silver thiocyanate was prepared from silver nitrate and potassium thiocyanate, and was dried at 100°C under vacuum (0.1 mm.) for 48 hours. A solution of chlororhenium (III) μ -tetra-n-butyrate chlororhenium (III) (0.8 gm.) in benzene (15 ml.) was refluxed for five hours (under nitrogen) with excess of silver thiocyanate (8 gm.) during which time the colour of the solution changed from orange to light brown, then to dark brown. The solution was filtered (under nitrogen) and the solvent removed on the vacuum pump; a very

dark brown-black solid was obtained, the yield being almost quantitative. The compound is soluble in acetone and benzene giving dark brown solutions

[Found: C, 23.2; H, 3.1; N, 3.7%. Required for $[\text{ReCl}_9\text{H}_{14}\text{O}_4\text{SN}]_2$; C, 25.8; H, 3.4; N, 3.3%].

Trichlorodiacetic acid rhenium (III)

The dark coloured solution remaining after removal of the orange crystals in the preparation of chlororhenium (III) μ -tetra-acetato chlororhenium (III) was filtered and evaporated in vacuo. The black residue was washed with Analar petroleum spirit (30-40°) in several portions and dried on the pump. The compound is soluble in acetone, alcohol, chloroform, and ether and is insoluble in water, benzene and carbon tetrachloride. The molecular weight was determined in acetone solution by the standard isopiestic method using azobenzene as reference. The conductivity measurement was carried out in nitrobenzene. Yield 1.5 gm. (about 44%). [Found: C, 11.0; H, 1.9; O, 16.0; Cl, 25.4; Re, 45.9%; mol. wt., 390 ± 40 . Required for $\text{ReCl}_3\text{C}_4\text{H}_8\text{O}_4$: C, 11.6; H, 1.9; O, 15.5; Cl, 25.8; Re, 45.1%; mol. wt., 412] $\Lambda(3.5 \times 10^{-3}\text{M}) = 1.3 \text{ mho.}$

Trichlorodipropionic acid rhenium (III).

The compound was separated from chlororhenium (III) μ -tetra-propionato-chlororhenium (III) in the

same way as for the acetic acid complex. The compound is very dark brown and is freely soluble in most common organic solvents for example acetone, chloroform, alcohol, ether and is insoluble in carbon tetrachloride and benzene. Yield is 1.6 gm. (about 44%). [Found; C, 14.0; H, 2.6; O, 14.6%. Required for $\text{ReCl}_3\text{C}_6\text{H}_{12}\text{O}_4$, C, 16.3; H, 2.7; O, 14.5%].

Chlororhenium (IV) μ -dioxo μ -diisobutyrate
chlororhenium (IV).

Rhenium trichloride (2 gm.) was refluxed with isobutyric acid (25 ml.) in presence of air for about four days; purple needlelike crystals precipitated slowly from the acid solution. This solution was filtered while hot (and the filtrate, an orange solution was worked up as below). The compound is soluble in alcohol, very slightly soluble in chloroform and dichloromethane and is insoluble in benzene, carbon tetrachloride and nitrobenzene. It is insoluble in cold water, and boiling water leads to its decomposition to rhenium dioxide. The latter type of decomposition occurs on addition of a base (small pellets of NaOH) to a solution of the compound in acetone or if the compound is shaken with cold aqueous sodium hydroxide. The compound was crystallised from chloroform and dried under vacuum. The yield is 0.5 gm. (about 23%). It sometimes happens that a small amount of $[\text{ReO}_2(\text{CH}_3)_2\text{CHCOO}]_2$ (orange

crystals formed in the same reaction) is precipitated with the product and this can be removed by dissolving the purple crystals $[\text{ReO}\{(\text{CH}_3)_2\text{CHCOO}\}\text{Cl}]_2$ in alcohol in which solvent $[\text{ReO}_2(\text{CH}_3)_2\text{CHCOO}]_2$ is insoluble. The compound gives non-conducting solution in acetone. This compound is stable to air and can be exposed to air for several months without decomposition. [Found: C, 14.9; H, 2.4; O, 14.4; Cl, 11.3; Re, 57.3%; mol. wt. 820 ± 100 . Required for $[\text{ReClC}_4\text{H}_7\text{O}_3]_2$, C, 14.8; H, 2.2; O, 14.8; Cl, 10.9; Re 57.3%; mol. wt. 649. M. p. 304°C]. $\Lambda(4.5 \times 10^{-4} \text{ M}) = 7.3 \text{ mho}$.

Chlororhenium (IV) μ -dioxo- μ -di-n-butyrato chlororhenium (IV).

Rhenium trichloride (2 gm.) was refluxed with n-butyric acid (25 ml.) in presence of n-butyric anhydride (1 ml.). The reaction was carried out in presence of air for four days, during which times purple crystals separated slowly from the acid solution. This solution was filtered while hot and the filtrate (an orange solution) was worked up as below. This compound has solubilities and properties similar to its isomer (chlororhenium (IV) μ -dioxo- μ -diisobutyratechlororhenium (IV)) and the yield is 0.5 gm. (about 23%). [Found: C, 15.3; H, 2.7; O, 15.8%. Required for $[\text{ReClC}_4\text{H}_7\text{O}_3]_2$: C, 14.8; H, 2.2; O, 14.8%]. M.p. 210°C .

Chlororhenium (IV) μ -dioxo- μ -dioctoato
chlororhenium (IV).

Rhenium trichloride (2 gm.) and octoic acid (25 ml.) were refluxed for four days in presence of air. After cooling, purple leaflets-like crystals of $[\text{ReO}(\text{CH}_3(\text{CH}_2)_2\text{COO})\text{Cl}]_2$ were the main product. Some orange leaflets-like crystals apparently $[\text{ReO}_2(\text{CH}_3(\text{CH}_2)_6\text{COO})_2]$ were formed but these were too small for analytically pure sample to be obtained. This purple compound is very soluble in acetone, chloroform, dichloromethane and benzene in the last of which it decomposes on boiling; and it is insoluble in carbon tetrachloride and petroleum spirit. The compound was crystallised from chloroform. It is unstable to air and changes to a sticky liquid when left exposed to it for two to three days. The yield is 0.1 gm. (about 4.5%). [Found: C, 25.9; H, 4.4; O, 12.7%. Required for $[\text{ReC}_8\text{H}_{16}\text{O}_3\text{Cl}]_2$: C, 25.2; H, 3.9; O, 12.6%].
M.p. 154°C.

Dichlororhenium (IV) μ -dihydroxy μ -di-
isobutyrate dichlororhenium (IV).

To a solution of chlororhenium (IV) μ -dioxo μ -di-isobutyrate chlororhenium (IV) (0.2 gm) in acetone (10 ml.) hydrochloric acid (5 ml., dilute or concentrated) was added. The purple solution turned blue and on removing acetone under vacuum blue crystals

separated. These were centrifuged off and washed with water several times and crystallised from chloroform and then dried in vacuo (at 100°C) for 48 hours. This compound is soluble in alcohol, chloroform, dichloromethane and acetone and is slightly soluble in benzene, it is insoluble in carbon tetrachloride and petrol, and gives non-conducting solution in nitrobenzene, $\Lambda (3.3 \times 10^{-4}M) = 3.6$ mho. Yield is 0.1 gm. (about 47%).
 [Found: C, 13.5; H, 2.8; O, 15.9%. Required for $[\text{ReCl}_2\text{C}_4\text{H}_8\text{O}_3]_2$; C, 13.3; H, 2.2; O, 13.3%].

Dichlororhenium (IV) μ -dihydroxy μ -di-n-butyrate dichloro-rhenium (IV)

The reaction was performed the same as for dichlororhenium (IV) μ -dihydroxy μ -di-isobutyrate dichlororhenium (IV) using chlororhenium (IV) μ -dioxo μ -di-n-butyrate chlororhenium (IV) (0.2 gm.) and the compound formed has properties and solubilities similar to its isomer, and the yield was of the same order (about 47%). [Found: O, 13.8; Cl, 18.2%. Required for $[\text{ReCl}_2\text{C}_4\text{H}_8\text{O}_3]_2$, O, 13.3; Cl, 19.6%].

Oxo-rhenium (V) μ -dioxo μ -di-n-butyrate oxorhenium (V)

After removal of the purple crystals of chlororhenium (IV) μ -dioxo μ -di-n-butyrate chlororhenium (IV) in the preceding preparation, n-butyric acid solution was cooled to room temperature and orange

crystals separated out. These were crystallised from n-butyric acid, washed several times with petroleum spirit (30-40°) until free from the carboxylic acid and then dried in vacuo. These crystals are slightly soluble in chloroform, dichloromethane and decompose in cold acetone, they are very sparingly soluble in cold benzene and chlorobenzene and dissolve in the last two solvents on boiling without decomposition. The compound is insoluble in cold water and boiling water decomposes it to ReO_2 . It is insoluble in alcohol, carbon tetrachloride, ether and petrol. It gives non-conducting solution in nitrobenzene. [Found: C, 16.1; H, 2.8; O, 20.2%; mol. wt. 590 ± 60 . Required for $[\text{ReC}_4\text{H}_7\text{O}_4]_2$: C, 15.7; H, 2.3; O, 20.9%; mol. wt., 610]. M.p. 257°C . Yield is 0.4 gm. (about 22%).

Oxo-rhenium (V) μ -dioxo μ -di-isobutyrate
oxo-rhenium (V)

This compound was separated from the isobutyric acid solution in the same way as oxo-rhenium (V) μ -dioxo μ -di-isobutyrate oxorhenium (V) and has properties and solubilities similar to its isomer. The yield is 0.4 gm. (about 22%). [Found: C, 15.7; H, 2.6; O, 20.3%. Required for $[\text{ReC}_4\text{H}_7\text{O}_4]_2$, C, 15.7; H, 2.3; O, 20.9%].

Polymeric complex of rhenium trichloride diacetate.

Rhenium pentachloride (2 gm.) was refluxed with acetic acid (25 ml.) in presence of acetic anhydride (1 ml.) under nitrogen, the reaction was carried out for two days. After cooling, the black solution was filtered off, the solvent was taken on the pump and the solid crystallised from chloroform. The compound is insoluble in acetone benzene, alcohol, carbon tetrachloride and water. It is unaffected by cold concentrated mineral acids (H_2SO_4 and HCl) but decomposed by bases to rhenium dioxide. It is slightly soluble in nitrobenzene and gives a non-conducting solution in the last solvent $\Lambda (8.2 \times 10^{-4}M) = 1.0$ mho. Yield 1.5 gm. (about 65%). [Found C; 12.0; H, 1.8; O, 15.8; Cl, 23.6%. Required for $ReCl_3C_4H_6O_4$, C, 11.7; H, 1.5; O, 15.6; Cl 24.0%]. Does not melt below $300^\circ C$.

Nitrogen Ligands

Oxohydroxodichlorodipyridine rhenium (V)

Pyridine (about 15 ml.) was added to a solution of rhenium pentachloride (2.0 gm.) in acetone (30 ml.) (G.P.R. grade) a green product precipitated rapidly ($\text{ReO}(\text{OH})\text{Cl}_2\text{py}_2$) and the solution turned orange, the green solid was filtered off (the solution was worked up as below) and crystallised from chloroform. This green compound is slightly soluble in acetone and pyridine and is insoluble in benzene, carbon tetrachloride, alcohol, tetrahydrofuran, water (hot or cold) and ether. It gives a non-conducting solution in nitrobenzene ($\Lambda(4.4 \times 10^{-4}\text{M}) = 0.9 \text{ mho}$, it is unaffected by cold concentrated hydrochloric and sulphuric acids. Yield was 0.5 gm (about 20%). [Found: C, 26.9; H, 2.2; N, 6.2; O, 7.0; Cl, 16.0; Re, 42.0%. Required for $\text{ReC}_{10}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}_2$: C, 26.8; H, 2.5; N, 6.3; O, 7.1; Cl, 15.8; Re 41.6%]. M.p. 230°C.

Dioxotetrapyridine rhenium (V) chloride dihydrate

After removal of oxohydroxodichlorodipyridine rhenium (V) complex (as described above) the acetone pyridine solution was left to settle for about 12 hours. Orange crystals precipitated, these are sparingly soluble in pyridine, acetone, chloroform alcohol, soluble in

water and decomposes on boiling in the last solvent to rhenium dioxide. It is insoluble in benzene, carbon tetrachloride, tetrahydrofuran, nitrobenzene and petroleum spirit. It can be crystallised from chloroform or water and gives a conducting solution corresponding to uni-univalent electrolyte in the last solvent ($\Lambda(1.0 \times 10^{-3} \text{ M}) = 61.0 \text{ mho}$). Yield was 2.1 gm. (about 63%). [Found: C, 39.7; H, 4.1; N, 9.6; O, 10.2; Cl, 5.9; Re, 31.9%. Required for $\text{ReC}_{20}\text{H}_{24}\text{N}_4\text{O}_4\text{Cl}$: C, 39.7; H, 4.0; N, 9.3; O, 10.6; Cl 5.9%]. Decompose at 125°C .

Dioxotetrapyridine rhenium (V)
tetraphenylborate.

To a solution of dioxotetrapyridine rhenium (V) chloride dihydrate (0.2 gm.) in water (15 ml.), a solution of sodium tetraphenylborate (0.2 gm.) in water (10 ml.) was added, a yellow precipitate separated at once. This was washed several times with water and crystallised from acetone, and was dried under vacuum for 48 hours at 100°C . Yield was almost quantitative. [Found: N, 7.0; O, 3.5%. Required for $\text{ReO}_2\text{C}_{44}\text{H}_{40}\text{N}_4\text{B}$: N, 7.0; O, 4.0%].

Oxotrichlorodipyridine rhenium (V)
monohydrate.

Concentrated hydrochloric acid (5 ml.) was added to dioxotetrapyridine rhenium (V) chloride dihydrate (0.3 gm.) the orange crystals of dioxotetrapyridine rhenium (V) first changed to red and some dissolved giving red coloured solution, on boiling light green powder precipitated out and the supernatant liquid became colourless. This green powder was insoluble in all solvents tried (e.g. acetone, alcohol, benzene, nitrobenzene, chloroform and dichloromethane). Yield was almost quantitative. [Found: C, 25.0; H, 2.5; O, 6.0; N, 6.4; Cl 21.7%. Required for $\text{ReC}_{10}\text{H}_{12}\text{Cl}_3\text{N}_2\text{O}_2$: C, 24.8; H, 2.5; O, 6.6; N, 5.8; Cl 22.0%].

Oxohydrodichloro- α - α -dipyridyl
rhenium (V)

α - α -dipyridyl (1.0 gm.) in acetone (10 ml.) was added to a solution of rhenium pentachloride (2.0 gm.) in acetone (10 ml.). Several products were formed, among them a green compound which can be separated by suspending the mixture in acetone and filtering off the green solution (the residue was so insoluble to give analytically pure sample). On removing acetone on the pump green powder separated out $\text{ReO}(\text{OH})\text{Cl}_2(\text{C}_5\text{H}_4\text{N})_2$, this is sparingly soluble

in chloroform and nitrobenzene and is insoluble in benzene, carbon tetrachloride and petrol. Yield was 0.5 gm. (about 20%). [Found C, 27.0; H, 2.7; O, 7.2; N, 6.4%. Required for $\text{ReO}_2\text{Cl}_2\text{C}_{10}\text{H}_9\text{N}_2$: C, 26.9; H, 2.0; O, 7.2; N, 6.3%].

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