CHLORIDES AND OXOCHLORIDE COMPLEXES OF RHENIUM

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by

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SCOPE AND CONTENTS:

A brief review of the rhenium-chlorine system is presented and a method to determine rhenium:chlorine atom ratios by neutron activation analysis is described. An infrared cell which is useful for highly reactive vapours at temperatures up to 400°C is also described. The compound claimed to be rhenium hexachloride is shown to be rhenium oxytetrachloride and a reliable preparation of β-rhenium tetrachloride is discovered. The hexachlororhenate(V) ion and several complexes containing rhenium(V), rhenium(VI) and rhenium(VII) are prepared. Chemical and physical evidence is used to predict structures of some of the above compounds.

.... to Pam and Jennifer who gave up
such a lot, and suffered so much
during my periods of frustration ....

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NOMENCLATURE

χ_g	The magnetic susceptibility of one gram of a compound
χ_m	" " " mole "
χ_m'	" " " " " after correction for diamagnetism of the atoms.
T	Temperature in degrees Kelvin
μ_{eff}	The effective magnetic moment of a compound
μ_T	The magnetic moment of a compound at T degrees Kelvin
py	pyridine
dipy	2,2'-dipyridyl
Θ	Weiss constant
g	gram
$t_{1/2}$	The half-life of a radioactive isotope
λ	The decay constant of a radioactive isotope
Å	Angstrom (10^{-8} cm)
cm	one centimeter
mm	one millimeter
L	Any neutral monodentate ligand
M	Any neutral bidentate ligand
X	A halogen atom

I INTRODUCTION

(a) General

Research into the chemistry of rhenium has played an important part in the rapidly developing fields of inorganic chemistry such as "cluster compounds" (1) and "less-common" co-ordination numbers (2). It is possible to prepare compounds of rhenium with formal oxidation states from -I to +VII and co-ordination numbers from 3 to 9 (3). When these properties are combined with a marked tendency of the element to disproportionate in many oxidation states, one is led into a very interesting field of study. The chlorides and oxychlorides of any element are a fundamental part of its chemistry and it is towards a better understanding of the rhenium-chlorine system that this thesis is devoted.

(b) History

The discovery of rhenium (4) and initial investigations into its chemistry (5,6,7,8,9,10) were made by W. Noddack and I. Tacke (later Frau Noddack) in the late 1920's. Subsequently an enormous amount of rhenium chemistry was published, mainly by German workers, as samples of the metal became more readily available. The first gram quantity was isolated in 1928 (8) and by 1933 potassium perrhenate was being produced commercially by a German company from molybdenum residues recovered from copper schists (11).

Noddack (12,13) chlorinated rhenium metal in the course of his first research and noted two chlorides. He described his experiments as follows:

"Durch Einwirkung von Chlorgas as Rheniumpulver einsteht bei gelindem Erwarmen ein tiefgrünes, leicht flüchtiges Chlorid von der Formel $ReC\ell_7$ das bei gewöhnlicher Temperatur grüne Kristalle bildet--- ---Bei Erhitzen von Rheniummetal mit Chlorgas auf 500° oder bei der thermischen Zersetzung von $ReC\ell_7$ entsteht ein braunes ebenfalls flüchiges Chlorid das angenährt die Zusammsetzung $ReC\ell_6$ ergab."

He also noted (5) that perrhenate (ReO_4^-) solutions, when heated with hydrogen chloride or potassium chloride, gave coloured solutions, but he did not investigate this further.

Briscoe et al (14) reinvestigated the reaction of rhenium metal with chlorine. They did not isolate either the hepta- or hexachloride claimed by Noddack but prepared a black crystalline "tetrachloride". They also observed green vapours of a volatile compound which crystallised in long needles and melted at 21°C, but did not isolate enough material for analysis

These green vapours were only noticed at the beginning of each chlorination. The two explanations which Briscoe and coworkers presented, were that either the green vapours were the volatile chloride of some metallic impurity, or were an oxychloride formed from oxygen contamination of their chlorine. Subsequent experiments in which osmium, molybdenum and tungsten (the most likely contaminants) impurities were added to the rhenium metal failed to increase the yield of green vapours, as did the addition of oxygen to the chlorine stream. In the same paper these workers describe the preparation of potassium hexachlororhenate(IV) by heating rhenium metal with potassium chloride in a chlorine stream.

Högenschmidt and Sachtleben (15) questioned the "tetrachloride" formulation. Their chlorination yielded a compound which appeared to be

Briscoe's tetrachloride, but on analysis they found a rhenium to chlorine ratio of 1:4·3. Enke (16) explained the colours observed by Noddack, when perrhenate ion and chloride ion were heated in solution. He added iodide as reducing agent and successfully prepared potassium, ceasium and thallous hexachlororhenate. The reaction was summed up by the equation:

$$MReO_4 + 3MI + 8HCl \longrightarrow M_2ReCl_6 + 2MCl + 3[I] + 4H_2O$$

(where $M = K^+, Cs^+, Tl^+$.)

Yost and Schull (17) published vapour pressure data of rhenium—chlorine mixtures. They observed green and red vapours, the molecular weights of which were determined. The results were interpreted to support the tetrachloride formula of Briscoe and equilibrium constants were calculated for the following system.

$$\begin{array}{ccccc} & & Re_2Cl_8\ (gas) & \rightleftharpoons & 2\,ReCl_4\ (gas) \\ & & \downarrow\uparrow & & \\ ReCl_6 & \rightleftharpoons & ReCl_4 + Cl_2 & & \end{array}$$

In 1932 Briscoe et al (18) published another paper in which they rescinded some of their earlier observations on the green vapours. In this publication they stated that the yield of the green vapours was increased by adding oxygen to the chlorine. They also noted that the compound could be prepared by warming rhenium "tetrachloride" with oxygen, or by chlorinating "rhenium pentoxide". From analytical and molecular weight data they formulate the compound as rhenium dioxotrichloride (ReO_2Cl_3).

This is the last paper published by this group of workers, so it seems appropriate to comment, at this point, on their results. The only compound to which they appear to have attached the correct formula was potassium hexachlororhenate and it is possible that they knew of Enke's (16) preparation of this compound by other methods. Briscoe's problem seems to have been one of analysis. He analysed for rhenium by gravimetry, weighing the rhenium as the dioxide dihydrate ($ReO_2 \cdot 2H_2O$) (19). This method was obviously unpopular as all other workers resorted to other methods, notably the nitron perrhenate gravimetric method, although no doubt about the dioxide method has been expressed in the literature. Confirmation that their rhenium analyses might have been incorrect is afforded by their description of a compound Re_2O_5 (20) which was later reformulated as ReO_3. Their description of this stoichiometric, very stable compound, agrees very well with that of ReO_3, but it was on the basis of rhenium analysis by the dioxide method that they proposed that it was a pentoxide.* Two recent reviews (22,23) of the oxides do not agree about the degree of hydration of the dioxide. Inconsistencies of the degree of hydration would cause discrepancies in the analytical results.

In 1932, Brukl and Ziegler (24) reacted Briscoe's "tetrachloride" with oxygen and successfully identified the only two rhenium oxychlorides known to the present day. Perrhenyl chloride ($ReO_3C\ell$) was found to be a colourless liquid, freezing at 4.5°C and boiling at 128°C at atmospheric pressure. They showed that the other oxychloride was rhenium oxytetrachloride ($ReOC\ell_4$). It was stated that $ReO_2C\ell_3$ prepared by Briscoe et al (18) was a

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* However, some recent work (21) has indicated that a stable mixture of ReO_3 and some other phase may be formed and that analytically this is closer to $ReO_{2.45}$.

mixture of ReO_3Cl and $ReOCl_4$, but Briscoe et al.'s description of their compound was identical with Brukl and Zeigler's description of $ReOCl_4$. Brukl and Zeigler also claimed that in cold aqueous hydrochloric acid rhenium oxytetrachloride gives a brown solution which is the acid of the oxohexachlororhenate(VI) dianion and further claimed to have isolated the potassium salt of this acid K_2ReOCl_6. This work has not been confirmed.

The following year Geilmann, Wrigge and Blitz (25,26) repeated the chlorination of rhenium metal and suggested that the tetrachloride prepared by Briscoe et al. was in fact a pentachloride. They further showed that on heating in nitrogen or under vacuum the pentachloride lost chlorine to form a trichloride. Much of the fundamental chemistry of the compounds was accurately described. Hydrogen reduction of the trichloride caused gradual loss of chlorine as hydrogen chloride. However, it was shown by X-ray diffraction that no phase intermediate between trichloride and metal was formed. They confirmed the work of Brukle and Ziegler, obtaining perrhenyl chloride and rhenium oxytetrachloride by reaction of pentachloride, or trichloride with oxygen. In addition an attempt was made to make rhenium tetrachloride by the thermal decomposition of silver hexachlorhenate, but a mixture of pentachloride and trichloride was obtained. No further simple chlorides or oxychlorides of rhenium were reported for three decades.

At this point it is convenient to divide this introduction into three other sections: chlorides, oxychlorides and chloro anions.

(c) Chlorides

The existence of all chlorides from $ReCl_2$ to $ReCl_7$ has been claimed . The only report of the dichloride (27) was a preparation of the hydrates $ReCl_2 \cdot 2H_2O$ and $ReCl_2 \cdot 4H_2O$. Very little evidence was presented to substantiate this formulation of the compounds and the report is unconfirmed. Fergusson (28) has expressed the opinion that these compounds may be dimeric in nature containing trivalent rhenium.

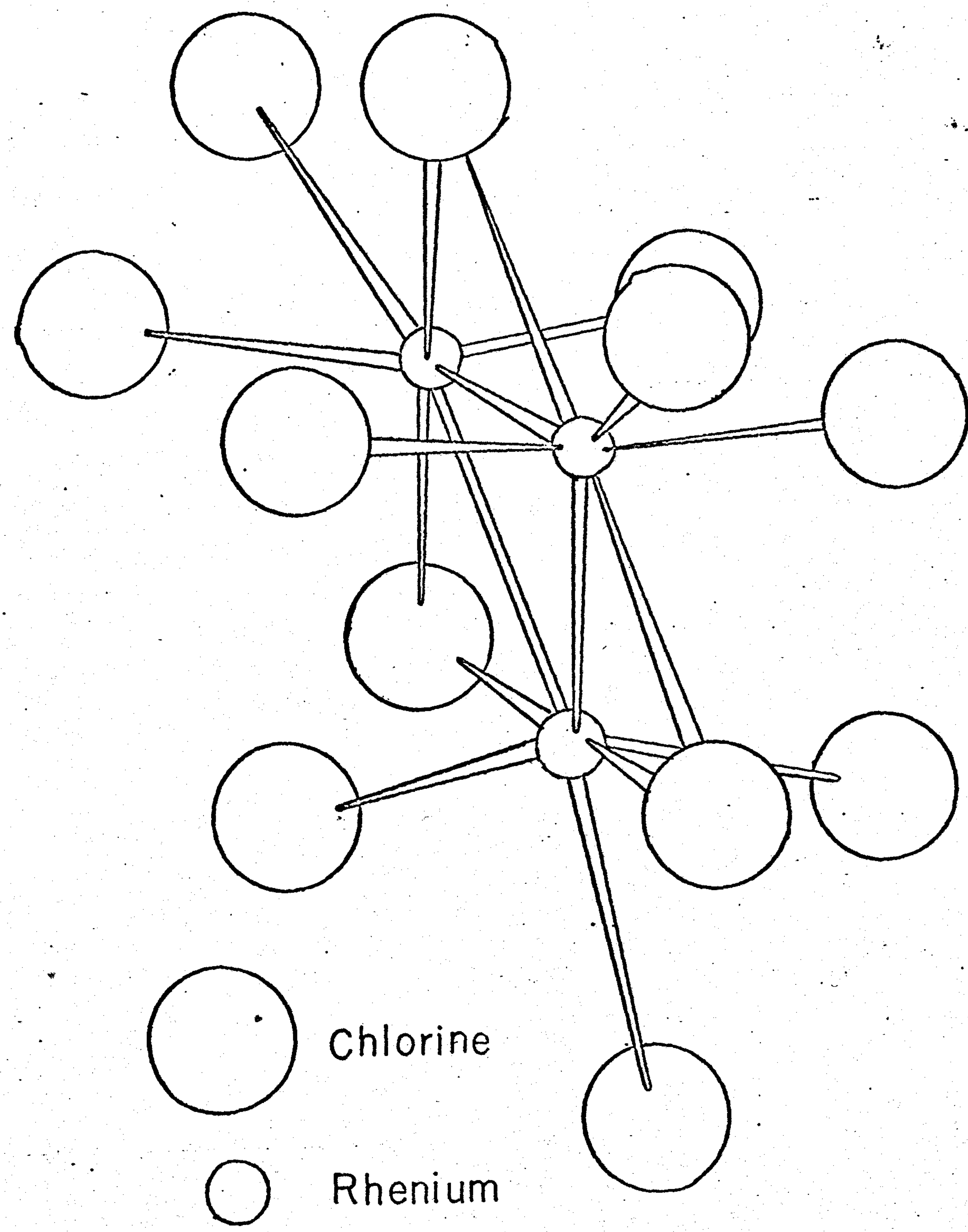
The preparation of rhenium trichloride by thermal decomposition of pentachloride (25) was described in section I(b). Other methods of preparation via reaction of sulphuryl chloride with the metal (29), or heating hexachlororhenate(VI)salts (30) are reported, but are not as efficient or convenient as the original preparative method. The compound is a red-purple micro-crystalline material, which is essentially non-volatile, but can be sublimed under high vacuum at 500°C. Several magnetic studies (31, 32,33) of this compound have been undertaken. Schuth and Klemm (31) found a small temperature-independent paramagnetism, but a later determination by Knox and Coffey (32) gave a slightly higher value with rather more dependence on temperature. Recently Colton and Brown (33) have suggested that there are two forms of the trichloride. One form, which was prepared directly from the pentachloride, had a susceptibility corresponding to Klemm and Schuth's measurements ($\sim 20 \times 10^{-6}$ c.g.s.) and a sublimed form, which had the magnetic characteristics described by Knox and Coffey ($\sim 495 \times 10^{-6}$ c.g.s.). X-ray diffraction studies failed to detect any difference between the two forms (33).

Trivalent rhenium contains four "d" electrons. Therefore, as a monomer, in any environment other than the presently unknown spin-paired tetrahedron, strong paramagnetism would be expected. Wrigge and Blitz (34) in 1936, explained this lack of paramagnetism by assuming dimerisation. Klemm and Frischmuth (35) stated the following year that they considered the trichloride to contain rhenium—rhenium bonds. Compounds of empirical formula $M^{+}(ReC\ell_4)^{-}$ where M=Cs, Rb, PyH (35,36) were known and the rubidium salt (35) had also been shown to be diamagnetic. A single crystal X-ray examination of this system was clearly needed and two independent groups (37,38,39) published, almost simultaneously, data to prove that the $(ReC\ell_4)^{-}$ ion was in fact a trimer with the geometry shown in Fig. 1 (page 8).

Further work (40,41,42) indicated that this trimeric cluster was common. The trichloride (41,42) itself has a similar structure with the trirhenium units bridged by some of the terminal halogens, so that each rhenium atom bonds to five chlorine atoms as in the ion $(Re_3C\ell_{12})^{3-}$. Mass spectral investigations at 280°C (43) have shown that the trimeric units still exist in the gas phase at this temperature, but this is hardly surprising as the compound can be sublimed without change at about 500°C (except for the magnetic changes mentioned above).

It has been shown (44,45) that the most stable and most easily prepared chloride of technetium is the tetrachloride. This contrasts sharply with the rhenium system where all efforts before 1963 failed to produce rhenium tetrachloride, although as previously discussed, it was claimed by Briscoe et al in 1931. Croft (46) claimed to have intercalated rhenium tetrachloride with graphite in 1956, but he did not give analytical data, or any details of the preparation. This work remains unsubstantiated.

Figure I. Structure of the $(Re_3Cl_{12})^{\equiv}$ ion.



Colton and Brown (47) isolated a compound from the reaction of rhenium dioxide hydrate with thionyl chloride which they claimed to be a tetrachloride. The compound was described as a black solid which hydrolysed readily in air, and although it appeared crystalline, no X-ray powder diffraction pattern could be obtained.

The discoverers of this compound studied the magnetic susceptibility (48), and found it to obey the Curie-Weiss law only between 220°-300°K with μ_{eff} = 1.55 B.M. A later assessment (49) of this magnetic evidence by Colton and Martin was used to predict a trimeric cluster of rhenium atoms.

From simple molecular-orbital calculations, they predicted one unpaired electron per trimeric unit, which, they say, should give a magnetic moment of 1 B.M. per rhenium atom. By extrapolating a plot of reciprocal temperature against magnetic susceptibility to zero temperature, they found a temperature independent contribution to the susceptibility. This was subtracted and the magnetic moment recalculated to give a temperature independent moment of 1 B.M. This magnetic moment and a little, not very convincing chemical evidence was use to justify their prediction of a trimeric structure.

In 1966 Cotton (50) bought fifty grams of "rhenium(III)chloride" from the Shattuck Chemical Company, which on analysis proved to be rhenium tetrachloride. Enquiries revealed that the compound had been prepared by the normal method of preparation of rhenium trichloride, i.e.,"by thermal decomposition of the pentachloride in a stream of nitrogen at around 375°C". The exact details of the experimental conditions had not been recorded, and repetition of the preparation has proved impossible. The sample which Cotton obtained was sufficient for his group to determine a great deal of the chemistry of this compound. Its properties are so different from the properties reported by Colton, that Cotton now calls the earlier compound α-$ReC\ell_4$ and his Shattuck-produced compound β-$ReC\ell_4$. Cotton considered that the chemistry and preliminary X-ray data (50) indicated that the compound was a metal to metal bonded dimer similar to the octahalodirhenium dianion discussed in section I(e) (see Fig. 4, page 18).

Although Cotton's group used all the β-$ReC\ell_4$ which was available (51) before the single crystal X-ray structure had been fully refined, a later assessment (52) of the unrefined data showed that β-$ReC\ell_4$ did not possess the $(Re_2C\ell_8)^{2-}$ type of arrangement. The structure which is shown in Fig. 2 (page 11) contains dimeric units, but the rhenium atoms are bridged by three chlorine atoms. The dimeric units are strung together in infinite chains via bridging by one of the terminal chlorine atoms. The Re-Re distance reported was 2.73 Å (±0.03) and some metal-metal interaction was postulated.

One preparation of rhenium pentachloride has been described in section I(b). Another good method is by the reaction of rhenium heptoxide with carbon tetrachloride in a sealed tube (45). Rhenium pentachloride is a deep-brown or black, crystalline solid, with reported melting points of 220°C (53,54) and 260°C (55). The liquid boils readily to give red-brown vapours. The single-crystal X-ray structure has been reported recently (54). The solid is a chlorine bridged dimer (see Fig. 3, page 12) similar to niobium pentachloride (56). The structure of the compound in solution or in the gaseous state is not known.

FIGURE 2.

A Portion of the β-$ReCl_4$ Polymer.

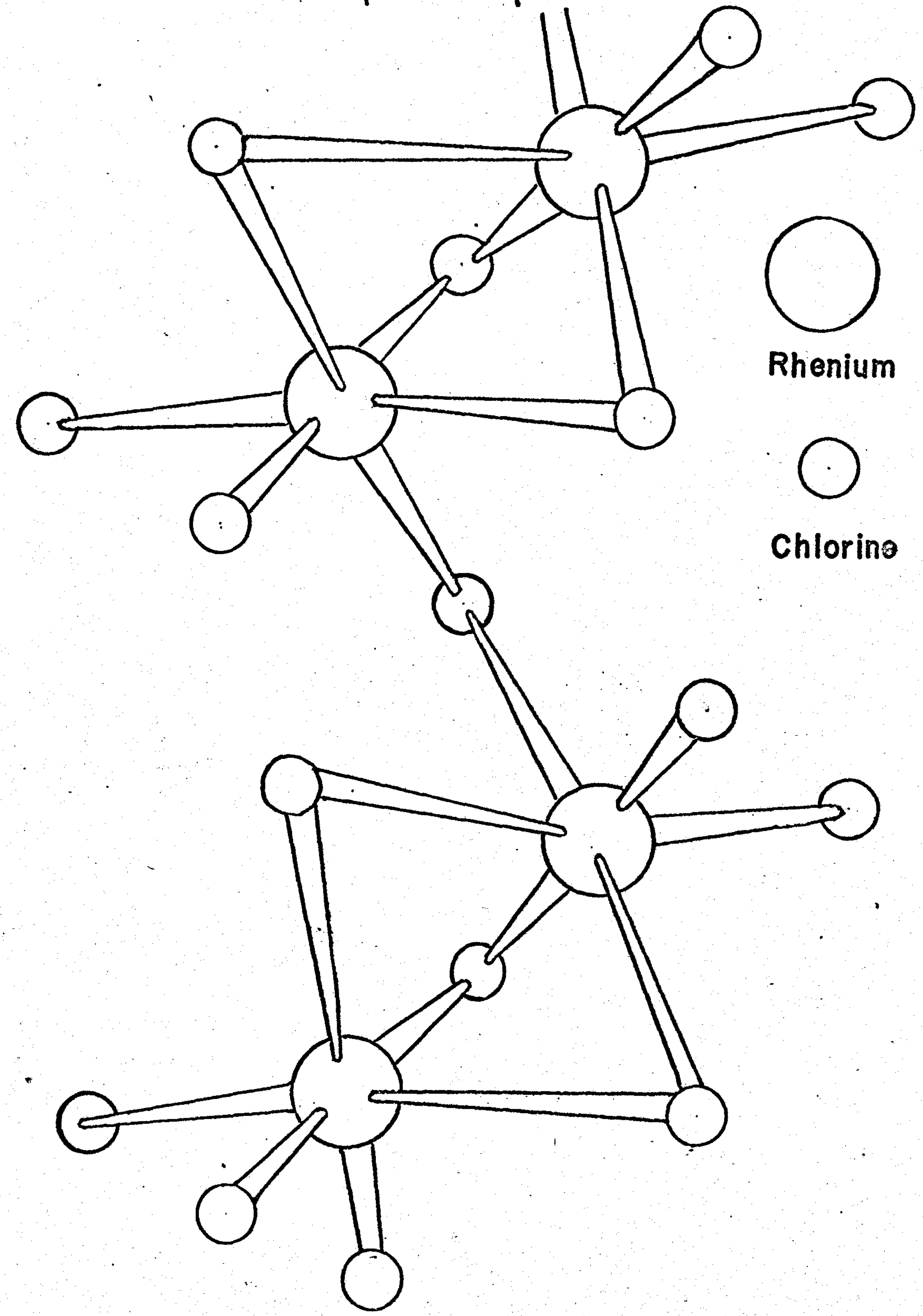
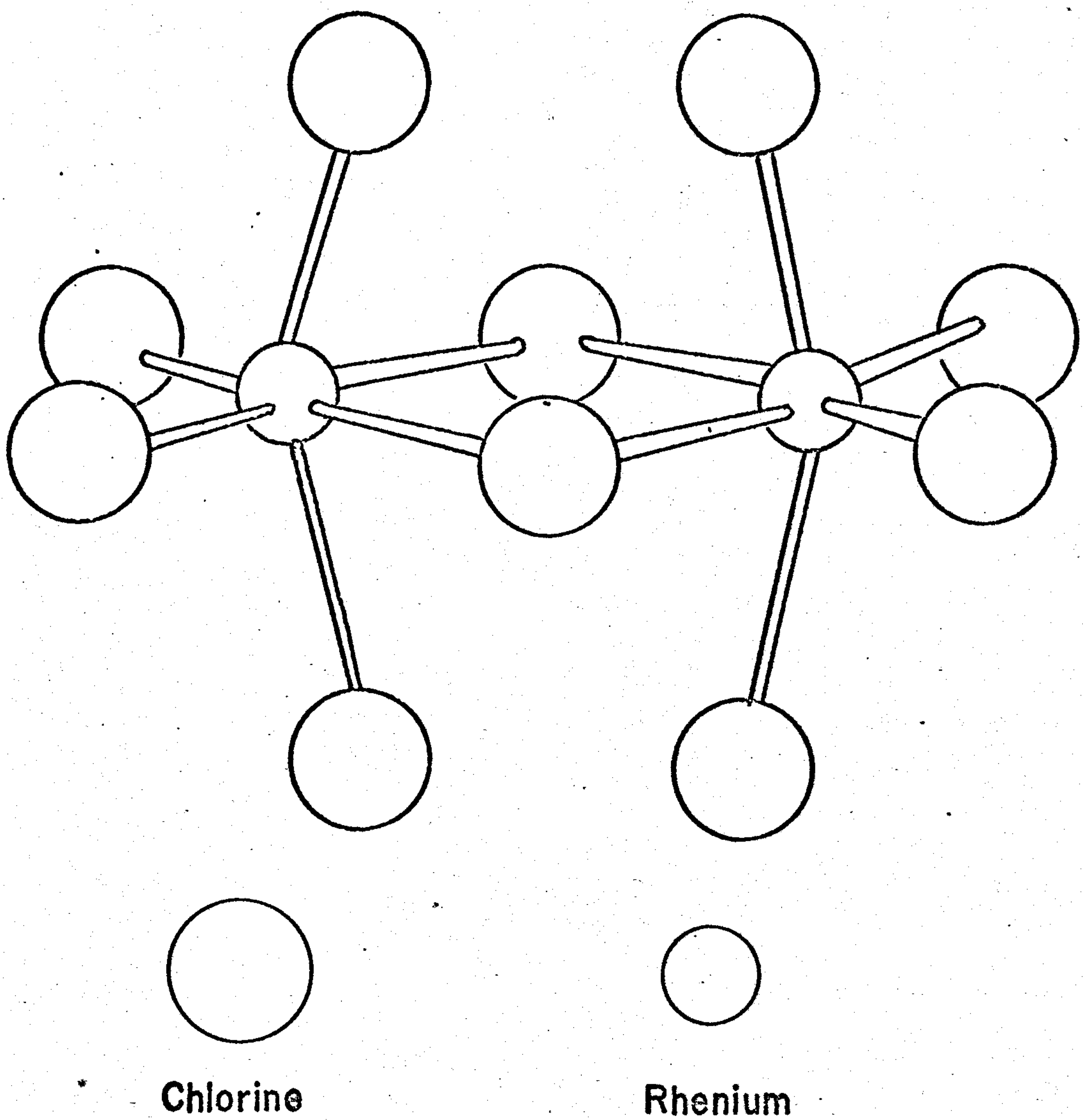


FIGURE 3. The Structure of Re_2Cl_{10}.



It is a highly reactive compound, instantly hydrolysed by water to rhenium dioxide and perrhenate ion (see section II) and has been used as the starting material for the preparation of several complexes (57,58). Three independent studies (31,32,38) have been made of the magnetic properties and these show small discrepancies. The reported magnetic moment was between 2.2 and 2.5 Bohr magnetons in each case. Brown and Colton (47) and Schuth and Klemm (31) found the Weiss constant to be 266° and 265° respectively, but Knox and Coffey (32) report a value of 164° with divergence from the Curie-Weiss law below 150°K. This divergence was confirmed by Brown and Colton (47) who showed it to occur at about 110°K. These authors attempt to explain Knox and Coffey's low θ values on the basis of hexachloride contamination.

The hexachloride of technetium was prepared by Colton in 1962 (59), by direct chlorination of a technetium mirror. At this time there existed the anomoly of a second row transition metal with a higher chloride than the corresponding third row metal. Technetium hexachloride on gentle heating was reported (59) to lose chlorine to give the tetrachloride. Because of this anomoly it was of interest to prepare rhenium hexachloride; the decomposition of hexachloride might also provide rhenium tetrachloride.

Colton noted the green vapours of Noddack (12,13) which were also reported by Schacheral (60). He further noted that the workers who observed these green vapours, prepared their own metal by hydrogen reduction of perrhenate salts. Geilmann et al (26), whose major chlorination product was the brown pentachloride, used commercial metal in a more massive form. In order to increase the yield of green vapours Colton (61) absorbed ammonium perrhenate solution on broken porous brick material and evaporated to dryness. The perrhenate was then reduced in a hydrogen stream at 200°C to dioxide, and at 600°C to leave the metal as an extremely fine deposit on the porous pot. After flushing with purified nitrogen, he chlorinated to obtain the desired compound in high yields with very small amounts of pentachloride produced.

This compound was analysed and claimed to be rhenium hexachloride which he described as "dark dichroic crystals, which melt a few degrees above room temperature to give a black liquid and green vapour" (61). It was found that on heating, the compound did not decompose in the manner of technetium hexachloride, but distilled unchanged. The only physical measurements made on the hexachloride were magnetic susceptibility studies (48), which showed that the hexachloride obeyed the Curie-Weiss law over the temperature range 98°K-297°K, with θ = 28° and μ_{eff} = 2.07 B.M. The authors admitted that this result was a little high for a d' system.

The spin-only moment for d' is 1.73 B.M. By Kotani theory (62) for a less than half-filled shell, any orbital contribution to the paramagnetism is negative, thereby lowering the magnetic moment. The magnetic properties of rhenium hexafluoride have been studied and a magnetic moment of 0.25 B.M. reported (63). This low magnetic moment is probably caused by large spin-orbit coupling effects.*

It seems strange that a change of ligand from fluoride to chloride should so drastically increase the paramagnetism. Colton and Brown (48) attempt to explain this by assuming that the hexachloride is distorted from the perfect octahedron, thereby destroying the spin-orbit coupling. This matter is discussed further in section IV.

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* It has been postulated that large spin-orbit coupling effects are present in hexafluoride molecules and are caused by the almost perfect octahedral symmetry of these molecules (64).

Noddack claimed that he prepared the heptachloride in his very early investigations (see Section 1(b)), but no further claims have been made. It may be assumed that this claim was erroneous.

(d) Oxychlorides

The discovery of the known oxychlorides was discussed in section 1(b). Perrhenyl chloride (ReO_3Cl) has been studied extensively by infra-red, Raman (65) and microwave spectroscopy (66). It has been shown to be a symmetric top with the following parameters:

$$\mathrm{Re - O} = 1.761\ \text{Å}$$

$$\mathrm{Re - Cl} = 2.230\ \text{Å}$$

$$\mathrm{Cl - \hat{Re} - Cl} = 108^\circ\ 20'$$

The original preparation was by the action of oxygen on rhenium trichloride (24). Other methods of preparation are by the action of a chlorine/oxygen mixture on the rhenium sulphides (67,68) and by direct chlorination of rhenium trioxide at 160-190°C (69). The reaction product in many cases contains purple and blue impurities which Wolf and coworkers (69) claim to be dissolved rhenium trioxide.

Rhenium oxytetrachloride has been studied very little since its discovery. Newer methods of preparation are by the reaction of chlorine-oxygen mixtures with the sulphides (67,68) and by the reaction of thionyl chloride with rhenium heptoxide or ammonium perrhenate (70). Melting points of the compounds have been reported from 21°C (26) to 29.3°C (36). The magnetic susceptibility was measured by Klemm and Schuth in 1934 (31), who found it to obey the Curie-Weiss law with $\theta = 25°C$ and $\mu_{eff} = 1.5$ B.M.

There is also a report in the literature (68) of a "volatile blue oxychloride, probably rhenium oxytrichloride", but this has never been isolated. Neither of the above well-known oxychlorides have been used as starting materials for the preparation of complexes.

(d) Chloro-anions

The hexachlororhenate(IV) anion was first reported in 1931 (14) and since then the hexachlororhenates $M^I_2ReX_6$ (M = alkali metal$^+$ or NH_4^+; X = Cℓ, Br or I) have proved to be (except for the perrhenates) the most stable, easily prepared, and important compounds of rhenium. Raman and infra-red measurements have been compared with those of the hexachlorosmate(IV) compounds (71). Discrepancies observed in the $(\nu_2 + \nu_3)$ combination band have been associated with a dynamic Jahn-Teller effect. This effect will be discussed further in section V. Chemical and physical properties of these compounds have been well studied and documented (72,73).

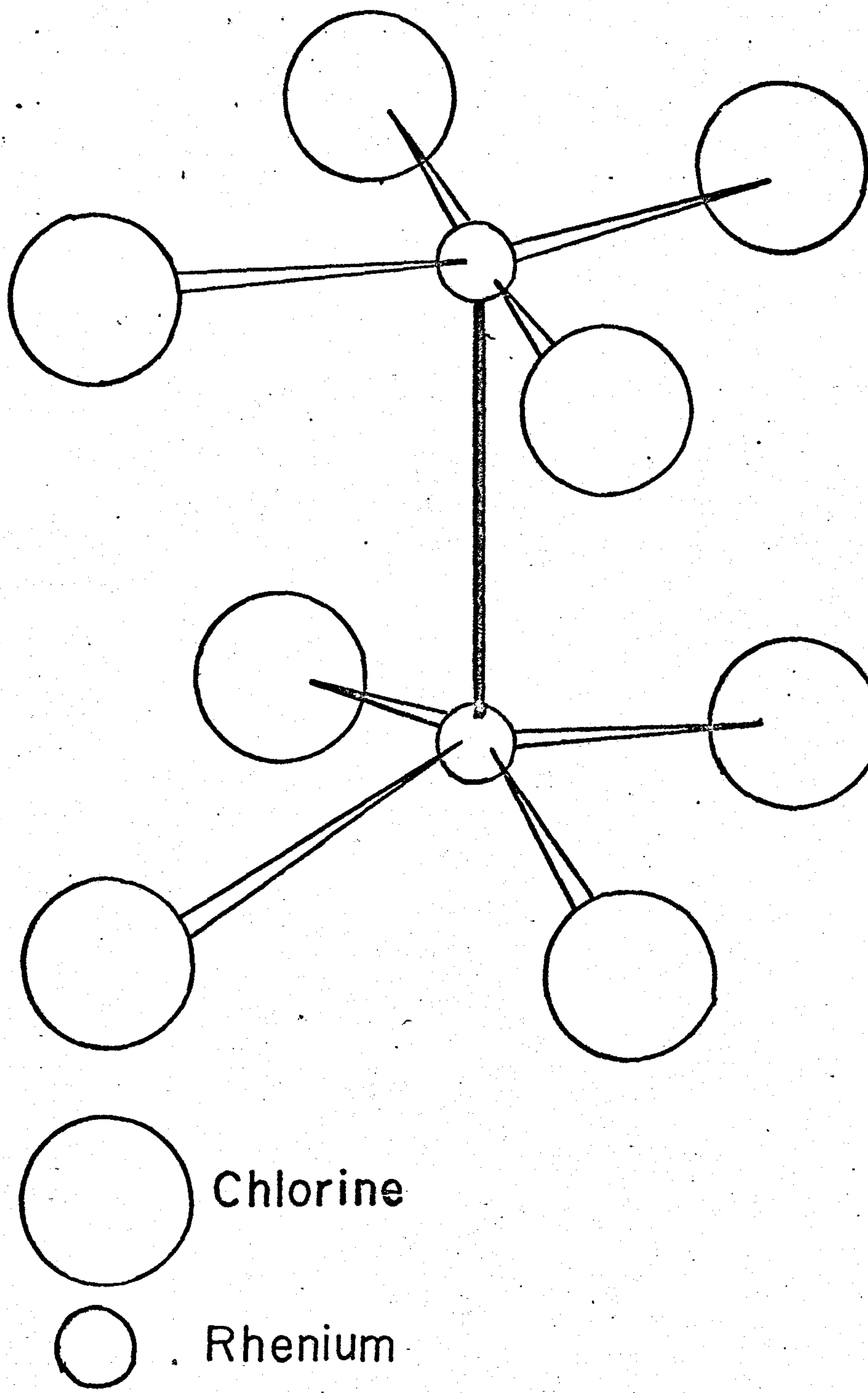
The structure of the $[Re_3Cl_{12}]^{3-}$ ion has been discussed under rhenium trichloride in section I(c) (see Fig. 1, page 8). Many studies of the system have shown that the trimeric unit is extremely stable. The compounds which have been prepared containing the trimeric rhenium cluster are summarised in (28).

Kotel'nikova and Tronev in the paper in which they reported $ReCl_2 \cdot 2H_2O$ (27), also reported other rhenium II containing compounds: $KHReCl_4 \cdot H_2O$, $KHReCl_4$ and PyH $HReCl_4$. In a subsequent paper, the single crystal X-ray structure (74) proved that the pyridinium salt was a dimer.

Cotton et al. (75) reinvestigated the compound and found the crystallographic data to be correct, although the compound contained trivalent, rather than divalent rhenium as claimed by Tronev (27). The structure of the anion (which is present in many compounds) is shown in Fig. 4, (page 18) (76). The novelty of this structure lies in the fact that the chlorine atoms are eclipsed, and the rhenium to rhenium internuclear distance is half an Angstrom shorter than in rhenium metal. This has led Cotton to postulate that the ion contains a quadruple bond (77).

This introduction provides a summary of the extent of rhenium-chlorine chemistry to date. It is hoped that the chapters following will help to broaden our knowledge of this topic.

Figure 4. Structure of the $(Re_2Cl_8)^=$ ion



II ANALYSIS

A good review of the many reported methods for the determination of rhenium has recently been published (78). The most popular are gravimetric methods utilizing the insolubility of tetraphenyl arsonium perrhenate (79) or nitron perrhenate (80). Chloride analysis is simple using silver nitrate as a precipitating agent for a gravimetric determination, or as a titrant in volumetric methods. When "classical wet methods" of analysis are referred to in this work, the methods employed were gravimetric methods using tetraphenyl arsonium perrhenate and silver chloride.

Numerous problems have been encountered in obtaining reliable analysis results by these methods. Some of the rhenium compounds studied are extremely sensitive to oxygen or water vapour, and are difficult to handle even in a good dry-box. It is therefore difficult to weigh samples accurately because of decomposition. Whenever it was possible to weigh a sample accurately, in our hands the above methods have often given results which were not reliable or reproducible. This was undoubtedly because the hydrolysis to chloride ion and perrhenate ion was incomplete, as ions such as $ReC\ell_6^{=}$ and $(Re_3C\ell_{12})^{3-}$ are formed (81).

Both rhenium and chlorine have two naturally occurring isotopes which can be activated by neutron capture. The relevant nuclear data are given in Table 1 (page 20).

It can be seen that either rhenium isotope will give an appreciable

Table 1.

Natural Isotope	Abundance (82)	Thermal neutron Capture Cross Section(barns)(83)	Half-Life of Activated Species (82)
^{185}Re	37.1%	104	92.8 hr.
^{187}Re	62.9%	66	16.9 hr.
^{35}Cl	75.5%	30	4×10^5 yr.
^{37}Cl	24.5%	5 ?	38 min.

Table 2.

Activation analysis of rhenium chlorine complexes.

Compound	Re% Theor.	Re% Found	Cl% Theor.	Cl% Found	Re:Cl (atoms)	Error (3σ)	No. of Detns.
$(ReCl_5)_2$	51.2	51.6	48.8	49.7	1:4.98	$\pm$ .06	12
$(ReCl_3)_3$	63.6	61.5	36.4	36.1	1:3.09	$\pm$ .12	10
$(C_5H_5N)_2ReOCl_3$					1:3.01	$\pm$ .14	5
$(NH_4)_2\ ReCl_6$	42.8	43.6	48.9	49.5	1:5.91	$\pm$ .15	9
$ReOCl_4$ *	54.1		41.4		1:3.92	$\pm$ .07	18
$ReOCl_4.POCl_3$	37.5	38.7	49.9	52.2	1:7.08	$\pm$ .35	6

*In the case of $ReOCl_4$, it was possible to analyse this compound for rhenium and chlorine by conventional methods after hydrolysis. Found Re 54.4% Cl 41.3, 41.1%.

amount of activity on short irradiation, but because of the long half-life of ^{36}Cl, of the chlorine isotopes, only ^{37}Cl will give significant amounts of activity on short irradiations. Several γ-ray peaks for each of the active isotopes ^{186}Re, ^{188}Re and ^{38}Cl appeared to be useful for counting, but the ones selected were at 2.16 MeV for ^{38}Cl and 0.155 MeV for ^{188}Re as they were almost free from interference by other isotopes. Initial irradiation experiments were performed on solid samples of known composition. Agreement with the theoretical results was very poor.

It was realised that the reason for the poor agreement with the theoretical results was "neutron flux depression" or "self-shielding" in the sample, caused by the high thermal neutron capture cross-section of rhenium. The McMaster reactor is not well-moderated, so there is an appreciable fast-neutron flux at the rabbit position. In general, apart from resonance absorption, it can be seen in Fig. 5 (page 22) that the ability of a nucleus to capture neutrons falls as the neutron energy increases. So if the neutron flux enters a highly absorbing solid, the slower neutrons will be preferentially absorbed. This will leave a larger proportion of high-energy neutrons, giving rise to an effective increase in the neutron temperature.

This effect would not be a problem in determining the Re:Cl atom ratio although it would affect absolute percentage determinations if the activation cross-sections of rhenium and chlorine varied in exactly the same way. Fig. 6 (page 23) shows that unfortunately they do not. The rhenium cross-section follows the normal V^{-1} relationship whilst that of

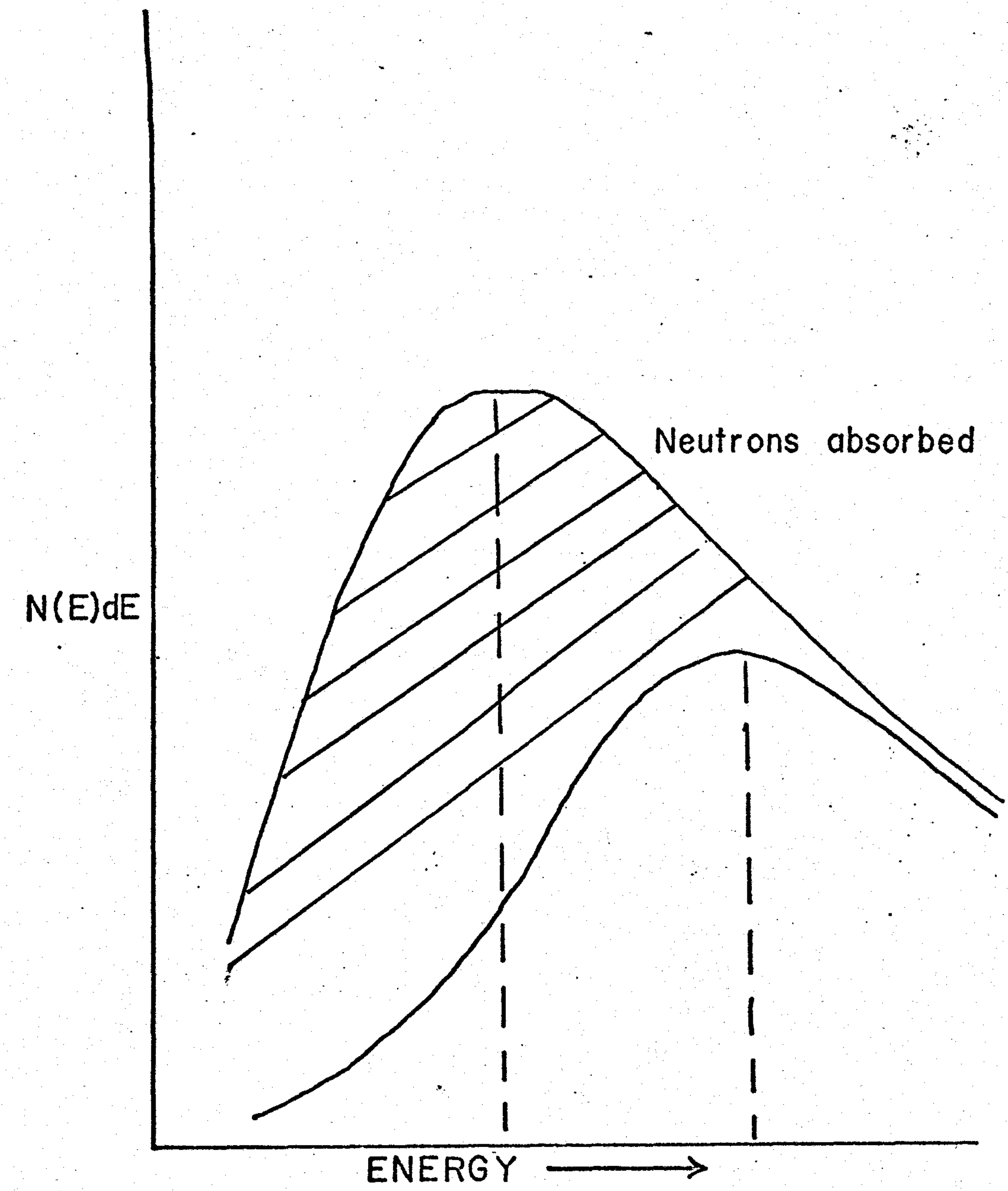
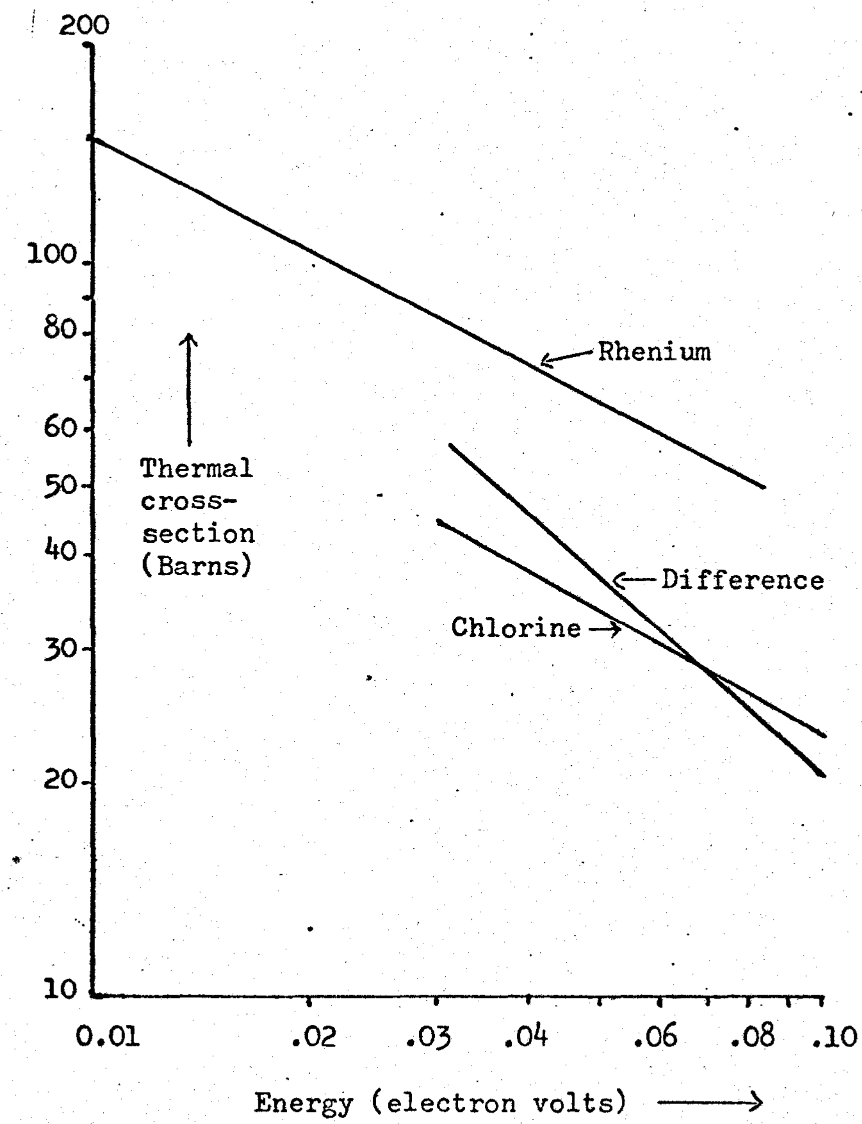


FIGURE 5.

Fig. 6.

Variation of Neutron capture cross-section with neutron energy.(83)



chlorine varies as $V^{-<1}$. This flux-depression effect had to be eliminated. The easiest way to overcome the problem is to perform the irradiations on solutions, where large aggregates of nuclei are not present. Any solvent may be used which does not contain easily activated nuclei. Elements which do not have easily activated nuclei are carbon, hydrogen, nitrogen and oxygen, which means that most common organic solvents (with the obvious exceptions, dichloromethane, chloroform and carbon tetrachloride), water, hydrogen peroxide or nitric acid may be used. Hydrogen peroxide was used extensively in this work, since it readily oxidised any insoluble lower rhenium oxides formed by hydrolysis, to the soluble perrhenate ion.

The neutron activation analysis method described here could give absolute amounts of rhenium and chlorine, but this was not the prime reason for the development of the method. The novelty lies in the determination of rhenium-chlorine atom ratios or stoichiometries without even weighing a sample. Details of the actual method employed appear in the experimental section IV(b) of this thesis and in (84).

Some results of this method of analysis applied to solutions are presented in Table 2 (page 20). The first four compounds were used to test the reliability of the method. Rhenium trichloride, ammonium hexachloro-rhenate(VI) and trichloroxobispyridinerhenium(V) are all air-stable and rhenium pentachloride is an air sensitive compound. The observed absolute percentages of rhenium and chlorine are compared with theoretical values, and the ratio of the number of atoms of rhenium to the number of atoms of chlorine is also given. The three sigma error value refers to the uncertainty in the number of atoms of chlorine, assuming that the number of rhenium atoms is exactly one. At least three independently prepared and purified samples of each compound were analysed and each determination was done in duplicate. The total number of duplicate analyses is given in the right hand column.

The two final analyses are for typical air-sensitive compounds which were analysed by this method, and whose composition has been confirmed by other techniques (see later). It can be seen that good agreement is obtained. In the case of rhenium oxytetrachloride it was possible to obtain a quantitative decomposition to chloride and perrhenate ions and the analysis was confirmed by classical wet methods.

We conclude that this is a very satisfactory and rapid method of determining the stoichiometry of rhenium-chlorine containing compounds when interfering elements are absent. Interference is only caused by elements which on neutron activation give appreciable amounts of γ-activity of energy close to 0.155 and 2.16 MeV. Potentially such a method is applicable to any compounds which contain elements which can be activated. It is not even necessary to determine both elements in the same irradiation, but in this case greater care has to be taken that both sample and standard are irradiated in exactly the same neutron flux. Because it is unnecessary to weigh the sample for analysis, this method should find wide application in the analysis of series of compounds which are very unstable.

The method has been extended to determine the formal oxidation state of rhenium. The following schemes of aqueous alkaline hydrolysis are well-established (85):

$$Re^{IV} \longrightarrow Re^{IV} \text{ (as } ReO_2 \text{ hydrate)}$$

$$3Re^{V} \longrightarrow 2Re^{IV} + Re^{VII} \text{ (as } ReO_2 \text{ hydrate + perrhenate ion } (ReO_4)^-)$$

$$3Re^{VI} \longrightarrow Re^{IV} + 2Re^{VII} \text{ (as } ReO_2 \text{ hydrate + perrhenate ion } (ReO_4)^-)$$

$$Re^{VII} \longrightarrow Re^{VII} \text{ (as } ReO_4^-)$$

The perrhenate ion is soluble and rhenium dioxide insoluble in water, therefore Re^{IV} is easily separated from Re^{VII} by filtration. The dioxide may be dissolved in hydrogen peroxide and both solutions made up to the same volume. The number of counts given in the ^{188}Re γ-ray peak at 0.155 MeV after irradiation of one millilitre of each solution are compared, and the ratio fitted to the above hydrolysis scheme. This determines the oxidation state of the rhenium in the original compound.

We have found that this hydrolysis scheme is not followed in all cases (see section V(b)) but is generally correct and is an excellent indication of valency if not concrete proof.

III APPARATUS CONSTRUCTED

(a) Vapour-phase infrared cell

Two major types of cell for recording infrared spectra of gaseous samples have been described (86,87). The first type (86) consists of a glass on metal cell-body with clamps to press the windows on, vacuum being held by O-rings. These cells had disadvantages in this work. First, it is very difficult to construct a cell which will hold high vacuum without using O-rings made of rubber. Some of the compounds investigated in this research attack this material. At the present time, teflon O-rings are too hard to hold good vacuum, and although teflon was not readily attacked, our compounds dissolved in or diffused into this material.

A typical example of the other type of cell is that described by Wildy (87). He attached lithium fluoride windows to a pyrex glass cell body using silver chloride as a cement, and a thin silver cylinder as a means of absorbing expansion strains. Wildy noted that molten silver chloride will "wet" glass which has been platinised or silvered and since his cell may be heated or cooled, the difference in the coefficients of expansion of glass and silver chloride is insufficient to cause the seal to break. From these facts it was reasoned that it should be possible to seal silver chloride windows directly to a pyrex cell body.

Several problems were encountered before the method of making the seal was found. Any metal (except the platinum on the glass) touching the window, fogged it, and made it opaque to infrared light. Springs which will operate above 250°C are extremely rare, thus a spring-loaded device, to hold the windows in place until melting, is impossible to construct. A G-clamp was found useless because of differences in the coefficients of expansion of the glass and clamp material.

The biggest problem to overcome was the extremely sharp melting-point of the silver chloride. When heated slowly in a furnace, as in Wildy's method, the bulk of the window melts at the same time as the edges in contact with the glass, and ruins the window. Unsuccessful attempts were made to lower the melting-point of the edges of the window by pressing in silver nitrate impurity. Although feasible, this course was not pursued as the following method was found to be foolproof.

The windows were laid flat on a clean glazed ceramic tile and heated in a muffle furnace to 320-325°C. The platinised end of the cell-body was heated in a blow-torch to just below the softening-point of pyrex (dull red ~500°C) and pressed squarely onto a silver chloride window as the latter was withdrawn from the furnace. The process was repeated for the other end of the cell. It was found that the cell-body fused about half a millimetre into the window and formed a seal which would hold a vacuum of 10^{-6} mm Hg for days. It was not found necessary to anneal the seal. The cell was fitted with a side-arm through which samples were distilled in. Cooling was applied by pouring liquid nitrogen onto the cotton-wool covered cell-body. Transmittance was of the order of forty per cent. Some of this loss can be accounted for by the small diameter of the cell, which would not allow passage of the full beam of the instrument. Windows of a larger diameter would overcome this, but these are expensive and forty per cent transmittance was sufficient for our work. The cell was heated by wrapping with asbestos paper and nichrome wire to which power was fed through a variac. The temperature at many variac settings were measured in an earlier experiment by placing a thermocouple in the cell. The cell is capable of recording spectra at temperatures over 400°C.

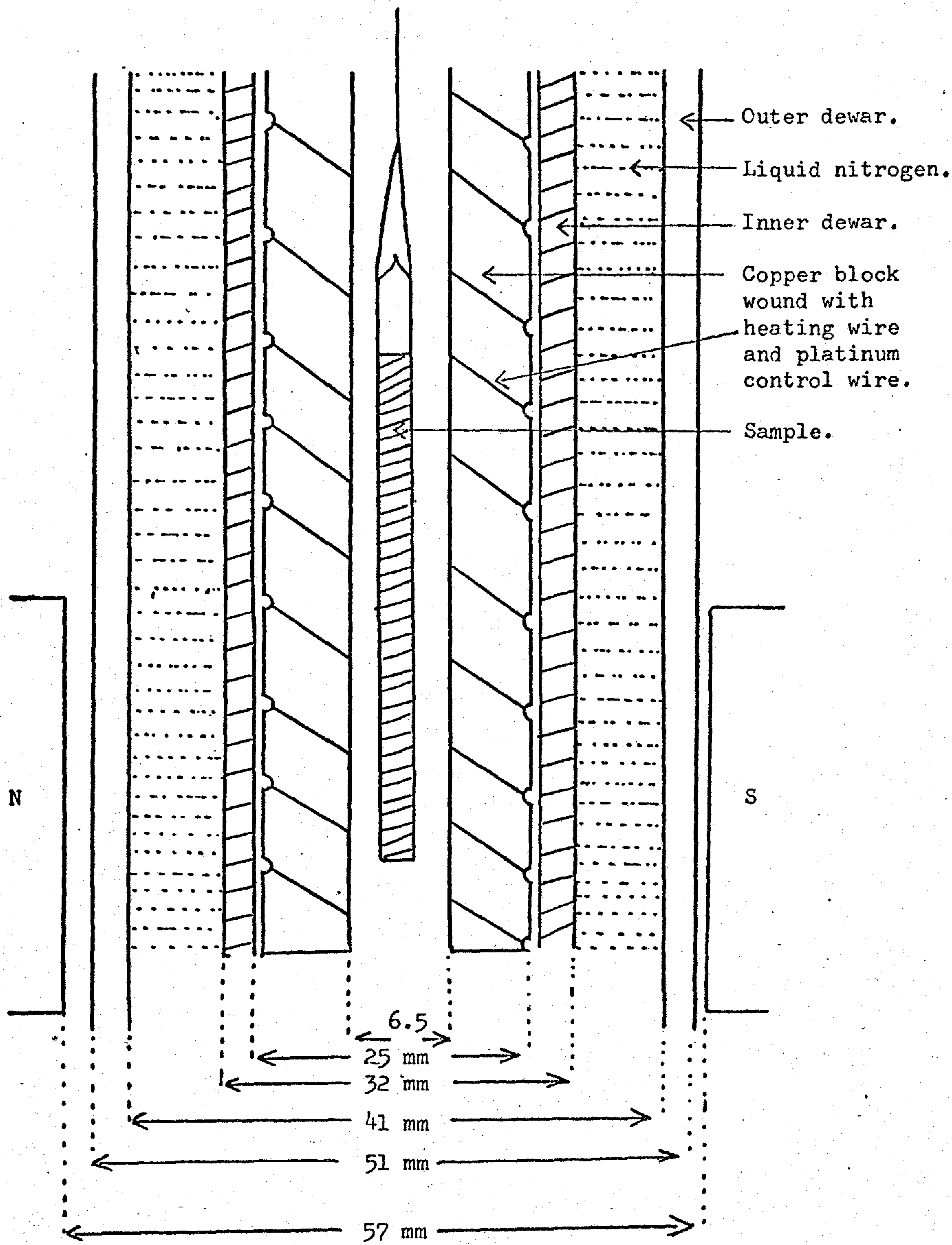
(b) <u>Gouy apparatus</u>

An Alpha Scientific Laboratories Incorporated variable temperature Gouy apparatus was purchased, but found to be totally unsuitable because of poor temperature control. We used the Alpha magnet and built accurate apparatus using the design of Earnshaw (88) and Newport Instruments Limited (Bucks.,England) (89). The pole gap on the Alpha magnet was smaller than that recommended as the minimum by Earnshaw (88). Consequently all our dimensions had to be scaled down as shown in Fig. 7 (page 30).

The diameter of the tubing normally used for samples was 3 mm O.D. although it was possible to use a tube of 5 mm O.D. Figgis and Lewis (90) consider that reproducible results cannot be obtained on samples of less than 3 mm diameter because of packing problems. We have obtained consistant results in these tubes of much smaller diameter by careful packing. The samples were finely ground before filling the tube which was then shaken in the vibrator of a HOOVER (Philadelphia, Pennsylvania) UNI-MELT melting-point apparatus to constant length. The tube was refilled and replaced in the vibrator until a constant ten centimetre length was

Fig.7.

Details of the temperature control unit used on the Gouy apparatus.



maintained. The small sample size also caused the changes in force, in and out of the magnetic field, to be small. A Sartorius ELECTRONO I microbalance, which can be read to one microgram was used to measure these changes. The small sample required was advantageous in this research as isolation of several grams of a pure product was difficult and expensive.

Temperature control was found to be excellent. The heating unit was built as described in (88) and (89) and the electronic controls were designed and built by Mr. Claus Schonfeld. The circuit is shown in Fig. 8 (page 32). The temperature was measured by a copper-constanton thermocouple cemented into a groove down the inside of the copper block. The thermocouple was calibrated by the highly sensitive platinum resistance thermometer used by Dr. R. J. Gillespie's group for hydrofluoric acid cryoscopy. This instrument is accurate to better than 0.001°C, and it was found that the temperature in the sample space of our apparatus could be held almost to this limit at low temperatures, i.e., from liquid nitrogen temperature to about -70°C. Between -70°C and room temperature the limit of the control became steadily poorer because of the greater heating and cooling applied. At around 0°C the control was at its worst, being about ±0.3°C.

(c) Dry-box

At the beginning of this work no dry-box was available in which the compounds could be handled. A "PLEXIGLASS" box was constructed with a circulating system and purification train through which the nitrogen atmosphere of the box could be passed. Heated, activated copper (91) was

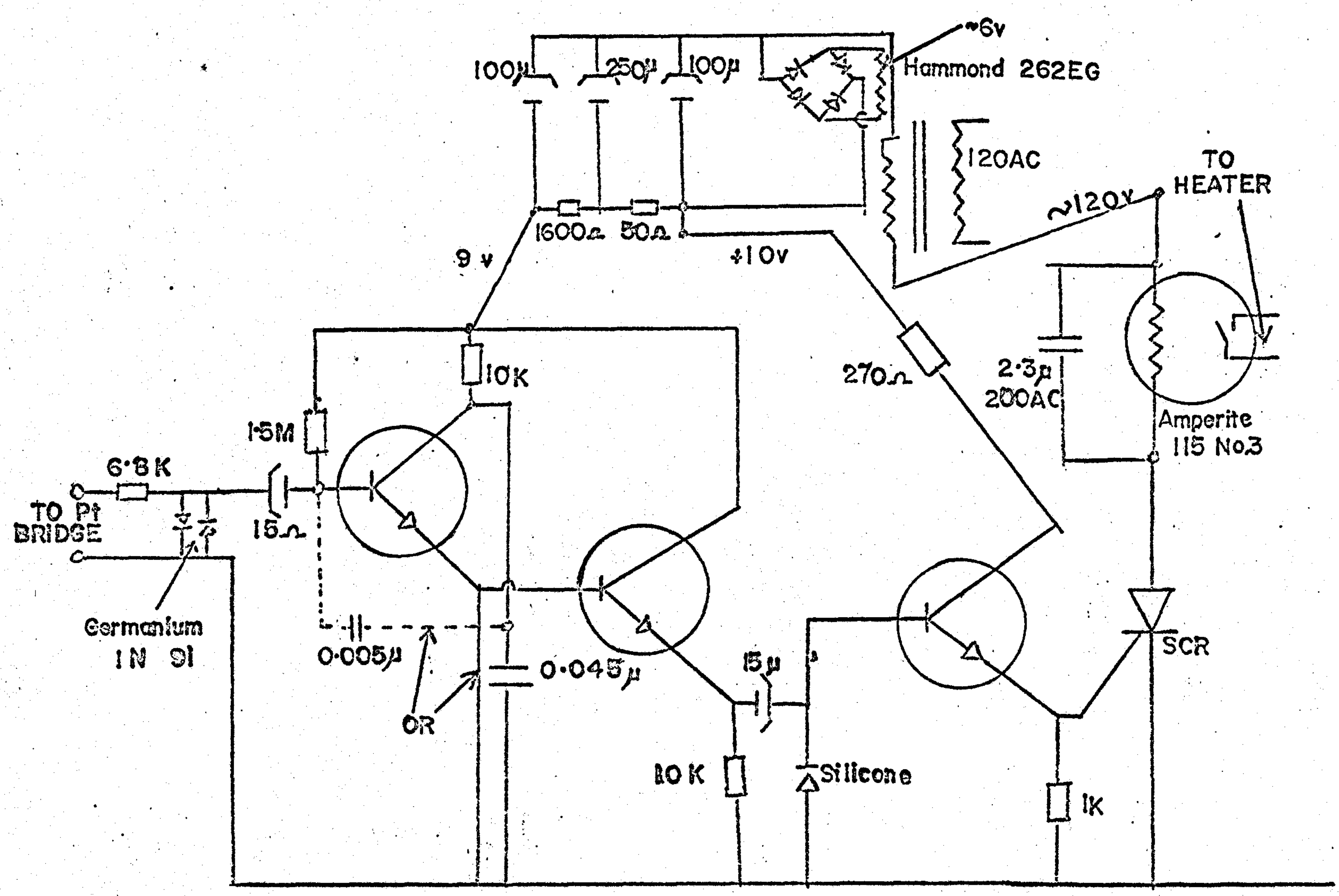


Fig. 8 Ciruit used to control the Gouy cryostat.

used to remove oxygen, the nitrogen was dried by molecular sieves and finally passed through a liquid nitrogen trap to remove other condensable contaminants. In place of a conventional inlet port a large polythene bag was used. In order to remove anything from the box, it was necessary to move the object down to the end of the bag and seal with a blow-torch. The use of a polythene bag in this manner is a technique normally employed by nuclear chemists to keep radioactive dust out of the air. In this case the sealed polythene bag made transportation of compounds under investigation from the dry-box much safer from decomposition by air. This was especially useful for transporting nujol mulls of sensitive materials to the Perkin Elmer 521 spectrometer (see section IV(d)).

IV EXPERIMENTS

(a) General techniques employed

Because of the extreme sensitivity of the compounds examined to moist air and stop-cock grease, etc., it was necessary to use special techniques in order to prevent decomposition of the compounds. The majority of the chlorides and oxychlorides investigated were volatile and thus vacuum distillation or sublimation was an excellent method of separation and/or purification. As grease was attacked it was not possible to use a permanent vacuum-line with stop-cocks and ground-glass joints. A typical vacuum-line used is shown in Fig. 9 (page 35).

The compound to be purified was contained in a tube sealed by the thin-walled capilliary at A. The line was pumped and heated with a Bunsen burner for at least twenty-four hours to remove surface moisture. The steel balls under B were then lifted with a magnet and dropped to break the seal at A, whilst the sample was cooled in liquid nitrogen, to prevent the vapours attacking the steel. The balls were replaced in the reservoir and removed by sealing at B. The U-traps were cooled in any convenient freezing-mixture and the sample separated and purified by trap to trap distillation. The sample was heated when necessary by water-bath, oil-bath or tube furnace.

Fig. 9 Typical vacuum line used.

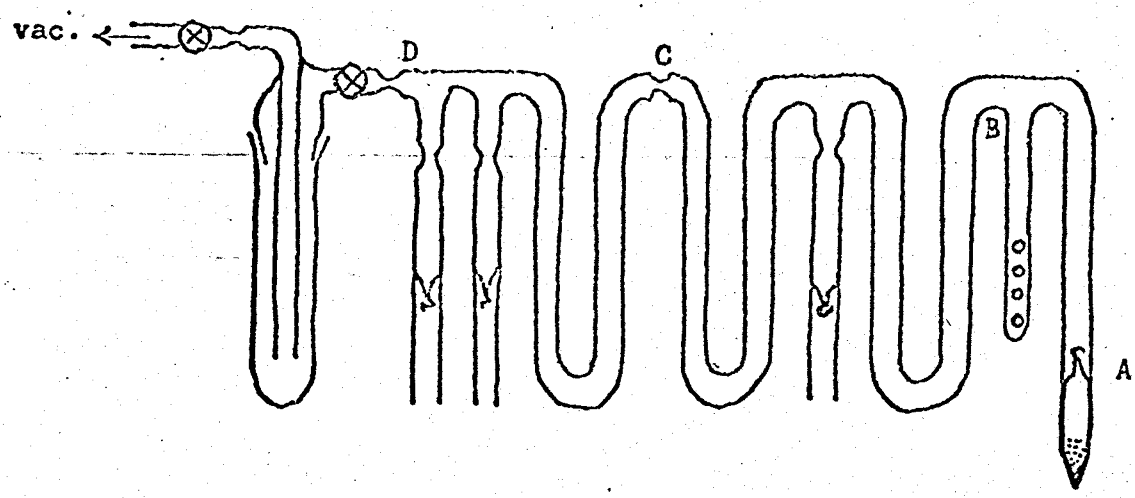
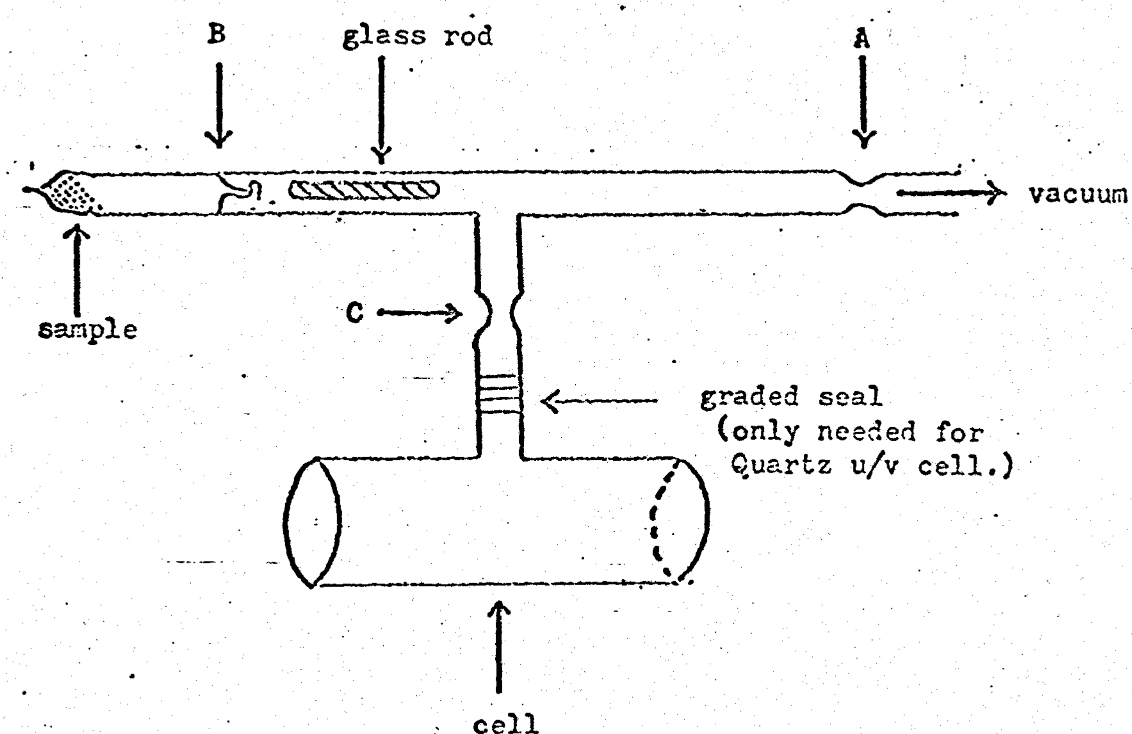


Fig. 10



Normally the sample was collected in the final trap by sealing at C and D and was transferred into the break-seals by standing the latter in a Dewar flask of liquid nitrogen. Less volatile compounds could be collected in earlier traps if required. Two break-seals were normally attached to the final trap, one to collect the main bulk of the product and one to collect a small sample for analysis.

Cells for vapour phase infrared and ultra-violet spectroscopy were filled on a vacuum line using the apparatus shown in Fig. 10 (page 35). The apparatus was evacuated and heated for at least 24 hours to remove surface moisture. The glass was sealed at A and the seal B broken with the piece of glass-rod by shaking. The cell was wrapped in cotton-wool, then liquid nitrogen poured onto the cotton-wool to provide cooling. When sufficient sample had distilled into the cell the glass was sealed at C.

Similar apparatus was used to fill Gouy tubes with $ReOC\ell_4$. The tube was sealed on the line in place of the cell and instead of distilling into the tube the compound was melted and poured in.

(b) Neutron activation analysis

Solutions of the compounds to be analysed were prepared by several methods. Air-stable materials were weighed and dissolved in a convenient solvent. Air-sensitive solids were transferred to a tared flask in a dry-box. Extremely sensitive compounds and compounds of which only a trace amount had been isolated were not weighed but destroyed in a break-seal, and the rhenium: chlorine atom ratio determined. These compounds were isolated in break-seals. The tube above the break-seal was filled with solvent (generally hydrogen peroxide) and the seal broken with a glass rod. A concentration of approximately one milligram of rhenium per millilitre of solution was found to be suitable. A standard solution of rhenium and chlorine was prepared by dissolving an accurately weighed amount of pure rhenium metal (99.9% by weight) in concentrated nitric acid, diluting, and dissolving an accurately weighed amount of ANALAR ammonium chloride.

One millilitre samples of standard and unknown were pipetted into separate two-fifths dram polyethylene capsules (obtained from Olympic Plastics, Los Angeles, California). The capsules were sealed by heating with a hot pyrex glass rod. The two capsules were placed axially in the reactor rabbit and irradiated for about forty-five seconds. The γ-ray spectra for sample and standard were observed using a 3" thallium-doped, sodium iodide crystal detector and a 400 channel analyser (Victoreen Instrument Corp., Tullamore Division, Model PIP 400). The peaks for $^{38}C\ell$ and ^{188}Re discussed in section II were plotted and the Compton background subtracted. A correction for decay of each sample was applied by multiplying by a factor derived from the expression:

$$\text{factor} = e^{\Delta t \lambda}$$

where Δt = difference in time between irradiation and counting

λ = the decay constant = $0.693/t_{1/2}$

$t_{1/2}$ = half-life of the isotope

The number of counts in the top channels of the peak given by the unknown were compared with the counts under a similar area of the peak given by the standard. The number of milligrams of rhenium and chlorine, and hence the percentage of rhenium and chlorine, and the rhenium:chlorine atom ratio were then calculated.

(c) Ultra-violet and visible spectra.

All spectra were recorded on a Carey model 14 instrument. Carey 1 cm quartz cells were used for solution studies and were filled in a dry-box. The cells were securely capped before transfer to the spectrometer. Gaseous spectra were recorded in all quartz cells of 10 cm path length with $1\frac{1}{2}$ inch diameter windows. These cells were filled by the method described in section IV(a). The gas-cells were heated by wrapping with asbestos paper and nichrome heating wire. Temperature control was obtained by feeding the power to the heating wire through a variac. The temperature was measured in an earlier experiment by placing a thermocouple in the cell at similar variac settings.

(d) Infrared spectra.

Routine spectra of air-stable compounds were recorded on a Perkin-Elmer-337 instrument. More accurate measurements of vapour-phase samples were performed on a Perkin-Elmer 521 instrument and far infrared studies were made on a Perkin-Elmer 301 spectrometer. Mull spectra of air-sensitive compounds were also recorded on the PE 521, as this instrument has a closed cell compartment through which a stream of dry nitrogen may be passed. This obviates decomposition of the sample in the spectrometer caused by reaction with moist air.

Vapour phase spectra were recorded using the cell described in section III and in (92). Spectra of solid samples were recorded as nujol mulls between potassium bromide or polyethylene plates. The nujol was dried by vacuum distillation from phosphous pentoxide. Mulls of sensitive materials were prepared in the dry-box and transferred to the instrument sealed in polythene as explained in section III. Solution cells were filled and transported in a similar manner.

Far infrared spectra of gaseous materials were measured in 10 cm path length pyrex glass cells fitted with polyethylene windows. The windows were heat-sealed to the glass body. Samples were distilled into the cell on the vacuum-line in the manner described in IV(a).

(e) Mass spectrometry.

Mass spectra were recorded on a Hitachi model RMU/6A by Dr. D. Clugston and Mr. R. Curran.

(f) Magnetic susceptibilities.

These measurements were made by the Gouy method on the apparatus discussed in section III. The samples were ground to a fine powder and packed in 3 mm (o.d.) quartz tubing to a length of approximately 10 cm, in a dry-box. The tube was capped, removed from the box and sealed. The sample-tube was then placed in the vibrator of a HOOVER (Philadelphia, Pa.) UNIMELT melting-point apparatus and shaken until the length remained constant. When the measurements were completed the sample was weighed and the tube calibrated with mercury tetrathiocyantocobaltate ($Hg[Co(CNS)_4]$) packed to the same length as the sample (93).

Diamagnetic corrections to the molar susceptibility were made using the values found in (94). When the Curie-Weiss law was followed, effective magnetic moments (μ_{eff}) were calculated using the formula:

$$\mu_{eff} = 2.84\ [\chi_m'(T + \theta)]^{1/2}$$

where χ_m' = the corrected molar susceptibility

T = absolute temperature

θ = Weiss constant.

In cases where the Curie-Weiss law did not apply, μ_T was calculated for each temperature T.

$$\mu_T = 2.84\ [\chi_m' T]^{1/2}$$

(g) Purification of reagents and solvents.

Acetone

Commercial grade acetone was stored over freshly regenerated molecular sieves (type 4A) and used without further purification.

Acetonitrile

"Analar" acetonitrile was purified by distillation from phosphorous pentoxide and potassium carbonate as described by Lewis and Smyth (95). The specific conductance of the purified material was found to be 6.2×10^{-8} ohm^{-1}cm^{-1}. This value compares favourably with the value of 5.9×10^{-8} quoted by Waddington (96) for pure acetonitrile.

Benzene

Reagent grade benzene was dried by distillation from phosphorous pentoxide, and stored in a dry-box over freshly regenerated molecular sieves (type 4A).

Carbon tetrachloride

Carbon tetrachloride was dried and stored in a similar manner to that used for benzene.

Chlorine

Commercial chlorine (supplied by Matheson, Whitby, Ontario) was dried by passing through concentrated sulphuric acid and phosphorous pentoxide traps, then into Stopcock B of the trap shown in Fig. 11.

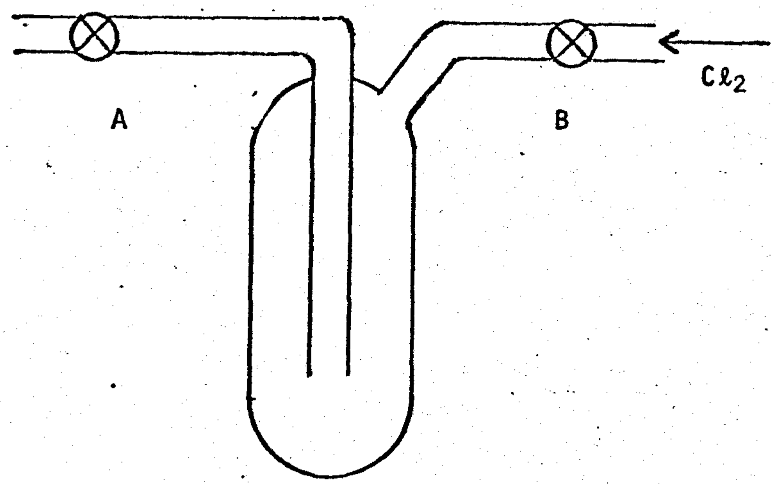


Figure 11

Chlorine was flushed through the trap until all air was expelled, then the Stopcock A was closed and the trap cooled in liquid nitrogen. When about 50 g of chlorine were solidified in the trap, Stopcock B was closed, a vacuum line was attached to Stopcock A and A was opened to pump oxygen out of the chlorine. When the pressure dropped to 10^{-4} mm Hg, A was closed and the chlorine allowed to warm up to -78°C in a dry ice/acetone bath. At this temperature chlorine is a liquid. The chlorine was refrozen in liquid nitrogen and reevacuated to 10^{-4}mm Hg. This process was repeated until no increase in pressure was observed when the trap containing solid chlorine was opened to the vacuum line. A steady stream from the trap was obtained by allowing liquid chlorine to boil off at -31.5 °C. This temperature was maintained by standing the chlorine container in a slush of "m"-toluidine.

Dichloromethane

Reagent grade dichloromethane was stored over molecular sieves (type 4A) and used without further purification.

Hydrogen

Commercial grade hydrogen (supplied by Canadian Liquid Air) was dried by passing through concentrated sulphuric acid and phosphorous pentoxide traps.

Nitrogen

Purified grade nitrogen (supplied by Canadian Liquid Air) was deoxygenated by hot activated copper in apparatus described elsewhere (91), and then dried by passing through concentrated sulphuric acid and phosphorous pentoxide traps.

Oxygen

Commercial grade oxygen (supplied by Canadian Liquid Air) was dried by liquefaction of the gas in a liquid nitrogen cooled trap similar to that described for chlorine. The oxygen was then allowed to evaporate slowly by controlled cooling with liquid nitrogen.

Pyridine

Reagent grade pyridine was dried by distillation from barium oxide as recommended by Leis and Currans (97).

Tetrahydrofuran

Reagent grade tetrahydrofuran was dried by distillation from lithium aluminum hydride, then stored over freshly regenerated molecular sieves.

Thionyl chloride

Thionyl chloride was purified by the method of Freidman (98) involving distillation from triphenyl phosphite.

All other reagents and solvents used were of the normal reagent grade.

(h) Preparation and purification of rhenium compounds used as starting materials.

Metallic rhenium

Rhenium metal was obtained commercially in powdered form and purified by reduction with hydrogen where indicated in the text. In all other cases, the powder was vacuum dried at 120°C for 24 hours before use. Suppliers of rhenium were Johnson, Matthey and Mallory (Toronto, Ontario), The University of Tennessee, and Chase Brass and Copper Company, Rhenium Division, Solon, Ohio.

Rhenium heptoxide: Re_2O_7

Some rhenium heptoxide was purchased from The University of Tennessee, and some from Koch-Light Laboratories, Colnbrook, Bucks, England, but the majority was prepared by burning rhenium in oxygen, in apparatus described by McLaren et al (99).

Rhenium trioxide: ReO_3

Rhenium trioxide was prepared by reduction of rhenium heptoxide by two different methods.

(i) Rhenium heptoxide was reduced with dioxan as described by Hiskey and Nechamkin (100). This method was found to be messy and high yields of trioxide were difficult to obtain.

(ii) It has been reported (101) that Re_2O_7 may be reduced to ReO_3 with carbon monoxide. It appeared that reduction by this method would be much easier in an autoclave than in the apparatus described. This proved to be correct.

Re_2O_7 was finely ground in a dry-box and transported to the autoclave in a stoppered bottle. The Re_2O_7 was placed in a glass liner and the autoclave sealed and flushed with carbon monoxide as rapidly as possible to minimise hydrolysis of the Re_2O_7 by atmospheric moisture. After reduction at 200°C and 500 psi carbon monoxide pressure for 24 hours the product was washed with water to remove unreacted starting material and dried at 110°C. Ninety percent yields of very pure rhenium trioxide were recorded.

<u>Rhenium dioxide: $ReO_2 x\ H_2O$</u>

Rhenium dioxide hydrate was prepared by aqueous hydrolysis of rhenium pentachloride as recommended by Colton and Brown (47).

<u>Perrhenyl chloride: $ReO_3C\ell$</u>

Perrhenyl chloride was prepared according to the method of Wolf, Clifford and Johnson (69) by direct chlorination of rhenium trioxide at 180°C. The pale yellow product was isolated in breakseals and purified by trap to trap distillation to give a colourless liquid product. Yields of pure compound were about seventy percent.

<u>Rhenium oxytetrachloride: $ReOC\ell_4$</u>

(a) Rhenium oxytetrachloride was prepared by Colton's method (70) from rhenium heptoxide and thionyl chloride. The product of this reaction was invariably contaminated by sulphur dioxide, which proved very difficult to remove by vacuum distillation. The presence of sulphur dioxide was readily detected by its gas-phase ultra-violet spectrum (102).

(b) Direct chlorination of rhenium metal gave low yields of rhenium oxytetrachloride if powdered rhenium was used, but gave high yields of rhenium oxytetrachloride if a rhenium mirror suspended on porous brick was used (see section V(a)). The oxytetrachloride was separated from pentachloride which was also produced, by pumping at reduced pressure, but separation from other volatile products was tedious. Thirty or forty trap to trap distillations were sometimes required to remove all impurities (see section V(a)).

(c) Rhenium pentachloride and dry oxygen were sealed in a Carius tube which was fitted with a break-seal. The tube was heated to 180°C in a furnace. The break-seal was then attached to a vacuum line, which was evacuated and heated for at least 24 hours before the seal was broken and the product distilled. This was the most convenient preparative method. Only two or three vacuum distillations were necessary to produce very pure oxytetrachloride in about 70 percent yield. The average Re:Cℓ ratio found for eighteen independant neutron activation analysis on $ReOC\ell_4$ prepared by all three methods was 1:3.92(±0.07). An analysis by convential wet methods after hydrolysis gave Cℓ = 41.3%, 41.1%; Re = 54.1%, 54.4%. $C\ell_4ORe$ requires Cℓ = 41.4%, Re = 54.1%.

<u>Rhenium pentachloride</u>

Some rhenium pentachloride was purchased from Alpha Inorganics, Beverly, Massachusetts, and Shattuck Chemical Company, but was generally prepared by one of the following methods.

(a) Powdered rhenium was chlorinated in the apparatus shown in Fig. 12 (page 47).

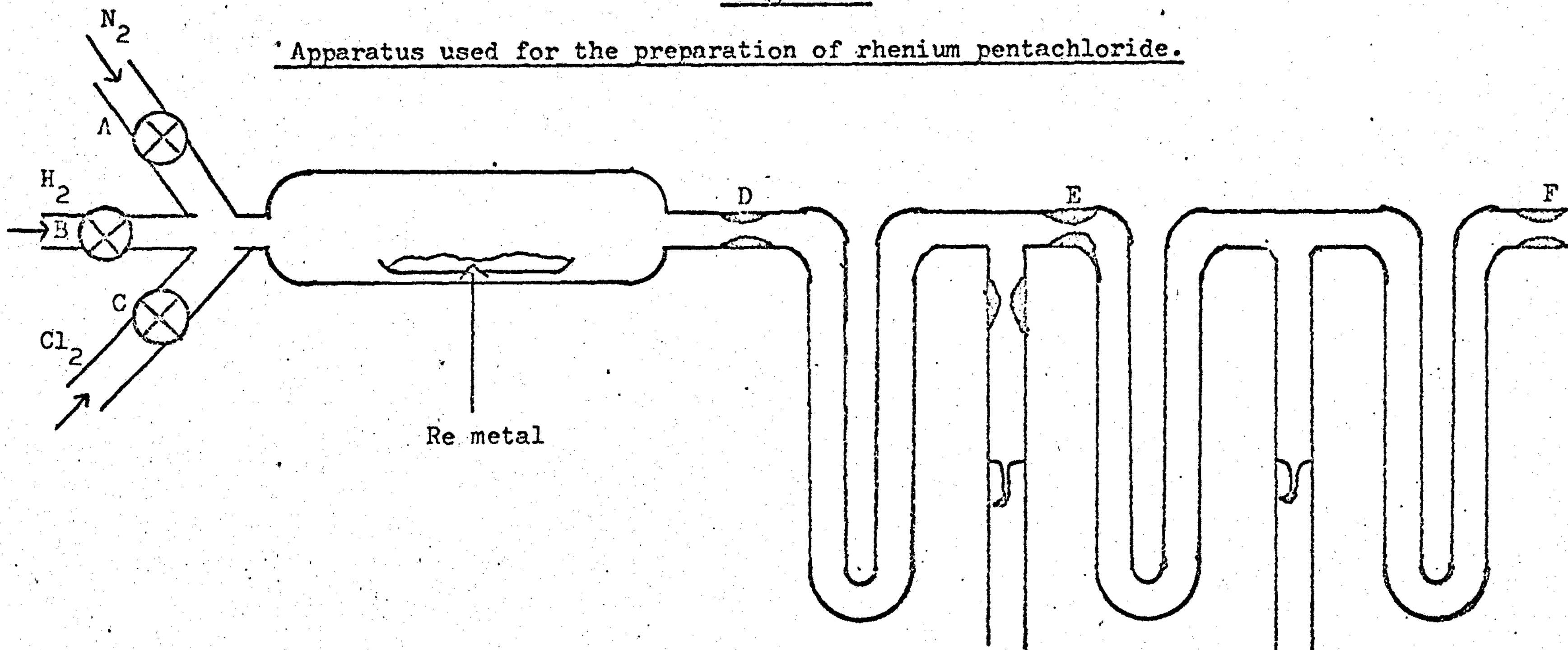
The rhenium was placed in a combustion boat as shown. Surface oxides were reduced by a stream of dry hydrogen passed over the metal at 500°C. The stopcocks A, B and C were closed and a vacuum applied at F for 24 hours to pump out all traces of moisture. The vacuum was released by opening the stopcock A to let in nitrogen. Chlorine was then passed over the metal at 500-550°C until all the metal had reacted. Almost all of the $(ReCl_5)_2$ produced remained in the first trap and the other traps were used to collect rhenium oxytetrachloride. Despite the precautions taken to keep oxygen out of the system, some $ReOCl_4$ was always formed. When the reaction was complete, the apparatus was sealed at D, E, and F. The traps were then attached to a vacuum-line and evacuated at room temperature. Chlorine and $ReOCl_4$ impurity distilled to leave $(ReCl_5)_2$ as a residue which was sealed in glass until required.

The rhenium pentachloride produced was in the form of very small crystals. The best method of purifying the material was to seal the pentachloride in a Carius tube with chlorine and distill it along the tube by applying a temperature gradient. By this method large plate-like crystals were formed.

(b) Rhenium heptoxide was reacted with carbon tetrachloride in a sealed tube as described by Knox, Tyree et al (45). Without

Fig. 12.

Apparatus used for the preparation of rhenium pentachloride.



modification this method gave high yields of pure rhenium pentachloride.

(c) Powdered rhenium was reacted with chlorine in a sealed tube. Rhenium powder was sealed in a vycor tube with an excess of chlorine, and the tube heated in a furnace at 600°C until all the metal had reacted (~0.2 g reacted in 24 hours). The tip of the tube was removed from the furnace and the temperature lowered to 300°C. Large plate-like crystals of rhenium pentachloride formed in the cooler end of the tube. A quantitative yield was obtained.

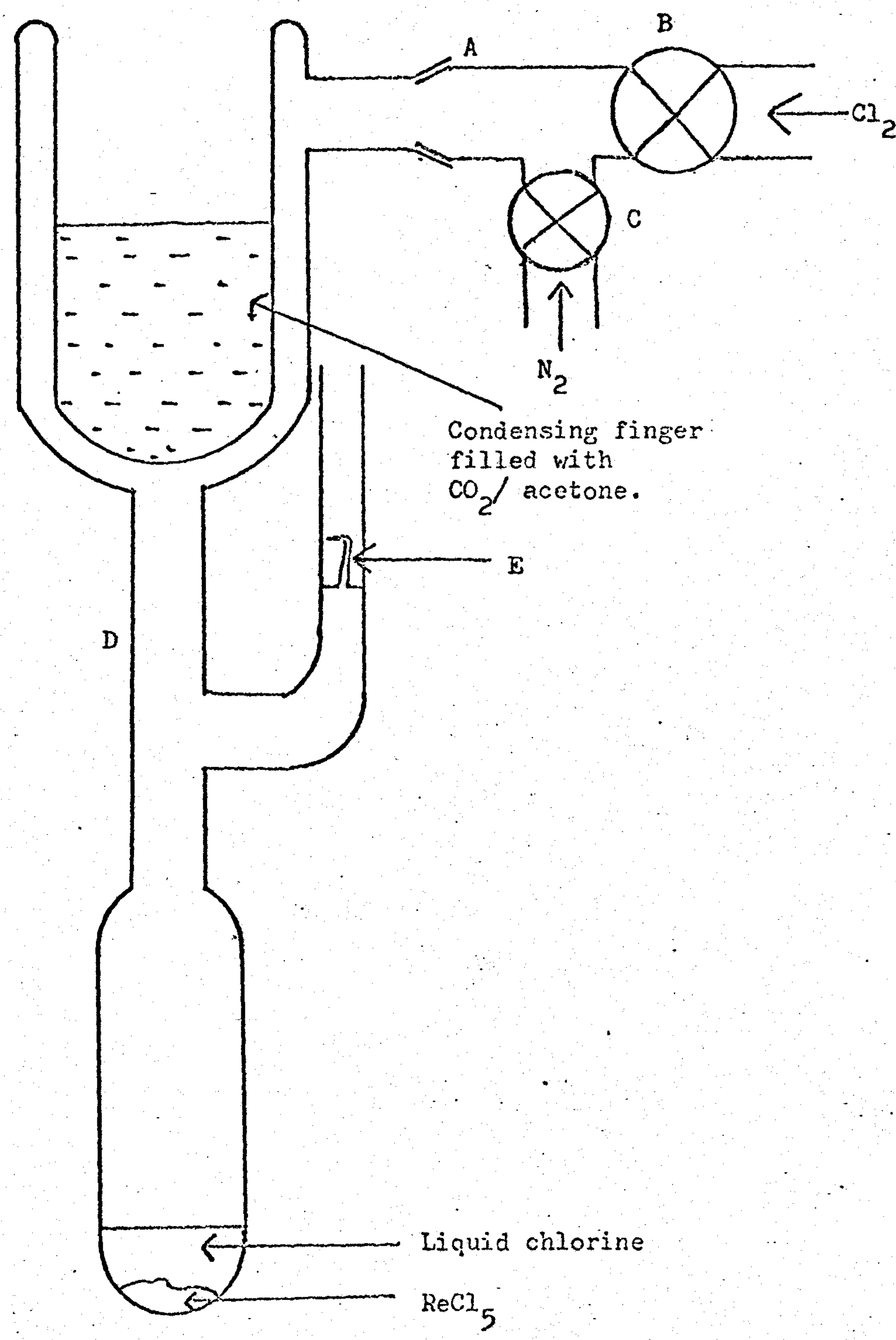
Rhenium pentachloride is a black crystalline material which melts at 261°C. An average of 12 analyses by neutron activation gave (see Table 2, page 20) Cℓ = 49.7%, Re = 51.6% (stoichiometry = 1:4.98 ± 0.06). $C\ell_5Re$ requires Cℓ = 48.8%, Re = 51.2%.

Reaction of $(ReC\ell_5)_2$ with liquid chlorine

The apparatus used is shown in Fig. 13. Rhenium pentachloride was powdered in the dry-box and transferred to the glassware through A. The apparatus was stoppered and removed from the dry-box. The stopper was removed and chlorine was blown into B immediately with C closed and the apparatus standing in a solid carbon dioxide/acetone refrigerant. When several millilitres of chlorine had been condensed, C was opened and the chlorine supply removed so that nitrogen could escape through B. The apparatus was removed from the CO_2/acetone bath and the condensing-finger D filled with this cooling mixture. Steady reflux of chlorine occurred.

Fig.13.

Apparatus for refluxing with liquid chlorine.



When the reaction was considered to be complete, the temperature of the condensing-finger was allowed to rise and the chlorine allowed to escape to atmosphere. The glass was sealed at D and the reaction mixture could be distilled through the break-seal E.

Rhenium trichloride: $Re_3C\ell_9$

Some rhenium trichloride was obtained from the Shattuck Chemical Company. This product was contaminated with approximately 12% rhenium pentachloride.

Rhenium trichloride was prepared by thermal decomposition of rhenium pentachloride. The decomposition may be performed in a stream of nitrogen or under vacuum (26). We have found it a little easier to use vacuum. Rhenium pentachloride was placed in the end of a long horizontal glass tube. Low vacuum (~10^{-2}cm Hg) was applied and the end of the tube containing pentachloride heated in a tube furnace to 200°C. About thirty or forty percent of the $(ReC\ell_5)_2$ decomposed to $(ReC\ell_3)_3$. The remainder distilled to a cooler part of the tube. The furnace was moved along the tube to heat the distilled $(ReC\ell_5)_2$. Again some of the $(ReC\ell_5)_2$ was decomposed and some distilled to a cooler part of the tube. The procedure was repeated to completion of the decomposition. Invariably some $(ReC\ell_5)_2$ was converted to $ReOC\ell_4$ by reaction with oxygen which leaked into the system. This $ReOC\ell_4$ was recovered from U-traps placed between the reaction tube and the pump.

Rhenium trichloride produced by this method was a deep purple, microcrystalline solid with a melting point greater than 300°C. The average of sixteen analyses by neutron activation analysis was $C\ell$ = 36.1%, Re = 61.5%

(Re:Cℓ = 1:3.04 0.10) Cl_9Re_3 requires Cℓ = 36.4%, Re = 63.6%.

(i) Preparation and purification of new compounds and new methods of preparation of known compounds

Rhenium tetrachloride

(a) Powdered rhenium metal and antimony pentachloride (mole ratio ≈1:2.5) were sealed in a "vycor" tube similar to that shown in Fig. 14.

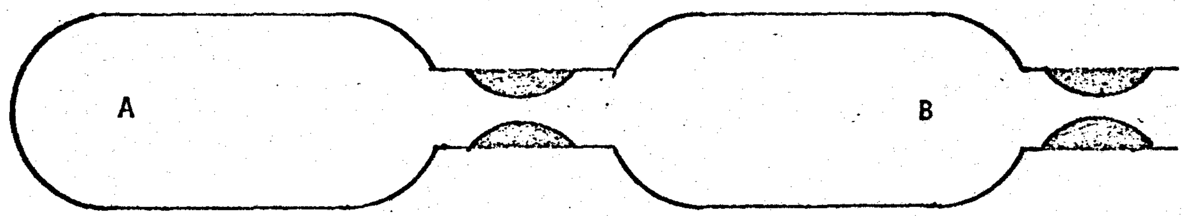


FIGURE 14

The sealed tube was heated in a tube-furnace at 600°C until all the metal had reacted (0.5g Re reacted in about 48 hours). The tube was moved along the furnace, so that the end B was out of the furnace and at room temperature. When all the products had condensed in B, the furnace temperature was reduced to 250°C and the tube position reversed, so that B was at the furnace temperature and A was at room temperature. Excess antimony pentachloride and some antimony trichloride distilled into A, leaving a black solid in B. The tube was opened in a dry-box, and the black solid transferred to a test-tube fitted with a ground-glass joint. The tube was stoppered, removed from the dry-box and transferred rapidly to a vacuum-line. The black solid was pumped at room temperature, and then at 165°C for 48 hours to remove all traces of antimony trichloride. The glass was then sealed and the product stored in a dry-box. Yields of 75% have been recorded.

(b) Approximately equimolar quantities of rhenium pentachloride and antimony trichloride were sealed in a pyrex glass tube similar to the vycor tube described in Fig. 14. The tube was heated for 48 hours at 300°C and the resulting black product purified in a manner similar to that described above.

Rhenium tetrachloride prepared by these methods has the properties of β-$ReC\ell_4$ described by Cotton et al (50). An average of 10 analyses by neutron activation gave Re = 56.8%, Cℓ = 43.3% (Re:Cℓ = 1:3.98) $C\ell_4Re$ requires Cℓ = 43.3%, Re =56.7%.

Conversion of rhenium tetrachloride to tetra-n-butyl ammonium octachlorodirhenate(III) $(n\ but_4N)_2(Re_2C\ell_8)$

Rhenium tetrachloride prepared by the above methods was reacted with tetra-n-butylammonium bromide by the method of Cotton et al (50). The blue product had an ultraviolet/visible spectrum identical to that of $(n\text{-}but_4N)_2(Re_2C\ell_8)$ prepared by a standard method (103). Analysis by A.B. Gygli, Toronto, Ontario, gave:

C = 33.1% H = 6.4% Cℓ = 23.1%

$C_{32}H_{72}C\ell_8N_2Re_2$ requires C = 33.6%, H = 6.4%, Cℓ = 24.8%.

Oxotrichlorobispyridinerhenium(V) : $ReOC\ell_3py_2$

(a) Rhenium oxytetrachloride was sealed under vacuum in a tube fitted with a break-seal, and the tube above the break-seal filled with pyridine. The seal was broken with a glass rod, causing the pyridine to be sucked onto the $ReOC\ell_4$. The tube was shaken vigorously to dissolve the $ReOC\ell_4$ and form a red solution. Heat was evolved during dissolution. After half an hour a green precipitate formed and continued to form until the red solution faded to a pale yellow. The green compound was filtered and washed with carbon tetrachloride; then pumped at 100°C for 24 hours to remove all solvent.

(b) $ReOC\ell_3py_2$ was prepared in exactly the same manner as in (a) using $ReOC\ell_4$--$OPC\ell_3$ as a starting material, instead of $ReOC\ell_4$.

Neither starting material was weighed but estimated yields were of the order of seventy percent. $ReOC\ell_3py_2$ prepared by either method is a green, air-stable, microcrystalline material of melting-point > 300°C. Analysis by Galbraith Labs. Inc., (Knoxville, Tennessee) gave:

C = 25.6% H = 2.3% $C\ell$ = 22.6% N = 5.9%

Neutron activation analysis gave $C\ell$ = 22.9%, Re = 40.0% [stoichiometry Re:$C\ell$ = 1:2.97(0.08)]. $C_{10}H_{10}C\ell_3N_2ORe$ requires C = 25.7%, H = 2.14%, $C\ell$ = 22.8%, N = 6.0%, Re = 39.8%. The compound showed the same infrared spectrum and solubility properties as a sample of $ReOC\ell_3py_2$ prepared by the original method (104).

Dioxotetrapyridine rhenium(V) chloride $[ReO_2py_4]C\ell$

The yellow filtrate from the preparations of $ReOC\ell_3py_2$ above were evaporated to low bulk. Large red crystals were deposited which after drying showed an infrared spectrum identical to that for $[ReO_2py_4]C\ell$ prepared by a standard method (105).

Oxoethoxobispyridinerhenium(V) $[ReO(OEt)C\ell_2py_2]$

$ReOC\ell_3py_2$ was refluxed with boiling absolute ethanol. After two hours all the green $ReOC\ell_3py_2$ had dissolved to give a blue solution. The solution was evaporated to low bulk and cooled to deposit large blue plate-like crystals. The product was filtered, washed with a little ice-cold absolute alcohol and dried in vacuum. Analysis by Galbraith Labs. gave C = 30.15%, H = 3.01%, Cℓ = 14.73%, N = 5.58%. $C_{12}H_{15}C\ell_2N_2O_2Re$ requires C = 30.3%, H = 3.2%, Cℓ = 14.9%, N = 5.9%, Re = 39.0%.

The product was obtained in 80% yield as air-stable blue plate crystals,melting-point = 185°C. The melting-point and infrared spectrum were identical with those of a sample of $ReO(OEt)C\ell_2py_2$ prepared by the original method (57).

Oxotrichloro(2,2′-dipyridyl)rhenium(V) [$ReOC\ell_3$dipy]

2,2′-dipyridyl and rhenium oxytetrachloride were dissolved in carbon tetrachloride in a dry-box, and the solutions mixed. A yellow compound precipitated from the solution. The precipitate was filtered, washed with carbon tetrachloride and vacuum-dried. Analysis of the product by Galbraith Laboratories gave C = 25.3%, H = 1.8%, Cℓ = 22.4%, N = 5.60%. Neutron activation analysis gave Cℓ = 22.7%, Re = 40.6%. $C_{10}H_8C\ell_3N_2ORe$ requires C = 25.8%, H = 1.9%, Cℓ = 22.9%, N = 6.0%, Re = 40.1%. The infrared spectrum was identical to that of a sample prepared by the original method (106).

The $ReOC\ell_4$ starting material was not weighed but the yield of yellow-green air-stable microcrystalline solid, melting-point = >300°C, was estimated as approximately seventy-five percent.

μ-oxobis[oxodichloro(2,2′-dipyridyl)rhenium(V)] [(dipy)$ReOC\ell_2$—O—$C\ell_2ORe$(dipy)]

$ReOC\ell_3$dipy was refluxed with boiling absolute ethanol. Very slowly the solution changed to a pale orange colour and a green compound was precipitated. The green compound was filtered, washed with ice-cold absolute ethanol and vacuum dried. Analysis by Galbraith Laboratories gave C = 27.8%, H = 2.1%, Cℓ = 16.2%, N = 6.3%. Calculated for $C_{20}H_{16}Cl_4N_4O_3Re$, C = 27.5%, H = 1.8%, Cℓ = 16.3%, N = 6.4%, Re = 42.6%. Yield of green, air-stable crystalline material, melting point >300°C, was sixty percent.

Trioxochlorobispyridinerhenium(VII) [$ReO_3Cl py_2$]

Pyridine and perrhenyl chloride were dissolved in carefully dried carbon tetrachloride and mixed. A white precipitate formed immediately. The precipitate was filtered, washed with carbon tetrachloride and pumped on a vacuum-line at room temperature to remove volatile impurities. The compound was then sublimed at 100°C in vacuum. The ReO_3Cl starting material was not weighed, but the yield of pure, air-unstable, very pale yellow compound, melting point = 155°C (decomp.) was approximately forty to fifty percent. Analysis by A. B. Gygli gave C = 28.0%, H = 2.9%, Cℓ = 8.4%, N = 6.3%. Neutron activation analyses gave Cℓ = 7.9%, Re = 43.4%. Calculated for $C_{10}H_{10}ClN_2O_3Re$, C = 28.1%, H = 2.3%, Cℓ = 8.3%, N = 6.5%, Re = 43.6%.

Trioxochloro 2,2′-dipyridyl rhenium(VII) [$ReO_3Cl dipy$]

2,2′-dipyridyl and perrhenyl chloride were dissolved in carefully dried carbon tetrachloride and the solutions mixed. The heavy white precipitate which formed immediately was filtered, washed with carbon tetrachloride and pumped at room temperature for 24 hours to remove volatile impurities. The ReO_3Cl starting material was not weighed but yields of white, involatile, air-stable compound, melting point 280°C (decomp.), were estimated at sixty to seventy percent. Analysis by

Galbraith Laboratories gave C = 26.7%, H = 1.7%, Cℓ = 8.4%, N = 6.1%. Neutron activation analysis gave Cℓ = 8.0%, Re = 43.1%. Calculated for $C_{10}H_8C\ell N_2O_3Re$, C = 28.2%, H = 1.9%, Cℓ = 8.3%, N = 6.6%, Re = 43.8%.

Oxotetrachloro(oxotrichlorophosphorus V)rhenium(VI) [$ReOC\ell_4(OPC\ell_3)$]

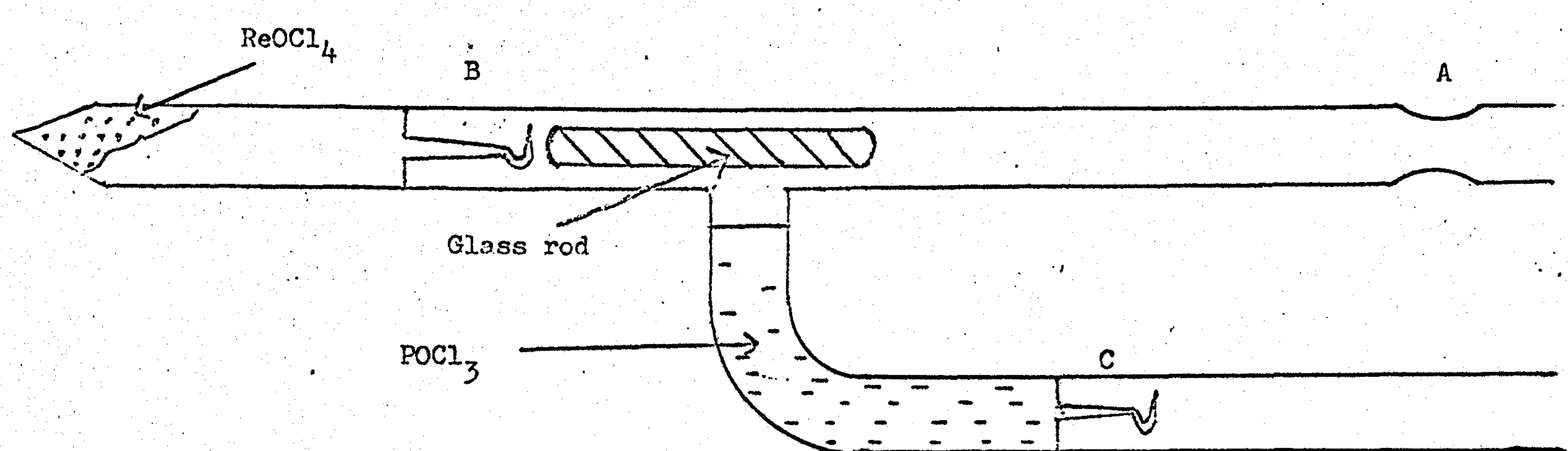
(a) Powdered phosphorus pentachloride was weighed in a dry-box into the bulb A of a pyrex glass tube similar to the tube shown in Fig. 14 (page 51) but with a break-seal fitted to A. Powdered rhenium heptoxide was weighed and transferred to the bulb B (mole ratio 5 $PC\ell_5$: $1Re_2O_7$) and the apparatus sealed at C before the reactants were allowed to mix. The tube was then shaken until the solids reacted with evolution of heat to form a red-brown semi-liquid mass. The tube was attached to a vacuum line and after pumping and heating for at least 24 hours, the seal was broken and the reaction products fractionated. Phosphoryl chloride and unreacted phosphorus pentachloride were volatile at room temperature. The $ReOC\ell_4$---$OPC\ell_3$ sublimed more slowly at room temperature and was freed from phosphorus chlorides after three or four trap to trap sublimations. The yield of $ReOC\ell_4$---$OPC\ell_3$ was about fifty percent.

(b) $ReOC\ell_4$---$OPC\ell_3$ was prepared in a manner analogous to (a) using ReO_3 instead of Re_2O_7 as starting material.

(c) By direct synthesis from $ReOC\ell_4$ and $POC\ell_3$ in pyrex apparatus shown in Fig. 15. The glass was vacuum dried, the $POC\ell_3$ poured in and the tube sealed at A. The apparatus was shaken to break the seal B. The reactants mixed to form a red solution and heat was evolved. The apparatus was attached to a vacuum-line and after pumping and baking for at least 24 hours the seal C was broken and excess $POC\ell_3$ pumped off at ice temperature.

Fig. 15.

Apparatus for the preparation of $ReOCl_4$-$OPCl_3$ by direct synthesis.



The $ReOCl_4$---$OPCl_3$ was purified by sublimation and isolated in break-seals. Yields of approximately seventy percent were recorded.

$ReOCl_4OPCl_3$ forms long fine needle crystals with a melting-point of 90.5°C. Analysis by Galbraith Laboratories gave Cl = 53.5%, P = 5.8%. Analysis by A. Bernhart gave P = 6.2% (see Chapter VI(a)). Neutron activation analyses gave (mean of 12 analyses) Cl = 52.2%, Re = 38.7% (Re:Cl = 1:7.08 ±0.35). Calculated for Cl_7O_2PRe, Cl = 49.9%, P = 6.2%, Re = 37.5%.

Tetrachlorophosphonium(V) hexachlororhenate ($[PCl_4]^+[ReCl_6]^-$)

(a) Powdered rhenium and phosphorus pentachloride (mole ratio 1:5) were sealed in a pyrex tube full of chlorine. The tube was placed in a tube-furnace at 500-550°C. It was arranged that the tip of the tube was at the end of the furnace, therefore at a lower temperature . A brown solid was deposited in the tip of the tube. When all the rhenium metal had reacted, and the product had collected in the tip of the tube, the temperature of the furnace was lowered to 200°C. The tube position was reversed so that the other end of the tube was in the air at room temperature. Unreacted phosphorus pentachloride condensed on this cool end of the tube. The tube was opened in the dry-box and the product transferred to a break-seal. The break-seal was transferred to a vacuum-line, and after evacuating the line for 24 hours to dry the glass, the seal was broken and the product pumped at room temperature to remove traces of phosphorus chlorides.

(b) Rhenium pentachloride and phosphorus pentachloride were sealed in a pyrex glass tube fitted with a break-seal. The tube was placed in a furnace and heated to 300°C. The product was separated from phosphorus chlorides by the procedure used in (a).

$(PC\ell_4)^+(ReC\ell_6)^-$ prepared by either method may be purified by vacuum sublimation at 150°C. Analysis by neutron activation (mean of ten determinations) gave: Cℓ = 62.8%, Re = 32.8%. Analysis by Galbraith Labs gave: Cℓ = 51.0%, P = 5.6%. Calculated for $C\ell_{10}PRe$, Cℓ = 62.0%, P = 5.4%, Re = 32.6%.

<u>Ditetrachlorophosphonium(V) octachlorodirhenate(III) $(PC\ell_4)_2^+(Re_2C\ell_8)^{2-}$</u>

(a) $RePC\ell_8$ was prepared by the method of Machmer (107). The product was separated from phosphorus chlorides by the procedure used for $RePC\ell_{10}$ above.

(b) Rhenium pentachloride and phosphorus trichloride were sealed in a pyrex glass tube fitted with a break-seal. The tube was placed in a tube-furnace and heated to 300°C. The product was separated from phosphorus halides by the procedure used for $RePC\ell_{10}$ above.

Neutron activation analysis (mean of 4 determinations gave Cℓ = 55.3%, Re = 37.1% (Re:Cℓ = 1:7.7), $C\ell_8PRe$ requires Cℓ = 56.6%, P = 6.2%, Re = 37.2%.

V CHLORIDES AND OXYCHLORIDES

(a) Rhenium hexachloride and rhenium oxytetrachloride

It was mentioned in section I that the observed magnetic moment (48) of rhenium hexachloride was anomalous. We wished to reexamine this system, to check the magnetic measurements and if found correct, perhaps find an explanation of the anomaly. We also wished to discover why rhenium hexachloride did not thermally decompose to a tetrachloride and chlorine. Technetium hexachloride decomposes in this manner very easily:

$$TcC\ell_6 \xrightarrow[\text{warming}]{\text{gentle}} TcC\ell_4 + C\ell_2 \ (59).$$

The conditions of Colton's(61) chlorination (described in section I(c)) were reproduced. The major product resembled the compound described by Colton, and just a little pentachloride was produced. In many early experiments, before the activation analysis (section II) and gas-phase infrared cell (section III) had been developed, the first test applied to the product was to measure the infrared spectrum of a solution prepared in a dry-box. Invariably peaks were observed in the range 900-1050 cm^{-1}. This region of the infrared is far too high for any heavy metal-chlorine vibrational frequency (108), but is the normal region of heavy metal-oxygen stretching vibrations (109). Therefore these absorptions were the result of oxygen contamination of the product.

Because of this contamination, more and more rigorous conditions were applied to keep moisture and oxygen out of the reactants, solvents, and products. At this time no dry-box was available in which this compound could be handled without fuming and decomposition. The initial reason for the use of break-seals and grease-free vacuum systems (see Experimental section IV(a)), and for the development of special infrared and analysis techniques was to try to obtain this compound in a pure form, and obtain accurate analysis figures.

Early analysis results by classical wet methods were not accurate but indicated that the ratio of rhenium to chlorine atoms was about 1:4. When the neutron activation method was refined enough, many analyses were performed. It was found that it was possible to obtain a rhenium:chlorine ratio of 1:6, unless the product was carefully separated from volatile contaminants (see later in this discussion). Samples which were purified by many trap to trap vacuum sublimations (thirty or forty in some cases), which formed large black crystals, and had a very sharp melting-point at 32°C were found to have a rhenium:chlorine ratio of 1:4. On hydrolosis with ammonium hydroxide solution, the compound gave a $Re^{VII}:Re^{IV}$ ratio of 2:1 which is typical of rhenium(VI) (see section II).

Gaseous infrared spectra recorded using the gas cell described in section III, filled on a vacuum-line with no possibility of oxygen entering the system (see experimental section IV(a)), showed one large peak centred at 1040 cm^{-1}. The peak was split with a P branch at 1047 cm^{-1} and an R branch at 1033 cm^{-1}. The absorption occurs at a little lower energy in solution; 1033 cm^{-1} in carbon tetrachloride and 1029 cm^{-1} in titanium tetrachloride. This absorption peak, which is reproduced in Fig. 16 (page 63) can only be caused by a rhenium-oxygen vibration. From the above evidence, it was realised that this chlorination product was rhenium oxytetrachloride. Subsequent investigations showed that it was possible to obtain classical wet analyses for rhenium and chlorine, on a sample transferred in the new Vacuum/Atmospheres (Los Angeles, California) dry-box, from a sealed tube to a previously weighed flask. These analyses confirmed the formulation of the chlorination product as $ReOC\ell_4$.

The vapour-phase ultra-violet/visible spectra of this chlorination product, and $ReOC\ell_4$ prepared by reaction of rhenium pentachloride with oxygen, were found to be identical. The absorptions observed are listed in Table 3 (page 64).

Further support for this formulation is afforded by a study of the magnetic susceptibility of the compound. The susceptibilities of samples of $ReOC\ell_4$ prepared by direct chlorination, and by the reaction of pentachloride with oxygen, are recorded in Table 4 (page 65). These results are plotted as a function of temperature in curves (a) and (b) of Fig. 17 (page 66). Curve (c) of this figure is a plot of the magnetic data reported by Klemm and Schuth in 1934 (31), and (d) is a reproduction of the data which Brown and Colton (48) obtained for "rhenium hexachloride". These "hexachloride" figures have been recalculated assuming Brown and Colton's compound to be rhenium oxytetrachloride. The recalculated results are presented as curve (e). The Weiss constants and the calculated effective magnetic moments are presented in Table 5 (page 67). It can be seen in this table that the Weiss constants are all between 24° and 28°.

Fig. 16. Re = O absorption in vapour-phase infra-red spectrum of $ReOCl_4$ showing P, Q and R branches.

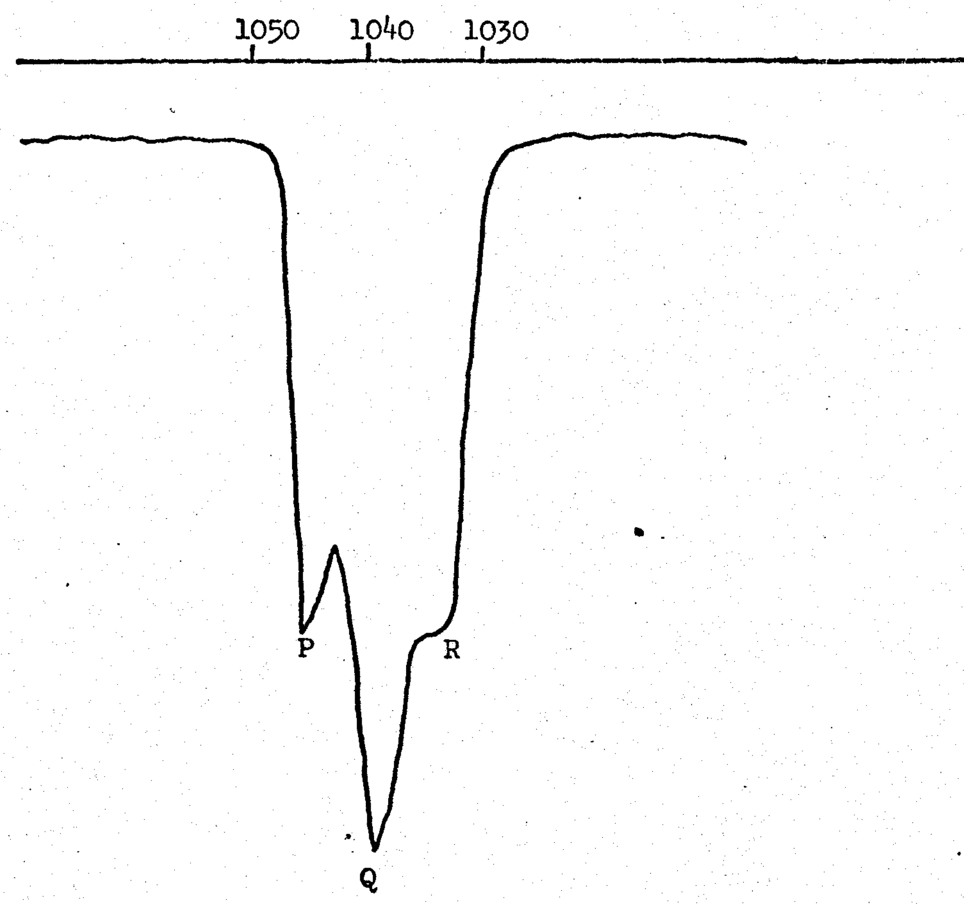


Table 3

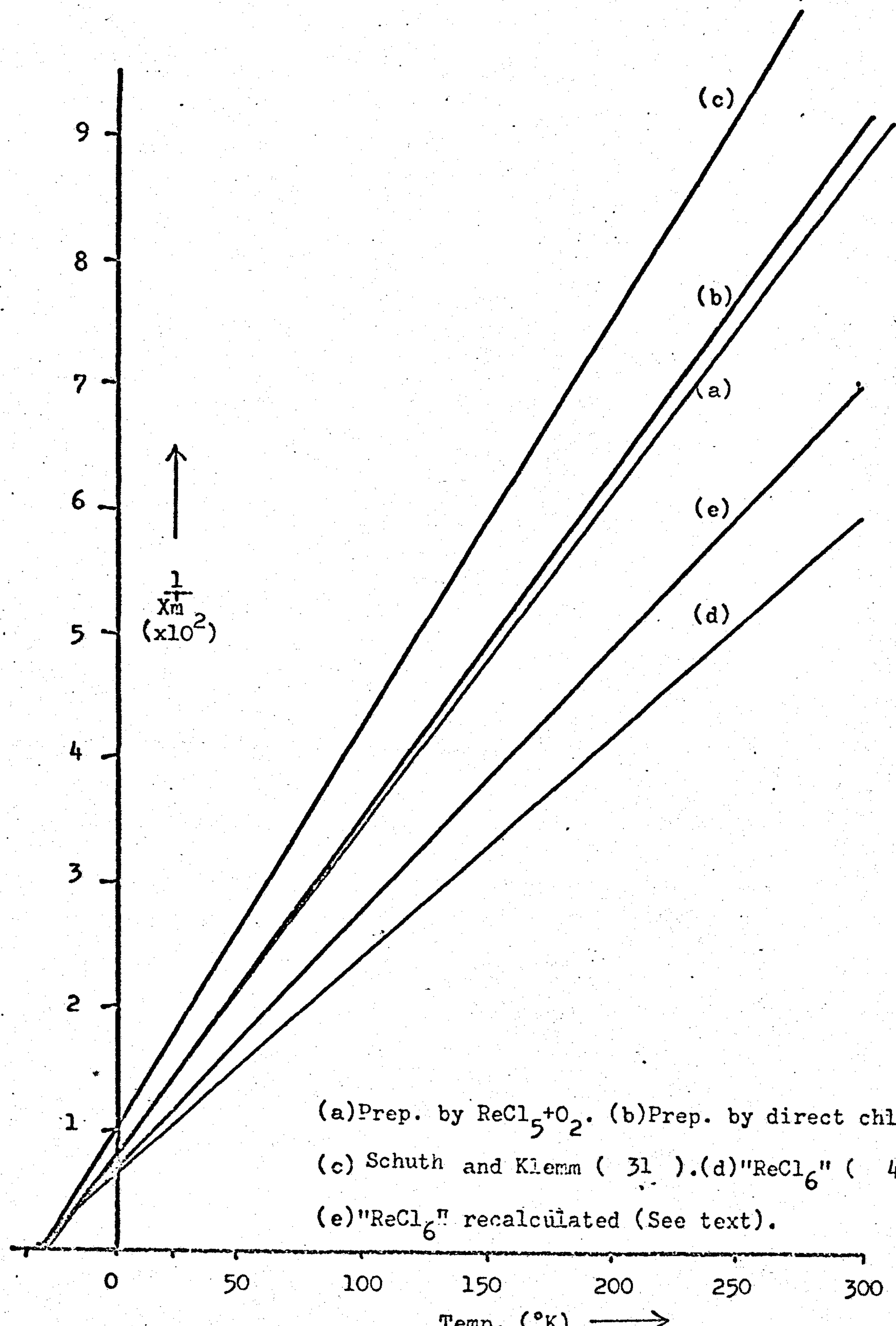
Vapour phase u/v visisible spectrum of $ReOCl_4$.

Temp.	Wavelenth Region		
(°c)	7000 - 5500 Å	5500 - 4000 Å	4000 - 1850 Å
- 78	No absorption observed.	No absorption observed.	Steady rise in absorption from 3600 Å to total absorption at 1850 Å. Shoulders at 2790 & 2460 Å.
+ 23	No absorption observed.	Large broad absorption band from 3775 - 5400 Å with peak at 4420.	Total absorption from 3000 Å - 1850 Å.
+ 80	Very weak, very broad band 5700 - 6400.	Large absorption band 3700 - 5450 total absorption from 4000 - 5100 Å.	Total absorption from 3400 - 1850 Å.

Table 4. The magnetic susceptibility of $ReOCl_4$.

Prepared by $ReCl_5$ & O_2 (This work) *		Prepared by direct chlorination. (This work)*		$ReOCl_4$ Schuth and Klemm (31)		"$ReCl_6$" Brown and Colton (48)		"$ReCl_6$" Recalculated (See text)	
Temp. (°K)	χ'_m ($\times 10^6$ cgs)	Temp. (°K)	χ'_m ($\times 10^6$ cgs)	Temp. (°K)	χ'_m ($\times 10^6$ cgs)	Temp. (°K)	χ'_m ($\times 10^6$ cgs)	Temp. (°K)	χ'_m ($\times 10^6$ cgs)
80	3334	80	3292						
100	2815	100	2780	90	2540	98	4368	98	3739
120	2432	120	2405			113	3876	113	3302
140	2134	140	2113			134	3358	134	2841
160	1906	160	1881			158	2942	158	2504
180	1719	180	1701			177	2672	177	2271
200	1576	200	1556	199	1310	201	2403	201	2040
220	1450	220	1431			225	2201	225	1870
240	1339	240	1293			251	1982	251	1670
270	1209	270	1192			266	1872	266	1571
293	1150	293	1117	293	928	297	1695	297	1430

Fig. 17. Magnetic susceptibility of $ReOCl_4$.



(a)Prep. by $ReCl_5+O_2$. (b)Prep. by direct chlorination.

(c) Schuth and Klemm (31).(d)"$ReCl_6$" (48).

(e)"$ReCl_6$" recalculated (See text).

Table 5.

Compound	Weiss constant.	μ_{eff}
$ReOCl_4$. Schuth and Klemm. (31)	25°	1·5
$ReOCl_4$ ($xReCl_5 + O_2$).	24°	1·7
$ReOCl_4$ (by direct chlorination).	27°	1·7
$ReCl_6$ Colton and Brown(48).	28°	2·07
Ref.(48)recalculated on $ReOCl_4$ basis.	28°	1·9

The effective magnetic moments from the measurements of Klemm and Schuth, this work and the recalculated figures of Brown and Colton are not in precise agreement. This is understandable when one considers the method of filling the sample tube. Because of the low melting-point of the compound, both other groups of workers and ourselves have found it impossible to grind the solid and pack a tube in the normal manner. The method used was to seal the quartz sample tube through a graded seal onto pyrex apparatus, which contained the $ReOC\ell_4$ under a break-seal (see experimental section IV(a) and Fig. 10 page 35). The apparatus was evacuated and heated to remove surface moisture. The seal was then broken, and the compound melted, and poured into the tube as a liquid. Thaw-melt techniques were employed in an attempt to obtain a continuous 10 cm length of rod of solid compound, but as the solid has a smaller specific volume than the liquid, some empty space was apparent in all cases. Within this limitation, the agreement of the μ_{eff} values is quite reasonable.

It seemed strange that the major product of chlorination of rhenium should be altered so much, just by using metal with a higher specific surface area. The first conclusion drawn was that a higher chloride was formed which attacked the glass or ceramic to abstract oxygen. A small amount of volatile yellow material, from which it was difficult to separate the $ReOC\ell_4$, had often been observed during trap to trap sublimations, and it now seemed possible that this was a higher chloride. By many careful sublimations a few milligrams of this compound were isolated. Activation analysis gave a rhenium:chlorine ratio of 1:~50 and the γ-ray spectrum of ^{24}Na was observed. A few more milligrams were isolated and the mass spectrum recorded. The spectrum showed peaks at almost every mass number up to 200. Dr. Shaw of the Geology Department of McMaster kindly performed an emission spectrographic analysis of the compound and reported that it contained:

several per cent of Si and Aℓ

about one per cent of Na and Ti, and

traces of Sn, Mg, Pb, Fe, Be, V, Cu, Ni, Co and Cr

Obviously the yellow "compound" was "ceramic chloride", and the oxygen in the major chlorination product was the result of attack on the porous brick.

It seemed possible that a higher chloride was formed, which immediately attacked the porous pot. The experiment was repeated using pyrex wool in place of the porous brick, but this reaction produced rhenium pentachloride in high yield with little rhenium oxytetrachloride. No higher chloride was observed. It was shown that chlorine did not attack the ceramic by sealing these materials in a pyrex glass tube and heating at 500 - 550°C, the temperature of the chlorination, for 24 hours. No reaction was observed. A similar reaction was attempted between rhenium pentachloride and ceramic but no conclusions could be drawn, as the pentachloride decomposed to trichloride and chlorine at temperatures lower than the reaction temperature.

A most reasonable explanation of this attack was offered by Chatt (110). He suggested that rather than a higher chloride being formed which then attacked the ceramic, the rhenium metal was acting as a reducing agent. An analogy can be drawn to the role of carbon in a blast-furnace where the carbon and in this case, rhenium, preferentially absorb the oxygen of the oxides present. A rhenium oxide, which is subsequently chlorinated, must have a very high free energy of formation at 550°C in order to extract oxygen from such stable refractory oxides as silica and alumina.

Despite all the precautions taken to exclude oxygen, a little $ReOC\ell_4$ was produced in all chlorination reactions. It has been noted by others (14)(25) and confirmed by us, that the $ReOC\ell_4$ was produced only at the beginning of the reaction. The presence of a very stable oxide phase offers a possible explanation of this observation, if this oxide is not reduced by hydrogen and reacts with chlorine much more rapidly than does rhenium metal.

An attempt was made to record the infrared spectrum of gaseous rhenium oxytetrachloride in the polyethylene region. However, the compound attacked or dissolved in the polyethylene, causing the windows to turn black after about fifteen minutes, thus preventing the transmission of infrared radiation. By freezing the sample, then heating it and measuring the spectrum rapidly, it was possible to observe a very strong absorption peak at 368 cm^{-1}. A similar strong peak was observed at 372 cm^{-1} for carbon tetrachloride and titanium tetrachloride solutions. This peak is in the region associated with metal-chlorine stretching vibrations and was therefore assigned as such.

The anomalous magnetic moment of "rhenium hexachloride" has been explained but we are left with a larger anomaly. The second row transition metal, technetium, has a higher chloride than the third row metal of the same group. However, technetium hexachloride was prepared by the same workers who claimed rhenium hexachloride and the description of the technetium compound was very similar to the description of "rhenium hexachloride". In the light of the results of this work, a reexamination of the technetium system appears to be needed.

Several methods have been used in unsuccessful attempts to prepare rhenium hexachloride. Rhenium pentachloride, β-tetrachloride and trichloride have been sealed in pyrex glass tubes with chlorine and heated at temperatures from 100°C to 500°C. In all cases the tube filled with red-brown vapours which are typical of pentachloride. When one part of the tube was cooled, large black plate-like crystals formed in the coolest sections. These were shown to be pentachloride and this method was an excellent way to purify the compound. It was considered that possibly, the hexachloride was thermally unstable, so a low temperature preparation was attempted. Powdered rhenium pentachloride was refluxed in liquid chlorine in apparatus described by Fig. 13 (page 49) and under rhenium pentachloride in Section IV (h). Some rhenium pentachloride dissolved in the liquid chlorine but only the original reactants could be isolated. Ultraviolet light was shone on the refluxing mixture in an attempt to induce chlorination by chlorine radicals, but the course of the reaction was unaffected.

It was noted that the melting-point of $ReOC\ell_4$ was lowered slightly unless the first five or ten per cent of the distilled product was discarded. This led us to believe that there must be a volatile impurity. By sublimation from traps at varying temperatures, it was found possible to isolate a trace of this compound. At -40°C (maintained by a chlorobenzene slush) a trace of yellow compound distilled over. This compound turned bright blue when allowed to warm up to above 0°C. The blue compound was non-volatile.

Only trace amounts could be isolated, making identification difficult. However, neutron activation analysis of both the blue and yellow varieties gave a rhenium:chlorine ratio of $\approx$ 1:3 and a ReVII:ReIV ratio of $\approx$ 1:2. Therefore both yellow and blue compounds appear to have the formula $ReOC\ell_3$. Many derivatives of this oxychloride are known (28) but the oxychloride itself has not been isolated previously. However, as mentioned in Section I (d), Glukhor (68) suspected a "volatile blue oxychloride, probably rhenium oxytrichloride". It is possible that the change in colour and volatility is a polymerisation effect.

In general, interpretation of magnetic and electronic spectral data of third row transition metals is complicated, because energy splitting caused by coupling of spin and orbital angular momenta are of the same order as the splittings caused by ligand field effects (111). Strong spin-orbit coupling in a d' system can cause large reductions in the paramagnetism. Somewhat weaker spin-orbit coupling could be treated as a perturbation of the ligand-field effect thereby reducing the paramagnetism (62).

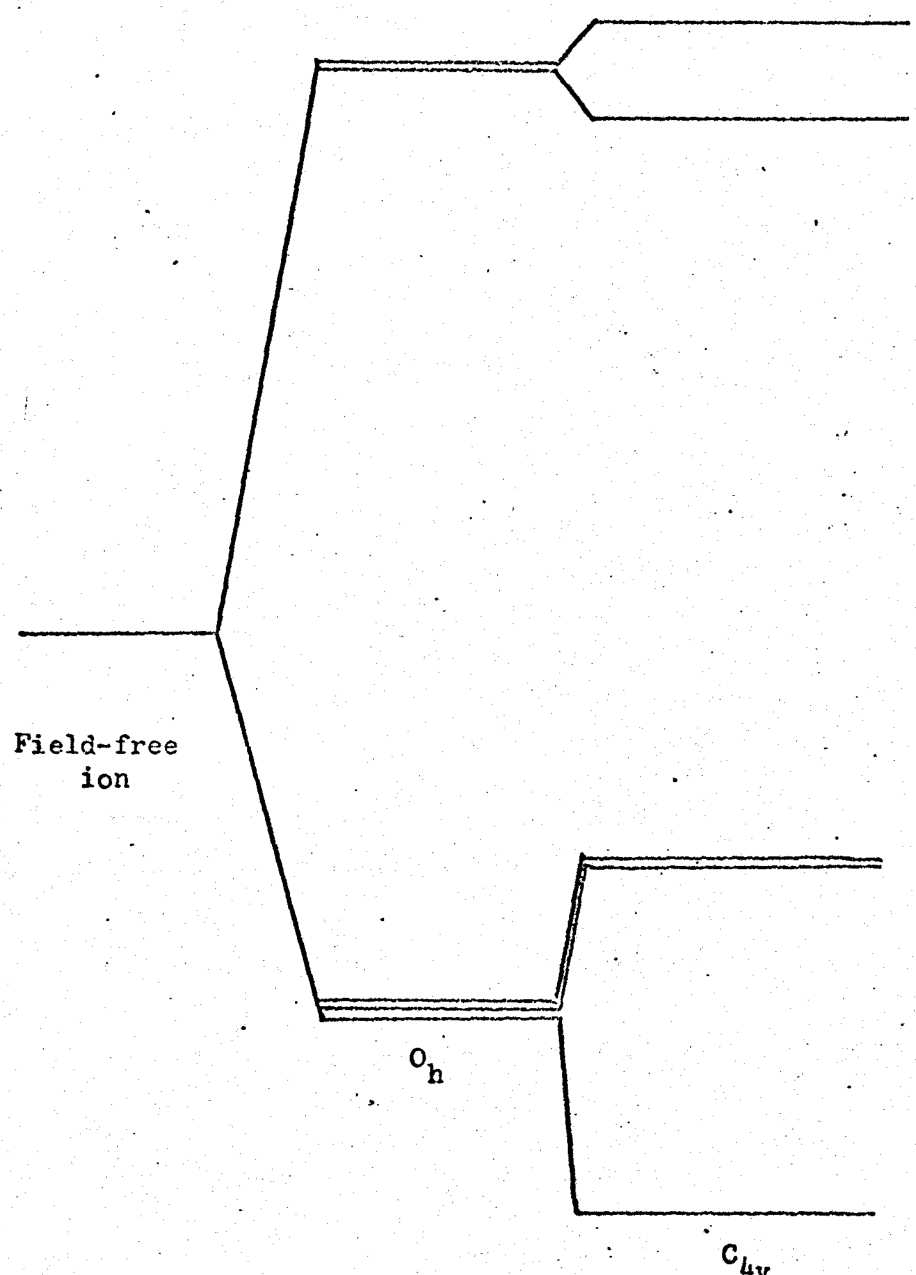
However, the effective magnetic moment found for $ReOC\ell_4$ is very close to the spin-only value of 1.73 B.M. This shows that spin-orbit coupling is negligible in this compound. Multiple bonding between the central metal and oxygen in d^2 complexes of the type L_2ReOX_3 (where L is a neutral ligand and X is a halogen) has been used to explain diamagnetism in these compounds (105). The $d_{\pi}-p_{\pi}$ rhenium to oxygen bonding shortens the Re-O bond length and reduces the symmetry from O_h to C_{4v} to produce "a non-bonding b_2 orbital of low energy to be filled by two electrons" (112). The splitting of energy levels on lowering the symmetry is shown in Fig. 18 (page 74).

The very high energy ν_{Re-O} absorption and the lack of any absorptions at lower energy indicate that polymerisation via oxygen bridges is unlikely (in solution and in the vapour phase). Unless such polymerisation of $ReOCl_4$ is assumed, this compound is five co-ordinate and two structures are possible. It may be a square pyramid (C_{4v}) or a trigonal bipyramid (D_{3h}). If C_{4v} the ligand field splittings will be the same as those discussed above, and shown in Fig. 18. The ground-state of a C_{3v} molecule containing one d electron has been calculated to be $^2E''$. Therefore if C_{3v}, $ReOCl_4$ would have an orbitally degenerate ground-state and would be expected to have some (negative) orbital contribution to magnetic moment, but if C_{4v} would be expected to be very close to the spin-only value.

The theory proposing multiple M = O bonding via $d_{\pi} - p_{\pi}$ interactions (105, 112) states that this bonding weakens the bond to the ligand "trans" to the oxygen. Work in this laboratory has shown that the rhenium-chlorine bond length is increased (76) and the "trans" halide ion may be replaced by alkoxide easily (114). Compounds of the type L_2ReOX_3 which have labile "trans" halide ions have Re = O infrared stretching frequencies between 958 cm^{-1} and 991 cm^{-1} (28). A series of compounds $[Re^{V}OX_4 \ldots L]^-$ (where X = Cl or Br and L is a neutral ligand) in which a short Re = O

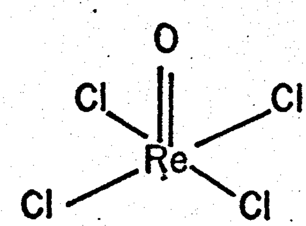
Fig. 18.

The splitting of energy levels on lowering symmetry from O_h to C_{4v}.



bond and a very long Re ... L bond have been proven (115, 116, 117) have Re = 0 infrared absorptions at about 1020 cm^{-1} (11). The gas phase infrared spectrum of $ReOC\ell_4$ has an Re = 0 absorption at 1040 cm^{-1}, although this is somewhat lower in solution.

This very high energy Re = 0 bond indicates that there is no ligand "trans" to the oxygen in the gas phase, although in solution a solvent molecule may be weakly co-ordinated in this position. We consider that this infrared and magnetic data indicate that $ReOC\ell_4$ has the square pyramidal geometry:



(b) Rhenium Pentachloride

As discussed in the introduction to this thesis (Section I (c)), rhenium pentachloride is well-known and has been studied extensively. The solid state structure has been determined by x-ray diffraction of a single crystal. The melting point was quoted as 260°C by Lebedev in 1960 (55). However, the very recent paper (52), in which the crystal structure is presented, quotes a melting point of 220°C. This low value is also quoted in Colton (53). The melting-point observed by us was 261°C which supports the earliervalue. We must conclude that the material prepared by the later authors was very impure.

The authors of the structural paper were supplied with pentachloride which "was prepared by the thermal decomposition of $ReC\ell_6$ in a dry nitrogen atmosphere". The original discoverer of "$ReC\ell_6$" noted that the compound did not decompose on heating but distilled unchanged (61). We have shown (see above) that the compound claimed to be rhenium hexachloride was actually rhenium oxytetrachloride, and can confirm that this compound does not decompose on heating.

The above preparation of pentachloride is therefore confusing, but a simple explanation does offer itself. As mentioned above, it is almost impossible to prepare rhenium pentachloride, free from oxytetrachloride, by direct chlorination of rhenium metal. Other methods of preparation (see experimental Section IV) will also yield a product contaminated with oxytetrachloride unless rigorous efforts are made to exclude oxygen. The oxytetrachloride has an intense dark colour and in a mixture of pentachloride and oxytetrachloride no pentachloride can be observed. When the oxytetrachloride was distilled off "by heating in a dry nitrogen atmosphere" to leave a residue of pentachloride, it would appear that the "hexachloride" had decomposed to pentachloride.

We have reexamined the magnetic properties of rhenium pentachloride which have been studied previously (31, 32, 48). The results, which are listed in Table 6, give a Weiss constant of 265° and an effective magnetic moment of 2.31 B.M. These results are in agreement with the published data.

(c) <u>Rhenium Tetrachloride</u>

This compound was discussed in Section I (c). The preparation

Table 6.

The observed magnetic susceptibility of rhenium pentachloride.

Temp. (°K)	χ_m (x10^6 c.g.s.)
102	1812
128	1689
144	1639
168	1544
192	1473
218	1414
250	1345
264	1309
291	1261

of α-$ReCl_4$ described by Brown and Colton (47) has been repeated, but no compound of this stoichiometry was isolated. The products of several reactions were examined by infrared spectroscopy and neutron activation analysis. The analyses were inconsistent and rhenium to chlorine ratios from 1:2 to almost 1:5 have been recorded. The infrared spectra of nujol mulls of the products showed broad diffuse peaks in the region 800 - 1000 cm^{-1}, which lead us to believe that the compound contains oxygen.

Many properties of β-$ReCl_4$ have been described (50) but no reliable preparative method is known. When rhenium powder was reacted with a large excess of phosphorus pentachloride and chlorine in a sealed glass tube, a compound of $ReCl_5$ and PCl_5 was isolated which existed in the solid state as PCl_4^+ $ReCl_6^-$ (see Section VI (b)). The ion PCl_4^+ is well known and characterised (118). On the other hand $SbCl_4^+$ is not nearly as well known but the anion $SbCl_6^-$ is extremely stable and easily formed (118). It was considered that under the same conditions as the phosphorus pentachloride reaction, antimony pentachloride might attack rhenium powder to form $ReCl_4^+$ $SbCl_6^-$. The latter compound could be a good starting material for the preparation of rhenium tetrachloride.

Rhenium was sealed in a pyrex tube with antimony pentachloride and chlorine gas (mole ratio 1 Re: 5 $SbCl_5$). The tube was slowly heated to 450°C. At about 400°C, red-brown vapours of rhenium pentachloride could be observed, and a thin film of brown solid deposited on the walls in the neck of the tube, which was slightly cooler than the rest of the tube. After several days heating at 450 - 500°C all the metal reacted, and the tube contained an antimony pentachloride wet brown solid, and red vapours of rhenium pentachloride. Preferential cooling of different areas of the tube did not separate the product from excess antimony chlorides as easily as excess phosphorus chlorides were separated in the corresponding phosphorus pentachloride reaction. The antimony pentachloride wet solid was pumped on a vacuum-line at temperatures up to 170°C. Some product distilled up the tube at this temperature but a little black crystalline involatile residue remained.

Activation analyses showed that the volatile product had a rhenium:chlorine ratio of 1:5.2. This and a few simple chemical tests indicated that this product was probably rhenium pentachloride contaminated with antimony trichloride.

The involatile product was analysed by neutron activation and a rhenium to chlorine ratio of 1:4.01 was found. The infrared spectrum of a nujol mull of this residue showed that no absorption occurred in the range 4,000 - 400 cm^{-1}. Rhenium tetrachloride would not be expected to absorb in this region.

None of the reactions of β-$ReC\ell_4$ which Cotton et al. (50) had reported appeared to be very characteristic. The best "spot-test" for $ReC\ell_4$ seemed to be the reaction with tetra"n"butylammonium bromide to give the blue Re(III) compound $[(but)_4N]_2Re_2C\ell_8$. Following Cotton's method, the reaction was performed with our compound and a blue product obtained. Analysis of the blue product for carbon, hydrogen and chlorine by a commercial analyst and a comparison of the ultra-violet/visible spectrum with that of $[(but)_4N]_2Re_2C\ell_8$ prepared by a standard method (103) confirmed the formulation. The black crystalline product was therefore considered to be β-rhenium tetrachloride and further examination of the product from later reactions provided confirmation. Table 7 compares the properties of rhenium tetrachloride prepared in this manner with the properties of Cotton's "accidental" rhenium tetrachloride.

Subsequent reactions in which the temperature and mole ratio of rhenium to antimony pentachloride were varied showed that only a very small excess of $SbC\ell_5$ (mole ratio $Re:SbC\ell_5 = 1:2.5$), no excess chlorine and temperatures of about 600°C were the optimum conditions for $ReC\ell_4$ formation. Under these conditions, using "vycor" tubing, half a gram of rhenium powder can be chlorinated in 48 hours.

It was considered that the probable mechanism of formation of $ReC\ell_4$ was via:

$$SbC\ell_5 \rightleftarrows SbC\ell_3 + C\ell_2$$

$$Re + 2\frac{1}{2}C\ell_2 \rightarrow ReC\ell_5$$

$$ReC\ell_5 + SbC\ell_5 \rightarrow ReC\ell_4^{+}\ SbC\ell_6^{-}.$$

followed by reduction of $ReC\ell_4^{+}$ (as monomer or polymer) to $(ReC\ell_4)_n$, possibly by $SbC\ell_3$. Rhenium pentachloride was sealed in vycor tubes with $SbC\ell_5$ and $SbC\ell_3$. No reaction occurred between $ReC\ell_5$ and $SbC\ell_5$ even after heating at 600°C for a week. However, reaction occurred between $ReC\ell_5$ and $SbC\ell_3$ to give $ReC\ell_4$ at 300°C. No intermediates have been isolated and therefore the formation of $ReC\ell_4$ appears to be simple reduction of $ReC\ell_5$ by $SbC\ell_3$.

Table 7.

Test.	Cotton et al (50).	Our observation.
1. Moist air.*	Sticky black mess obtained.	Sticky black mess obtained.
2. Acetonitrile.	Insoluble.	insoluble. After a day a little dissolves to give a green solution.
3. T.H.F.	Insoluble.	As for CH_3CN.
4. Benzene.	Insoluble in non-polar solvents.	Insoluble.
5. Carbon tetra -chloride	Insoluble in non-polar solvents.	Insoluble.
6. Methanol.	Soluble with decomposition.	Slowly soluble $\longrightarrow$ purple/red $\longrightarrow$ green solution with black ppt.
7. Absolute ethanol.	Soluble with decomposition.	Slowly soluble $\longrightarrow$ green, $\xrightarrow{\text{12 hrs.}}$ red.
8. Acetone.	Soluble with decomposition.	Slowly soluble $\longrightarrow$ blue $\xrightarrow{\text{12 hrs.}}$ red/purple.
9. D.M.S.O.	Soluble with decomposition.	Slowly soluble $\longrightarrow$ purple $\xrightarrow{\text{12 hrs.}}$ red.
10. Hydrochloric acid.	Soluble with decomposition.	Soluble $\longrightarrow$ blue.
11. Heat to 300° in N_2.	Probably decomposes to $ReCl_3$ & $ReCl_5$.	Decomposes to $ReCl_3$ and $ReCl_5$.

The only reported reaction which we repeated was the reaction to form $[(\text{t-butyl})_4N]_2\ (Re_2Cl_8)$ mentioned in the text.

* In a personal communication Prof. Cotton informed us that this is the most characteristic reaction of β-$ReCl_4$.

This postulate is substantiated by the very low yields of $ReCl_4$ if chlorine is added to the Re + $SbCl_5$ reaction mixture. It has been stated that rhenium is not attacked by chlorine when sealed in a static system (119). This statement is not true as we have chlorinated rhenium in this manner (see rhenium pentachloride in experimental Section IV (h)) and chlorination of the metal in our reactions with PCl_5 and $SbCl_5$ is probably by molecular chlorine produced by the vapour phase equilibria:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

$$SbCl_5 \rightleftarrows SbCl_3 + Cl_2$$

If more chlorine is added to the Re + $SbCl_5$ system than is necessary to chlorinate all the metal, the dissociation of $SbCl_5$ to $SbCl_3$ and Cl_2 will be hindered and $SbCl_3$ reduction of $ReCl_5$ drastically curtailed.

If $ReCl_4$ is produced by reduction of $ReCl_5$ by $SbCl_3$ as postulated above, excess $SbCl_5$ should not affect the yield. However, it was found that a large excess of $SbCl_5$ did cut the yield considerably. If the Re + $SbCl_5$ reaction product was very wet with $SbCl_5$, the distillate on the vacuum line was not colourless $SbCl_5$, but an intense green colour. This colouration must have been caused by a rhenium compound but separation of it from $SbCl_5$ has not been possible.

The published crystal structure (52) (see Fig. 2, page 11) shows that each rhenium atom is situated in a pseudo-octahedral field. Rhenium (IV) is a d^3 system and in this environment should exhibit paramagnetism equivalent to three unpaired electrons, whether the ligand field splitting is large or small.

The magnetic properties of several hexachlororhenate(IV) salts have been examined (120, 121, 122) and all show similar properties. They have an effective magnetic moment of 3.2 B.M. to 3.8 B.M. and a temperature dependence which approximates to the Curie-Weiss law. Some antiferromagnetic interaction has been demonstrated (122). In general, β-$ReC\ell_4$ would be expected to show magnetic behaviour similar to these hexachlororhenate(IV) salts.

The magnetic susceptibility of β-$ReC\ell_4$ was measured over the temperature range 100 - 293°K. Table 8 shows that the susceptibility is independent of temperature. Strong temperature independent paramagnetism is present however, giving a magnetic moment which varies from 0.90 B.M. at 100°K to 1.55 B.M. at room temperature.

Temperature independent paramagnetism arises from the second (high-frequency) term of the Van Vleck equation. This term, also known as the second order Zeeman effect, is the result of mixing-in of paramagnetic higher energy states. Therefore, the magnetic data indicates that β-$ReC\ell_4$ contains no unpaired electrons. Cotton et al. (52) cite a minimum Re-Re interatomic distance of 2.73Å and consider this to be short enough to indicate some metal-metal interaction. This metal-metal interaction is confirmed by our observations. The singly occupied t_{2g} orbitals on a pair of tri-chlorine bridged rhenium atoms must interact to form molecular orbitals in which the electrons are paired, forming metal-metal bonds. The bond-length 2.73Å is longer than other observed Re-Re bonds (see reference (76) for a full discussion), which indicates

Table 8.

The magnetic susceptibility of β–$ReCl_4$

Temp. (°K)	X'_m ($x10^6$)	μ_T (B M)
100	1010	.90
125	1010	1.01
150	1010	1.10
175	1010	1.19
200	1010	1.28
225	1010	1.35
250	1010	1.43
275	1010	1.50
293	1010	1.55

that only relatively weak bonds are formed.

The far infrared spectrum of a nujol mull was recorded between polythene plates. The absorption peaks absorbed were:

369	cm^{-1}	strong
294	"	weak
244	"	weak
158	"	medium
166	"	weak shoulder

However, the polythene plates were attacked. It was not possible in this case (as it was for rhenium oxytetrachloride vapour) to measure the spectrum before attack of the polythene took place. Therefore, it cannot be stated, with certainty, which of the above absorptions can be attributed to β-rhenium tetrachoride, and which are caused by decomposition products. The strong absorption at 369 cm^{-1} is in the range associated with metal-chlorine vibrations but is much higher than the 318 cm^{-1} of ν_{Re}-Cℓ in the hexachlorrhenates (71), and observed for several rhenium complexes in this laboratory (114). However, this absorption occurs at the frequency found for $\nu_{Re-C\ell}$ in rhenium oxytetrachloride. At this stage, it cannot be determined whether this absorption is a rhenium tetrachloride vibration, or a vibration of rhenium oxytetrachloride or some other decomposition product.

The x-ray diffraction pattern of powdered β-$ReC\ell_4$ has been recorded and indexed by Dr. C. J. L. Lock and Mr. P. Frais. The results, which are presented in Table 9 (page 86), are very close to the theoretical

Table 9.

X-ray diffraction data of powdered β-$ReCl_4$

#	d_{hkl} (a)	Int. (b)	Cal d_{hkl} (c)	(hkl) (c)	#	d_{hkl} (a)	Int. (b)	Cal d_{hkl} (c)	(hkl) (c)
1.	6.288	7	6.282	(010)	23.	1.957	11	1.957	(131)
2.	6.012	43	6.073	(002)	24.	1.894	~9	1.892	(215)
3.	5.528	100	5.580	(011)	25.	1.831	6	1.834	$(\bar{2}24)$
4.	4.478	18	4.468	(110)	26.	1.791	20	1.797	$(\bar{1}33)$
5.	4.225	31	4.247	$(\bar{1}11)$	27.	1.768	12	1.767	(224)
6.	3.386	<3	3.403	(013)	28.	1.751	14	1.752	$(\bar{2}06)$
7.	3.151	~10	3.141	(020)	29.	1.719	7	1.717	$(\bar{3}14)$
8.	3.036	~10	3.037	(004)	30.	1.703	10	1.702	(026)
9.	2.939	~10	2.944	(113)	31.	1.671	~5	1.673	(017)
10.	2.774	16	2.800	(022)	32.	1.625	~5	1.625	(126)
11.	2.721	32	2.728	(121)	33.	1.585	~5	1.585	(323)
12.	2.674	~9	2.683	(104)	34.	1.550	~4	1.552	$(\bar{3}24)$
13.	2.606	~11	2.620	$(\bar{2}12)$	35.	1.510	~9	1.510	(141)
14.	2.559	~11	2.558	(114)	36.	1.487	~5	1.489	(330)
15.	2.367	<3	2.379	$(\bar{2}13)$	37.	1.463	~5	1.464	(043)
16.	2.270	~9	2.271	(213)	38.	1.439	~5	1.440	$(\bar{2}35)$
17.	2.227	~7	2.234	(220)	39.	1.414	~5	1.415	(413)
18.	2.161	<3	2.170	$(\bar{1}15)$	40.	1.393	~5	1.393	(325)
19.	2.094	16	2.094	(030)	41.	1.376	~5	1.377	(404)
20.	2.067	17	2.064	(031)	42.	1.365	~11	1.366	(422)
21.	2.034	11	2.036	$(\bar{3}02)$	43.	1.331	<3	1.334	$(\bar{4}15)$
22.	1.991	20	1.989	(223)					

(a) Values calculated from our photographs.

(b) Values estimated from our photographs.

(c) Values calculated from Cotton's (52) unit cell parameters.

values, calculated from the single crystal x-ray data of Cotton et al.(52).

(d) Perrhenyl Chloride - ReO_3Cl

It has been reported that perrhenyl chloride decomposes in sunlight to turn purple (26). Wolf, Clifford and Johnson (69) consider that compound will remain colourless for several weeks if sealed in a greaseless system. They expressed the opinion that the purple colouration was caused by dissolved rhenium trioxide. By our observation, freshly prepared, undistilled perrhenyl chloride slowly discolours to a blue/purple, but a product which has been vacuum-distilled several times has remained colourless for several months.

Distillation of ReO_3Cl, freshly prepared by chlorination of ReO_3, left a white, nonvolatile at room temperature, crystalline residue. Neutron activation analysis of this residue revealed that it contained only a trace of chlorine and 75.6 per cent of rhenium. The infrared spectrum showed only a very broad band at $\sim$ 922 cm^{-1}. The theoretical percentage of rhenium in rhenium heptoxide is 77.5 per cent and the infrared spectrum shows only a broad bond at $\sim$ 922 cm^{-1}, similar to that for the white residue above. This residue dissolved in water to form a colourless perrhenic acid solution. In spite of the white appearance, instead of the normal yellow colour, it was concluded that a little rhenium heptoxide is formed by the action of chlorine on rhenium trioxide.

When an aqueous solution is evaporated to dryness, perrhenic acid cannot be isolated (35) and deep green and purple colours develop. These colours are also observed if Re_2O_7 is exposed to moist air and are probably hydrates of a rhenium oxide. No work on the formulation of these compounds has been published.

The purple colour to which ReO_3Cl "decomposes" is very similar to the above. Exposure to even the faintest trace of moist air by slow leakage on diffusion is sufficient to cause Re_2O_7 to turn blue and we consider that the blue colour to which ReO_3Cl "decomposes" is caused by the contaminant which we have isolated, i.e. rhenium heptoxide.

Since this work has been completed, a paper has appeared in the literature (123) which contains some physical measurements made on rhenium oxytetrachloride. The room temperature magnetic moment and spectra of rhenium oxytetrachloride solutions were measured. Electronic reflectance spectra and the infrared spectrum of a nujol mull were also recorded. In general, the published data is in agreement with that in the text. These authors also consider that the data indicate that rhenium oxytetrachloride has C_{4v} symmetry.

VI PHOSPHORUS HALIDE COMPLEXES

(a) Oxotetrachloro(oxotrichlorophosphorus rhenium(VI) $ReOCl_4$-$OPCl_3$

Whilst still under the impression that the product of direct chlorination of a metallic film was rhenium hexachloride, attempts were made to prepare rhenium oxytetrachloride by other methods. It was found that the reported preparation, by reaction of rhenium heptoxide with thionyl chloride (70), gave an impure product. An examination of the vapour-phase ultra-violet spectrum, invariably showed sulphur dioxide (102) to be present. The original method of preparation; by reacting rhenium trichloride with air or oxygen (24) was reported to give mixed products. These must be separated to prepare pure rhenium oxytetrachloride. It has been stated that if rhenium chloride is sealed with carefully dried oxygen at 180°C (124), rhenium oxytetrachloride is the sole product. Our work confirms this statement. Under these conditions rhenium pentachloride was converted quantitatively to rhenium oxytetrachloride, and this was found to be the best method of preparation.

Preparation of oxytetrachloride was attempted, by chlorination with phosphorus pentachloride.

Rhenium heptoxide was mixed with phosphorus pentachloride in a dry-box. It was unnecessary to seal the two solids in a tube and heat, as they reacted exothermally at room temperature to give a red-brown semi-liquid mass. Rhenium trioxide and PCl_5 reacted in a similar manner to give a similar product. Separation of the mixture of products by vacuum distillation gave phosphoryl chloride, unreacted phosphorus pentachloride and a dark red-black compound, which sublimed slowly at room temperature. After three or four sublimations this compound was pure. It crystallised in fine needles which melted sharply at 90.5°C. Analysis for phosphorus and chlorine by a commercial analyst gave a P:Cℓ ratio of 1:8. However several neutron activation analyses gave a Re:Cℓ ratio of 1:7, and the infrared spectrum of a mull of the compound indicated a formula $ReOC\ell_4$-$OPC\ell_3$. Therefore a sample was sent to another analyst who found a P:Cℓ ratio of 1:7, thus supporting the above formulation. Further confirmation was obtained by synthesising the compound from $ReOC\ell_4$ and $POC\ell_3$.

As discussed in Section IV (a), Cotton et al. (115, 116, 117) have described a series of rhenium (V) compounds $[ReOX_4 \ldots L]^-$, where X = bromide or chloride and L = a neutral ligand such as H_2O or CH_3CN. They postulated that the rhenium-neutral ligand bond was long, and the ligand, which was "trans" to the oxygen atom was very weakly bound. This postulate was proven by a single cystal x-ray structural determination (115). We consider that the infrared data presented in Table 10 (page 92) indicates that $ReOC\ell_4$ - $OPC\ell_3$ has a similar type of structure.

The infrared data shows that the $POC\ell_3$ is bonded in the normal fashion (125) i.e. through the oxygen. The phosphorus oxygen frequency is lowered by ~ 40 cm^{-1}, as the bond is weakened by donation of electron density from the oxygen atom to the rhenium atom. The energy of the phosphorus -chlorine bond is increased slightly, as electron density is shifted from anti-bonding regions into the phosphorus -chlorine bonding

Table 10.

Infra - red spectra of $ReOCl_4.OPCl_3$.

CCl_4 Soln	Nujol Mull	$TiCl_4$ Soln	Vapour	$POCl_3$ [128]	$ReOCl_4$ vapour (This work)	Assignment
1300			1290	1290		
1248	1239	1258				$\nu_{(P-O)}$
1210	1202	1214				
1021	1020	1021	1040		1040	$\nu_{Re=O}$
1028						
612	610	605	584	581		ν_{P-Cl}
584						
484				486		

region, in order to maintain electrostatic neutrality of the ligand.

The infrared data also shows clearly that the compound exists as $ReOCl_4$-$OPCl_3$ in the solid state and in titanium tetrachloride solution. In the gas phase, it exists as discrete $ReOCl_4$ and $POCl_3$ molecules, whereas in carbon tetrachloride an equilibrium is evident between $ReOCl_4$, $POCl_3$ and the complex. This indicates that the $POCl_3$ is loosely bound.

ν_{Re-O} in the compounds $[ReOX_4 \ldots L]^-$, in which strong $p\pi - d\pi$ interactions between rhenium and oxygen are postulated, and a short Re-O bond has been proven, was found to be at $\sim$ 1020 cm^{-1}. ν_{Re-O} in $ReOCl_4$ - $OPCl_3$ is at the same frequency and indicates the similarity in structure between $[ReOX_4 \ldots L]^-$ and $ReOCl_4 \ldots OPCl_3$.

The magnetic suceptibility of $ReOCl_4 \ldots OPCl_3$ has been studied over a wide temperature range, and show that the compound obeys the Curie-Weiss law with $\Theta = 23°$ and $\mu_{eff} = 1.71$ B.M. The results are presented in Table 11 (page 94) and plotted as a function of temperature in Fig. 19 (page 95). For purposes of comparison, the variation of susceptibility of $ReOCl_4$ is also plotted. The close similarity in magnetic behaviour can be seen. Thus the addition of $POCl_3$ to $ReOCl_4$ in the sixth co-ordination position has not affected the magnetic properties. Spin-orbit coupling effects are again absent and no higher symmetry than the C_{4v} postulated for $ReOCl_4$ is apparent.

The infrared and magnetic evidence presented above lead us to believe that $ReOCl_4 \ldots OPCl_3$ is a rhenium(IV) analogue of the rhenium (V) compounds $[ReOX_4 \ldots L]^-$ prepared by Cotton's group. Therefore, it is considered that $ReOCl_4 \ldots OPCl_3$ has a pseudo-C_{4v} molecular symmetry with a trans $O = Re \ldots OPCl_3$ system:

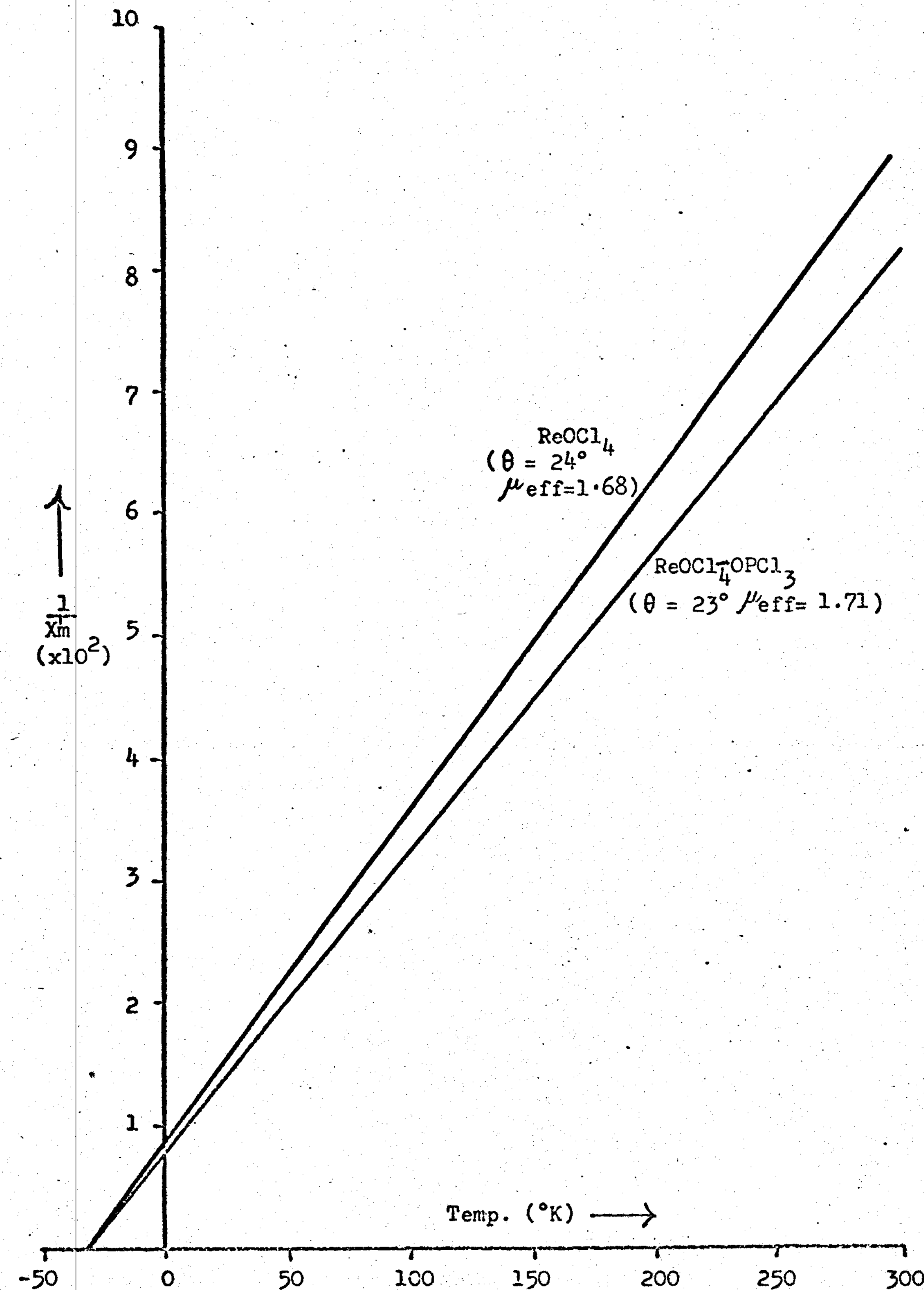
Table 11.

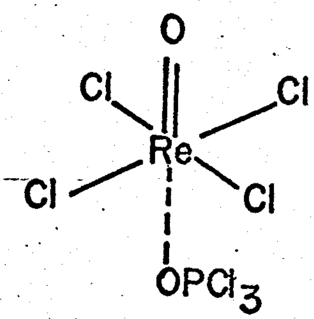
Magnetic susceptibility of $ReOCl_4$-$OPCl_3$.

(Mean of results for two indep. preps.)

Temp.(°K)	χ_m' ($\times 10^6$ c.g.s.)
80	3584
100	3086
120	2689
140	2320
160	2087
180	1880
200	1771
220	1620
240	1516
270	1315
293	1212

Fig. 19. Comparison of magnetic properties of $ReOCl_4$ and $ReOCl_4-OPCl_3$.





(b) Tetrachlorophosphonium(V) Salts of Chloro Anions

A method used in an attempt to prepare rhenium hexachloride was direct chlorination of rhenium metal with chlorine and phosphorus pentachloride under pressure. By heating powdered rhenium with a large excess ($Re:PCl_5=1:5$ of phosphorus pentachloride and chlorine gas in a sealed tube, a brown solid product was isolated. This solid was easily separated from phosphorus chlorides, and could be purified by vacuum sublimation at 165°C. The sublimed product formed a thin red film on the cooler glass walls. Neutron activation analysis showed that this compound was not rhenium hexachloride, as the Re:Cl ratio was 1:10. The infrared spectrum of a nujol mull of the compound showed only one absorption in the range 400-4000 cm^{-1}. This absorption peak was very strong and centred at 649 cm^{-1}.

This peak is at much higher energy than can be expected for a heavy metal-chlorine vibrational mode (108). It is too intense and too low in energy to be the result of a metal oxygen vibration resulting from oxygen contamination of the product. Neither phosphorus pentachloride (118), phosphorus trichloride (127) nor phosphorus oxytrichloride (128) absorb in this region but an absorption at 649 cm^{-1} is characteristic of the $PC\ell_4^+$ ion (118).

As the compound contains $PC\ell_4^+$, it must be $PC\ell_4^+ReC\ell_6^-$. The phosphorous content was confirmed by a commercial analysis (but formulation as $ReC\ell_5.PC\ell_5$ will also fit this analysis). It was not possible to confirm the formal oxidation state of rhenium by examining the hydrolysis products. When water was added a deep red solution formed which rapidly faded through orange and yellow to become colourless in three or four minutes. Any formal oxidation state of less than seven would be expected to precipitate rhenium dioxide (see Section II). The colour of this compound seemed to be rather intense for a rhenium(VII) (d°) compound, and the observed paramagnetism (see later) showed that unpaired electrons were certainly present. Therefore the reaction with water probably involves disproportionation to rhenium(VIII) and rhenium(IV) but the Re(IV) is oxidised to rhenium(VII) (as soluble, colourless perrhenate ion) by the phosphorus compounds present.

The compound was readily oxidized by air to perrhenate ion. This was shown by infrared spectroscopy. After recording the infrared spectrum, the cell was opened and the mull exposed to air. The odour of phosphoryl chloride was noticed and after ten minutes, the mull had changed from a very dark brown colour to white. The infrared spectrum was recorded again, and the only absorption peak was a broad band centred at 918 cm^{-1}. This peak is typical of perrhenates. The expected absorption peaks of phosphoryl chloride were not observed, presumably because all the phosphoryl chloride had volatilised.

The magnetic susceptibility of $RePC\ell_{10}$ was recorded over a wide temperature range and found to obey the Curie-Weiss law with $\Theta = 56$ and $\mu_{eff} = 2.67$ B.M. The data is presented in Table 12 and as a function of temperature in Fig. 20. For purposes of comparison, the magnetic properties of rhenium pentachloride, and a mean of four hexafluororhenate(V) salts (129) are also plotted. The available magnetic data of the hexafluororhenate ion shows that the Weiss constants were in the range 35° - 100°. and the effective magnetic moments between 1.62 and 2.24 .* Some antiferromagnetic interaction was suspected but no Néel points were reported.

The hexachlorotungstate(IV) ion is isolectronic with the hexachlororhenate ion. Kennedy and Peacock (130) have studied the magnetic properties of several salts of this ion. In this case more marked antiferromagnetic interactions are present. Weiss constants of 122° to 400°, and magnetic moments of 0.89 to 1.76,** have been observed. Although the magnetic properties of $RePCl_{10}$ resemble the properties of $(ReF_6)^-$, more than those of $ReCl_5$, a comparison of the magnetic properties of $RePCl_{10}$ with those of hexafluororhenate(V) or hexachlorotungstate(IV) does not offer strong support for the $(PCl_4)^+$ $(ReCl_6)^-$ formulation. However, the PCl_4^+

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* Because of the antiferromagnetic interactions, Peacock and Hargreaves (129) calculate their effective magnetic moments of 1.53-2.05 B.M. at 300°K from the relation $\mu_T = 2.84\sqrt{\chi'_m T}$. As the Curie-Weiss law was obeyed at higher temperatures, the values in this text were recalculated for purposes of comparison, from the more common relationship used in this work $\mu_{eff} = 2.84\sqrt{\chi'_m (T + \Theta)}$

** In this case the antiferromagnetic interactions appear to be too strong to justify recalculation of the effective magnetic moment from $\mu_{eff} = 2.84\sqrt{\chi'_m (T + \Theta)}$.

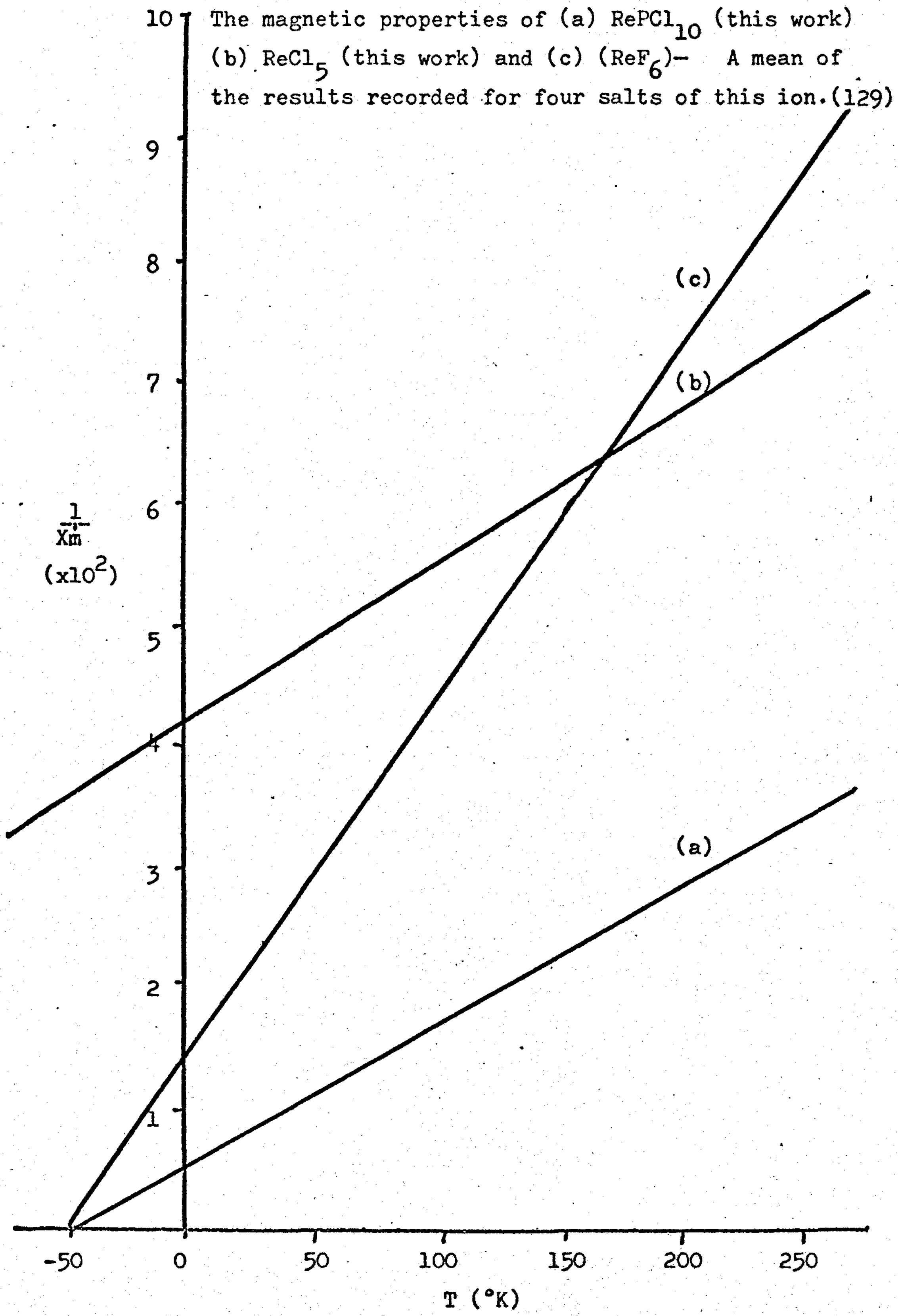
Table 12.

The magnetic susceptibility of $RePCl_{10}$.

Temp (°K)	χ_m' ($\times 10^6$ c.g.s.)
92	5972
103	5591
124	4904
136	4590
152	4276
166	4005
183	3706
197	3501
211	3324
226	3143
242	2982
258	2829
274	2729
290	2601

Fig. 20.

The magnetic properties of (a) $RePCl_{10}$ (this work) (b) $ReCl_5$ (this work) and (c) $(ReF_6)^-$ A mean of the results recorded for four salts of this ion.(129)



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ion is much larger than the metal cations of the $(ReF_6)^-$ and $(WCl_6)^{2-}$ compounds studied. It is possible that magnetic dilution by this large anion removes the antiferromagnetism present in the latter compounds. Magnetic studies of an alkali metal salt of $(ReCl_6)^-$ or of $(ReF_6)^-$ and $(WCl_6)^{2-}$ associated with a large cation must be made before this point can be verified.

It is well known that phosphorus pentachloride exists in the solid state as an ion pair PCl_4^+, PCl_6^- (131). Beattie and Webster (118) have shown, by conductivity and infrared spectroscopy, that this same ion pair occurs in acetonitrile solution. Conductance measurements of $RePCl_{10}$ in acetonitrile solution were attempted. The compound dissolves in acetonitrile to give a blood-red solution, which quickly fades to a pale yellow. Rapid transfer was made to a conductivity cell and an attempt made to make a measurement before the colour faded. A molar conductance of only 0.14 ohm^{-1} cm^{-1} was recorded. This value was the same for the faded yellow solution. Therefore it was not possible to dissolve a sample and measure the conductance rapidly enough, for this technique to give any indication of the molecular structure.

It was hoped that far infrared and possibly Raman spectroscopy would provide some confirmation of the hexachlororhenate(V) ion in $RePCl_{10}$, by comparison with the spectra of the hexachlororhenate(IV) ion. Woodward and Ware (71) studied the infrared and Raman spectra of the latter ion and the hexachlorosmate(IV) ion, and compared them with rhenium and osmium hexafluoride spectra. In the latter two compounds, which contain one and two d electrons respectively, anomalies in the ν_2

vibration have been attributed to a dynamic Jahn-Teller effect*.

These anomalies in the ν_2 vibration were a very weak Raman line, and a broadened and weakened $(\nu_2 + \nu_3)$ combination band in the infrared.

Hexachlororhenate(IV) hexachlorosmate(IV) ions contain t_{2g}^{3} and t_{2g}^{4} electrons. The t_{2g}^{3} system possesses only spin degeneracy and Woodward and Ware say that very little Jahn-Teller effect is expected. Hexachlorosmate(IV) with a t_{2g}^{4} system should show no Jahn-Teller effect. However, in both of these compounds the ν_2 vibration was so weak that it could not be observed in the Raman spectrum, and the $(\nu_2 + \nu_3)$ combination bond was broadened and weakened to the same extent as rhenium hexafluoride (t_{2g}^{1}) and osmium hexafluoride (t_{2g}^{2}). No reason for this departure from theory was forwarded.

It was anticipated that the hexachlororhenate(V) would have far infrared and Raman spectra similar to hexachlororhenate(IV) but the Jahn-Teller effects would be more marked. However, it has not been possible to observe a Raman spectrum. $RePC\ell_{10}$ is a very dark brown solid and decomposes at the point of impact of the laser beam. This is presumably because the compound is highly absorbing at 6328Å, the wavelength of the He/Ne laser exciting line. The compound was ground into phosphorous pentachloride in an effort to lower the absorption. It was hoped that the Raman spectra of $PC\ell_4^{+}$, $PC\ell_6^{-}$ and $ReC\ell_6^{-}$ would be observed, but decomposition in the laser beam still occurred, even when the $RePC\ell_{10}$ concentration was only one per cent.

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* Theoretically, for O_h molecules, the Jahn-Teller effect can affect the $\nu_2(eg)$ and $\nu_5(t_{2g})$ vibrations and electronic degeneracy permits Jahn-Teller distortions for t_{2g}^{1}, t_{2g}^{2}, t_{2g}^{3} but not t_{2g}°, t_{2g}^{4}, t_{2g}^{5} and t_{2g}^{6} (132). No Jahn-Teller effects have been observed for the ν_5 vibration.

The far infrared spectrum was recorded and the absorption peaks observed are listed with those of ceasium hexachlororhenate(IV) in Table 13. As in the case of β-rhenium tetrachloride (see Section V (c)), the observed spectra were poor because of attack on the polyethylene windows and little argument can be presented on the basis of this spectrum. In spite of the attack the $(\nu_2 + \nu_3)$ peak at 582 cm^{-1} was sharper than that which was observed at 584 cm^{-1} for hexachlororhenate(IV) and the $(\nu_2 + \nu_5)$ peak was extremely broad and extremely weak in both cases.

It was desirable that a more stable and lighter coloured hexachlororhenate(V) salt be made in order to study the spectral properties more fully. Rhenium pentachloride was sealed in pyrex glass tubes with chlorides of large cations. Ceasium chloride gave a hexachlororhenate(IV) salt as reported previously (14). Chlorides of the large organic groups tetraethylammonium, tetraphenylarsonium, benzyl—triethyl and tetra-n-butylammonium, all produced charred masses from which no stoichiometric compounds could be isolated. Consequently the only spectrum obtained of the hexachlororhenate(V) ion was the poor far infrared spectrum of $RePC\ell_{10}$, from which it is difficult to draw firm conclusions.

The only strong evidence for the formulation $PC\ell_4^+$ is the strong infrared absorption at 649 cm^{-1}, although a little support is given by the magnetic and far infrared data.

Experiments are in progress to compare the x-ray powder diffraction patterns of $RePC\ell_{10}$ with that of $PC\ell_4^+$ $PC\ell_6^-$. Also a single crystal x-ray structural determination is to be made if suitable crystals can be mounted.

Table 13.

The far infrared spectra of $RePCl_{10}$ and Cs_2ReCl_6.

Assign (71)	Cs_2ReCl_6(71)	Cs_2ReCl_6 (this work)	$RePCl_{10}$
$(\nu_2+\nu_3)$	584 mw	584 w	582 w
$(\nu_3+\nu_5)$	473 w	468 vw	490 vw
ν_3	313 vs	311 vs	318 vs
ν_4	172 s	170 s	161 s

A paper has since appeared in the literature which described a reaction of rhenium metal with phosphorus pentachloride in a sealed tube (107). The product of this reaction analysed as $RePCl_8$, and was claimed to be the first known phosphorus trichloride complex of rhenium, $ReCl_5.PCl_3$. The reaction conditions described for the preparation of this compound were somewhat different to the conditions used in the above preparation of $RePCl_{10}$. In this case, the reaction temperature was 600°C (in a "vycor" tube), whilst the temperature used in our preparation was 500°C. A smaller excess of phosphorus pentachloride ($Re:PCl_5$ = 1:3.5 against 1:5 in our reaction), and no excess chlorine, were sealed in the tube.

The reaction was repeated using these published conditions, and a product which looked very similar to $RePCl_{10}$ was isolated. The product was transferred to a vacuum line and it was found that this product was involatile up to 180°C. This contrasts with the product of our original reaction which sublimed in vacuum at 150°C. Numerous other chemical differences which are listed in Table 14 were found. These show that the reaction of rhenium with phosphorus pentachloride in a sealed tube gives different products when the reaction conditions are changed.

The infrared spectrum of $RePCl_8$ was recorded as a nujol mull in the range 400 - 4000 cm^{-1}. Again a very strong absorption band was observed at 649 cm^{-1}, but this time a small sharp peak at 710 cm^{-1} was also observed. The peak at 649 cm^{-1} again appears to be caused by the PCl_4^+ ion. Therefore the formula of this compound appears to be $PCl_4^+ ReCl_4^-$. Now, as has been discussed earlier, the $ReCl_4^-$ ion is

Table 14.

Comparison of the properties of $RePCl_{10}$ and $RePCl_8$.

	$RePCl_{10}$	$RePCl_8$
Heat in vacuum	Sublimes at 150°c	Involatile at 180°c
Water	Red solution which rapidly fades to yellow, to colourless.	Blue solution. After 2 minutes turns purple then colourless with black precipitate.
Acetonitrile	Red solution which rapidly fades to pale yellow.	Blue solution which turns green after 24 hours.
Preparation	Prepared by reaction of $ReCl_5 + PCl_5$.	Prepared by reaction of $ReCl_5 + PCl_3$
Infrared	One large absorption at 649^{-1} cm.	One large absorption at 649^{-1} cm plus small peak at 710^{-1} cm.

known in trimeric form (see Fig. 1; page 8) and dimeric form (see Fig. 4 page 18). The blue colour of an aqueous solution (before hydrolysis takes place) and in acetonitrile solution is fairly characteristic of the dimeric species (137). Using the method which Cotton et al. (50) used with β-rhenium tetrachloride the $RePCl_8$ was converted to the well-known (to us) tetra-n-butylammonium octachlorodirhenate(III). The composition of the latter compound was confirmed by a commercial analysis for carbon, hydrogen and chlorine and by the ultra-violet and visible spectra which were identical to that of the tetra-n-butylammonium compound prepared by a standard method (103). Therefore the compound was considered to be $(PCl_4)_2^+$ $(Re_2Cl_8)^{2-}$ rather than $ReCl_5.PCl_3$ as postulated by Machmer. The small peak at 710 cm^{-1} cannot be explained by this formulation and it is suspected that this absorption is an overtone or combination band.

However, Machner published magnetic data which showed that the compound was paramagnetic, with an effective magnetic moment of 2.37 B.M. and obeyed the Curie-Weiss law (Weiss constant = 24°). $ReCl_5.PCl_3$ would be expected to show paramagnetism, but $(PCl_4)_2Re_2Cl_8$ should be diamagnetic with the electrons paired in the rhenium-rhenium bonds. Diamagnetism (x_m = -530 x 10^{-6} at room temperature) has been observed for the tetra-n-butylammonium salt of this anion (103). The magnetic susceptibility of this compound and $RePCl_8$ has been measured over a wide temperature range and the results are presented in Table 15. It can be seen that $RePCl_8$, and to a very much smaller extent, $[(nbut)_4N]_2(Re_2Cl_8)$ show paramagnetism which decreases as temperature decreases. This type of magnetic behaviour is caused by a diamagnetic ground-state with another

Table 15.

The variation of the magnetic susceptibilities of $RePCl_8$ and tetra'n'butyl ammonium octachlorodirhenate III.

$RePCl_8$			$(n\ but)_4N\ _2\ (Re_2Cl_8)$		
Temp (°K)	X_m' (x10^6)	μ_T	Temp (°K)	X_m' (x10^6)	X_m' (x10^6)
100	614.2	0.69	93	-1191	-591
114	654.0	0.77			
135	712.7	0.88	134	-811.4	-211.4
157	763.4	0.99			
173	839.7	1.08	172	-719.0	-119.0
206	898.4	1.22	203	-684.8	-84.8
233	953.1	1.34	235	-658.3	-58.3
269	996.1	1.47	269	-568.5	+31.5
293	1024	1.60	290	-555.2	+44.8

energy level lying at slightly higher energy. As the temperature is increased, thermal energy is sufficient to allow some population of the higher level. No detailed description of the energy states involved is possible without more experimental work and much calculation, but the assumption of a diamagnetic ground-state appears to be reasonable.

The magnetic data reported here contradicts the data recorded by Machmer. However, Machmer's results were very similar to the results described above for $PC\ell_4^+ReC\ell_6$ (Table 12, page 99). We have found that for these two reactions, great care must be taken to reproduce experimental conditions exactly, in order to obtain the desired product. Preparation of pure $RePC\ell_{10}$ and $RePC\ell_8$ is easier by direct synthesis from $ReC\ell_5$ + $PC\ell_5$ and $ReC\ell_5$ + $PC\ell_3$, then by the reactions of rhenium metal with phosphorus pentachloride. It is considered that Machmer measured the magnetic susceptibility of $RePC\ell_{10}$, or probably a mixture of $RePC\ell_{10}$ and $RePC\ell_8$, not pure $RePC\ell_8$. As the preparation he employed involves reaction in a sealed tube, only small batches can be prepared at one time. Therefore, it is possible that he did not make his magnetic measurements on the batch which he analysed.

Comment must be made on the magnetic susceptibility of $((n\ \mathrm{but})_4\ N)_2(Re_2C\ell_8)$. The observed room temperature diamagnetism was -555×10^{-6} c.g.s. This is very similar to the value of -530×10^{-6} c.g.s. reported by Cotton et al. (103). As Cotton pointed out, the diamagnetic correction for the ligands is about -600×10^{-6} c.g.s. This leaves a corrected paramagnetic susceptibility of the compound of x'_m 45×10^{-6} c.g.s. This is a very small paramagnetism, but it was hoped that this value would become even smaller on cooling, and thus show a similar behaviour to $RePCl_8$ and support our proposed formulation as $(PCl_4)_2^+$ $(Re_2Cl_8)^{2-}$.

Table 15 shows that the susceptibility of $(nbut_4N)_2Re_2Cl_8$ was reduced on cooling. Diamagnetism is independent of temperature and theoretically the lowest susceptibility which this compound can possess is the diamagnetism of the ligands i.e. $x_m = -600 \times 10^{-6}$ c.g.s. or $x'_m = 0$. It can be seen that at 93°K the compound has $x'_m = -591 \times 10^{-6}$ c.g.s. This value is much lower than can be accounted for by inaccuracies in the diamagnetic corrections applied, and we can offer no explanation of this observation.

The x-ray diffraction pattern of a powdered sample has been recorded. This data, and the x-ray data of $RePCl_{10}$ are presented in Table 16 (page 111). The powder data has not been indexed but clearly shows that the compounds have different structures. X-ray powder photographs also showed that it was possible to prepare mixtures of the two compounds, unless care was taken to reproduce the conditions of the preparations exactly.

Table 16. Comparison of X-ray powder diffraction patterns.

$RePCl_{10}$				$RePCl_8$			
d_{hkl}	Int.	d_{hkl}	Int.	d_{hkl}	Int.	d_{hkl}	Int.
8.035	15	2.261	~20	10.282	vw	2.417	s
7.430	<3	2.224	~15	9.165	m	2.371	vw
6.677	39	2.193	3	8.080	vw	2.309	w
6.298	39	2.160	3	7.284	vw	2.273	vw
5.981	56	2.117	29	6.607	vs	2.238	w
4.980	76	2.082	<3	5.717	w	2.212	vw
4.742	51	2.048	13	5.200	m	2.181	w
4.493	52	2.012	28	5.025	s	2.159	vw
4.121	7	1.954	15	4.552	w	2.132	vw
3.958	7	1.916	29	4.353	w	2.099	m
3.848	<3	1.864	24	2.240	w	2.080	vw
3.661	9	1.827	18	4.143	vw	2.034	vw
3.588	8	1.798	10	4.013	w	2.006	m
3.393	<3	1.766	12	3.858	vw	1.973	vw
3.325	<3	1.760	<3	3.655	w	1.941	m
3.236	<3	1.721	41	3.576	vw	1.905	m
3.180	<3	1.692	10	3.453	vw	1.864	vw
3.042	<3	1.665	3	3.278	w	1.845	w
2.997	<3	1.640	32	3.220	w	1.828	vw
2.875	<3	1.611	5	3.100	vw	1.806	w
2.843	100	1.572	<3	2.993	w	1.779	vw
2.771	<3	1.544	6	2.931	w	1.749	m
2.682	26	1.519	11	2.858	w	1.734	vw
2.643	48	1.495	9	2.784	w	1.714	vw
2.563	30	1.478	9	2.747	w	1.695	vw
2.511	~10	1.460	13	2.679	w	1.667	w
2.458	19	1.439	3	2.611	vw	1.560	w
2.407	23	1.422	29	2.578	vw	1.501	w
2.382	4			2.543	w	1.429	vw
				2.522	2	1.365	vw
				2.475	vw	1.271	m

VII AMINE COMPLEXES PREPARED FROM OXYCHLORIDES

(a) Rhenium(V) Complexes

When oxotetrachloro(phosphoryl chloride)rhenium(VI) $ReOC\ell_4$-$OPC\ell_3$) was isolated, it was considered that a series of compounds $ReOC\ell_4$-L might be prepared by exchanging phosphoryl chloride with some other neutral ligand L. Ligands such as triphenylphosphine and alky or aryl phosphites reacted to give a black tar, from which it has been impossible to isolate pure products. It seemed that the rhenium compound oxidized and/or chlorinated the ligands. It is possible that if further experiments are carried out to determine the correct solvents and conditions, reasonable products may be isolated.

Two ligands, pyridine and 2,2' - dipyridyl, which are more resistant to oxidation than the ligands mentioned above, did give clean reactions to form easily isolated, stoichiometric compounds.

Dissolution of $ReOC\ell_4$-$OPC\ell_3$ in dry pyridine gave a red solution from which a green compound precipitated after standing for half an hour. As the green precipitate formed, the colour of the solution faded to a pale yellow. Later work showed that the reaction proceeded in exactly the same manner if $ReOC\ell_4$, instead of $ReOC\ell_4$-$OPC\ell_3$ was used as a starting material. After purification, the green compound was analysed by neutron activation and found to have a rhenium: chlorine ratio of 1:3. Carbon, hydrogen, nitrogen and chlorine determinations agreed with the formulation of the green compound as oxotrichlorobis(pyridine)rhenium(V).

($ReOC\ell_3\ py_2$), rather than the expected oxotetrachloropyridinerhenium(VI).

The infrared spectrum of a nujol mull showed absorptions normally found for pyridine complexes (134), and a strong sharp absorption peak at 966 cm^{-1}. This peak was assigned to a rhenium-oxygen stretching mode by comparison with the reported spectra (28) of the well-known series of compounds $ReOX_3L_2$ and $ReOX_3M$*, which have rhenium-oxygen stretching frequencies in the range 946 cm^{-1} to 991 cm^{-1}. The compound was found to be diamagnetic as is the case for the other compounds in this series (28). $ReOC\ell_3\ py_2$ has been prepared before by another method, but no magnetic or infrared data were reported for the compound. Chakravorti's (104) preparation was repeated and the product was found to have the same properties, melting point and infrared spectrum as the product of our reaction.

The yellow solution, left after filtration of the $ReOC\ell_4$-$OPC\ell_3$ plus pyridine reaction mixture, was evaporated to low bulk, and large red crystals deposited. An infrared spectrum of a nujol mull of these crystals was identical with that of the well-known (105) dioxotetrapyridinerhenium(V) chloride, $[ReO_2py_4]C\ell$. It was found that $ReOC\ell_3py_2$ reacted with excess pyridine to form $[ReO_2py_4]C\ell$ quantitatively. At room temperature, the time for complete reaction was several days, but the reaction was more rapid if the mixture was boiled in air. Thus the interconversion of these two compounds is extremely easy:

$$ReOC\ell_3py_2 \underset{\text{boil with conc. HC}\ell\ (104)}{\overset{\text{boil with pyridine}}{\rightleftarrows}} [ReO_2py_4]C\ell$$

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* Where x = halogen, L = a neutral ligand and M = bidentate neutral ligand.

When solutions of $ReOC\ell_4$-$CPC\ell_3$ (or $ReOC\ell_4$) and 2,2'dipyridyl in dry carbon tetrachloride were mixed, a yellowy green solid precipitated. Neutron activation analysis of the dried product gave a rhenium to chlorine ration of 1:3. Carbon, hydrogen, nitrogen and chlorine were determined by a commercial analyst and these results corresponded to a formula $ReOC\ell_3$ dipy. The infrared spectrum of this diamagnetic compound was similar to the spectrum of co-ordinated 2,2'-dipyridyl observed in other compounds (135), and also showed a strong sharp absorption at 975 cm^{-1}. $ReOC\ell_3\cdot$dipy has been prepared by two other methods (50,106). Chakravorti (106) did not report any infrared data for the compound which he prepared. This preparation was repeated. The product had an infrared spectrum identical to that of the compound prepared by our method and to that reported by Cotton et al. (50).

Both $ReOC\ell_3py_2$ and $ReOC\ell_3\cdot$dipy were refluxed with absolute alcohol. The pyridine compound reacted rapidly to give a blue solution. Gradual evaporation of the solution caused large blue crystals to deposit. The 2,2'-dipyridyl compound reacted much more slowly, but after three or four days, the solution turned pale orange in colour and a dark green crystalline material was precipitated. The solid products of both reactions were analysed for carbon, hydrogen, nitrogen and chlorine by a commercial analyst.

The analyses showed that both products were compounds which had been prepared previously by other methods (57). The blue pyridine compound was oxoethoxodichlorobis(pyridine)rhenium(V). ($ReO(OEt)$, $C\ell_2py_2$), and the green 2,2'-dipyridyl compound was μ-oxo-bis(oxodichloro-

2,2'-dipyridylrhenium(V). ($ReOCl_2dipy - O - ReOCl_2dipy$). The solubilities, melting points and infrared spectra of the compounds prepared by this method were identical with those of the compounds prepared by the original methods.

Johnson et al. (57) prepared the oxygen-bridged 2,2'-dipyridyl compound by reaction of 2,2'-dipyridyl with an acetone solution of rhenium pentachloride. These workers prepared μ-oxo-bis(oxodichlorobispyridinerhenium(V) by an analagous method. They noted that the oxygen bridge of the pyridine compound was cleaved by ethanol. The reactions observed by Johnson et al. and by us are combined in Fig. 21 (page 116). The reaction scheme in Fig. 21 shows that the oxygen bridged dimer of the 2,2'-dipyridyl series was formed in boiling ethanol. In contrast, the oxygen bridge of the pyridine series is easily broken by boiling ethanol.

Johnson et al. found that $ReOCl_2py_2 - O - ReOCl_2py_2$ could be prepared from phosphine complexes, in which it had been shown that the attack site, a chlorine atom, was "trans" to an oxygen atom. On this basis, they assumed a "trans" configuration for the oxygen atoms in the pyridine compounds, and proposed the reaction scheme reproduced in Fig. 22 (page 117).

We prepared the blue ethoxo-compound $ReO(OEt)Cl_2py_2$ from $ReOCl_4$-$OPCl_3$ via $ReOCl_3py_2$. The structure of the starting material (see Section VI(a)) has been shown to be A of Fig. 23 (page 118). The phosphoryl chloride and one chlorine atom are replaced by

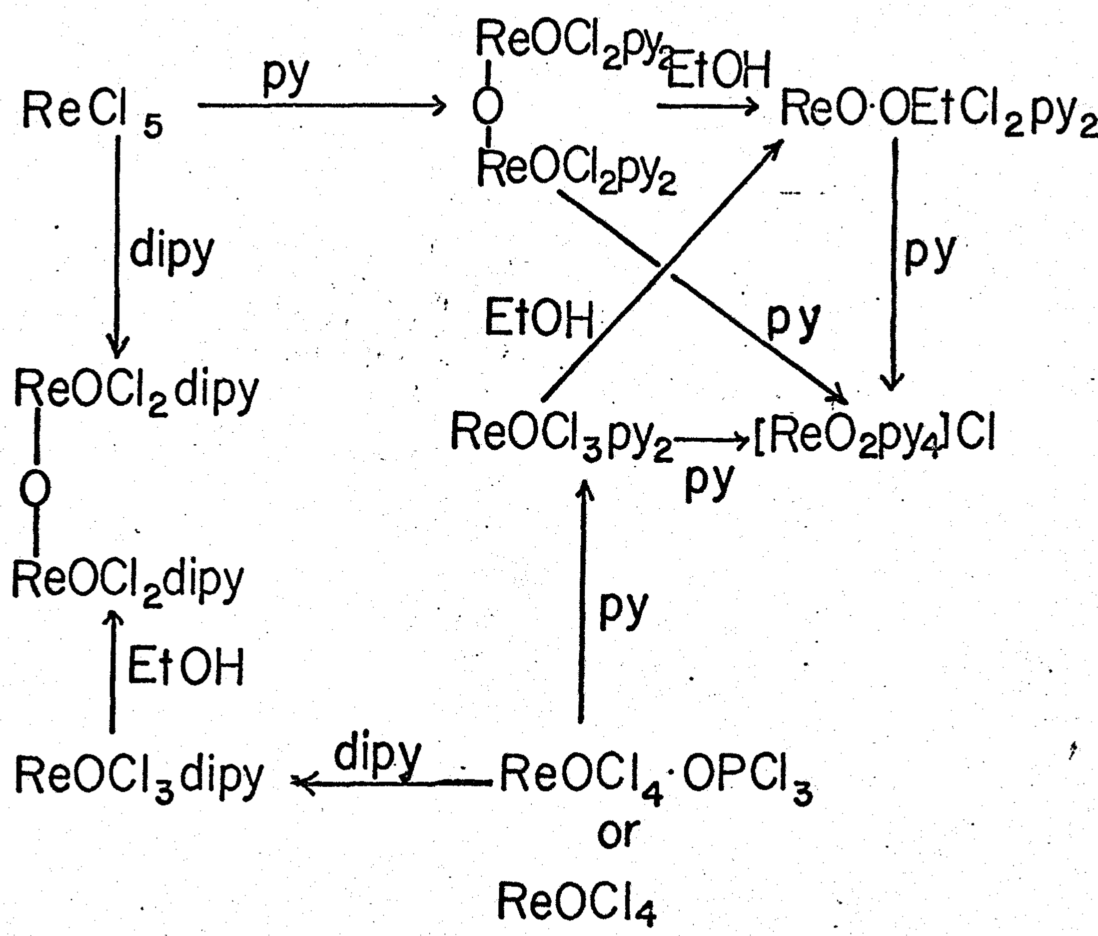


FIGURE 21. Reactions of Rhenium Penta-Chloride and Oxotetrachloro(phosphoryl-chloride)rhenium(VI) with Aromatic Amines.

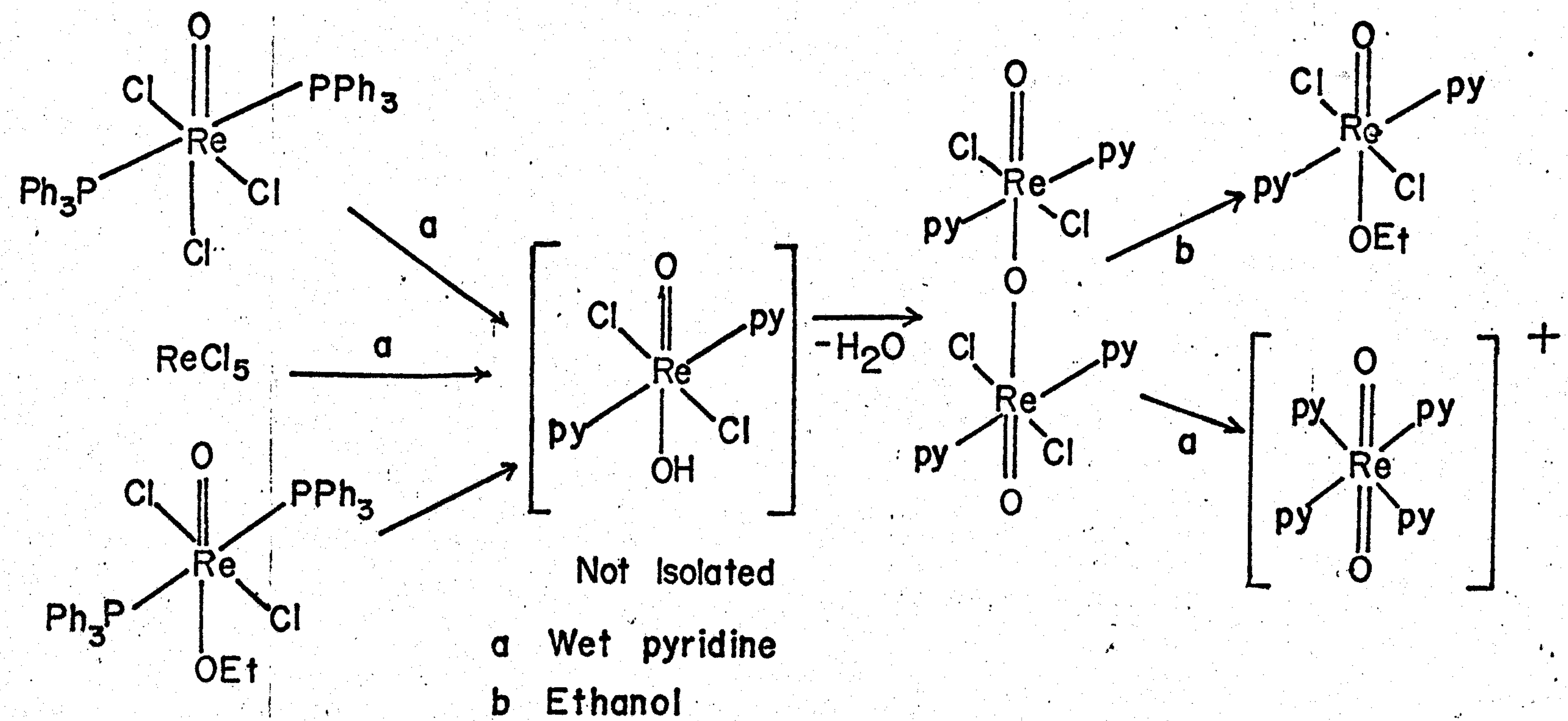


FIGURE 22· Reactions of phosphine and pyridine complexes of rhenium; scheme proposed by Johnson, Taha & Wilkinson (57)

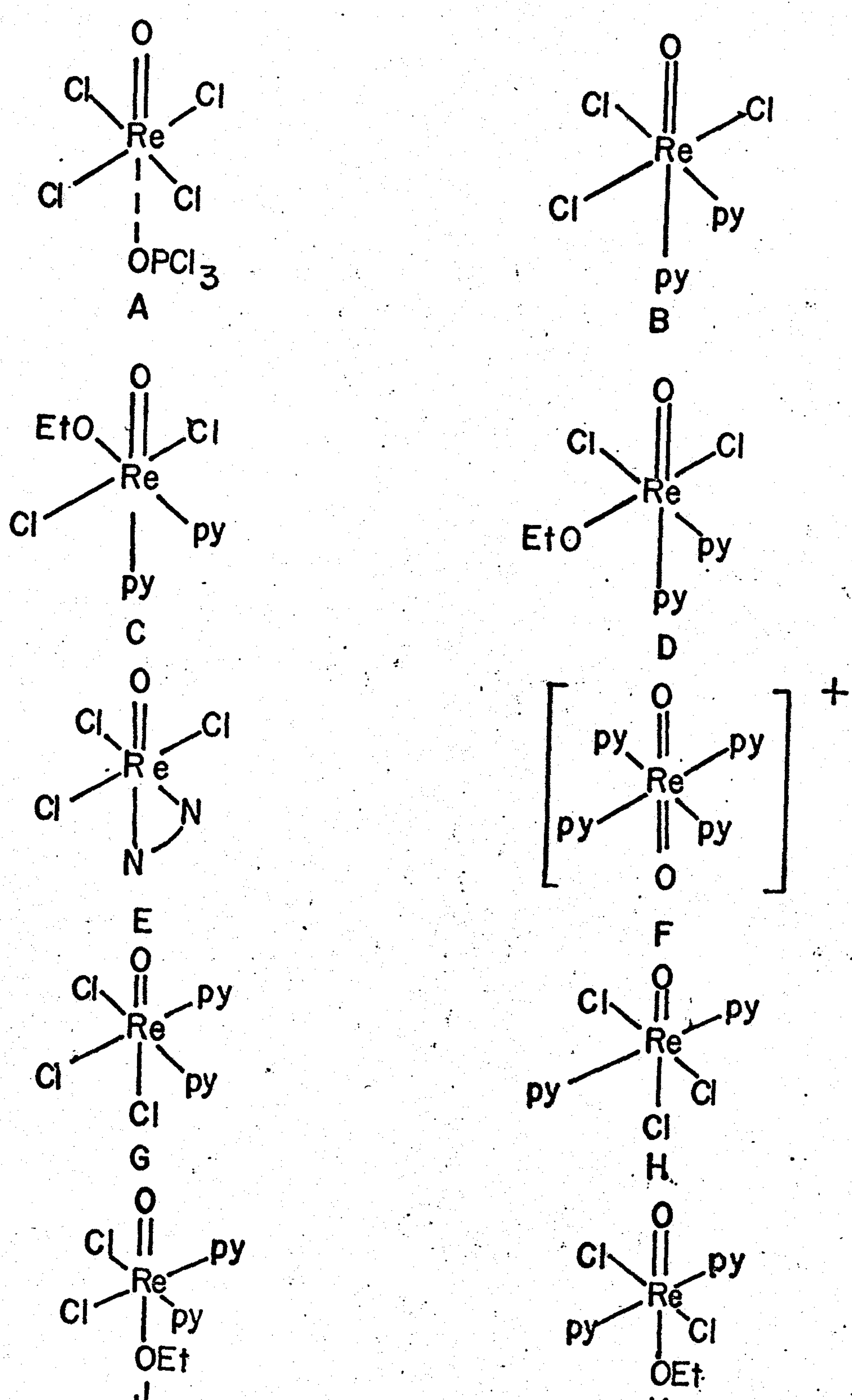


FIGURE 23. Possible Geometries of Some Pyridine Complexes of Rhenium.

pyridine. Unless rearrangement takes place during the reaction $ReOCl_3py_2$ must have the cis configuration B (Fig. 23 - page 118).

When one chlorine atom of this compound is replaced by ethoxide (again, unless rearrangement takes place) there are two possible geometrical arrangements of the product. These are shown as C and D (Fig. 23, page 118).

Neither of these structures are the same as the one proposed by Johnson, Taha and Wilkinson. If either C or D is the correct structure, the assumption of a trans configuration for the reaction scheme proposed by these workers must be questioned.

As Johnson et al. pointed out, in the 2,2' dipyridyl compound, "the ligand nitrogen atoms must necessarily be cis rather than trans." They did not however propose any cis configuration. If the same arguments are applied to the 2,2' dipyridyl reactions as were applied to the pyridine case, the geometrical arrangement of $ReOCl_3$dipy is E (Fig. 23, page 118).

If the structures B and E are correct, little difference would be expected in their reactivity with alcohol. We have shown, however, that one chlorine of the pyridine compound is replaced very easily to give an ethoxy species, but several days of refluxing are necessary to replace one chlorine of the 2,2'-dipyridyl compound by an oxygen bridge.

The reaction of $ReOCl_3py_2$ with excess pyridine to give $[ReO_2py_4]Cl$ does not support structure B as the trans structure of $[ReO_2py_4]Cl$ has proven by single crystal x-ray diffraction (136). Rearrangement would be necessary during the formation of this compound in order to remove the py = Re - O trans system if $ReOCl_3py_2$ had the cis structure B.

The multiple bonding between transition metals and oxygen, and the labile nature of halide ions "trans" to the multiply bonded oxygen was discussed in Section V (a). The ease of replacement of one chlorine ligand of $ReOCl_3py_2$ by ethoxide ion, lead us to believe that this chlorine ion is "trans" to the oxygen atom. In this case rearrangement must take place during the reaction of $ReOCl_4$-$OPCl_3$ with pyridine. There are then two arrangements, G and H (Fig. 23, page 118), possible for $ReOCl_3py_2$, which are reconcilable with the ease of replacement of chloride ion by ethoxide ion, and the formation of "trans" $[ReO_2py_4]Cl$.

We have no evidence which suggests that H and K are the correct structures, rather than G and J, but Johnson et al. suggest that H and K are the correct geometries.

No rearrangement to a "trans" form analogous to H is possible for $ReOCl_3$dipy but rearrangement to a cis form analogous to G is. This compound, however, does not possess a chloride ligand which is easily replaced by ethoxide and no compound analogous to $[ReO_2py_4]Cl$ has been observed when the compound was reacted with excess 2,2'=dipyridyl. These observations support the retention of configuration E. The structures which we consider to be correct are summarised in Figs. 24a and 24b (pages 121 and 122).

All three structures for $ReOCl_2$dipy - O - $ReOCl_2$dipy are possible and we have no evidence to indicate which one is correct.

The structure proposed for the dimeric compounds by Johnson et al. and above show that the pyridine compound has two oxygen atoms trans to the bridging oxygen. On the other hand the 2,2'-dipyridyl compound

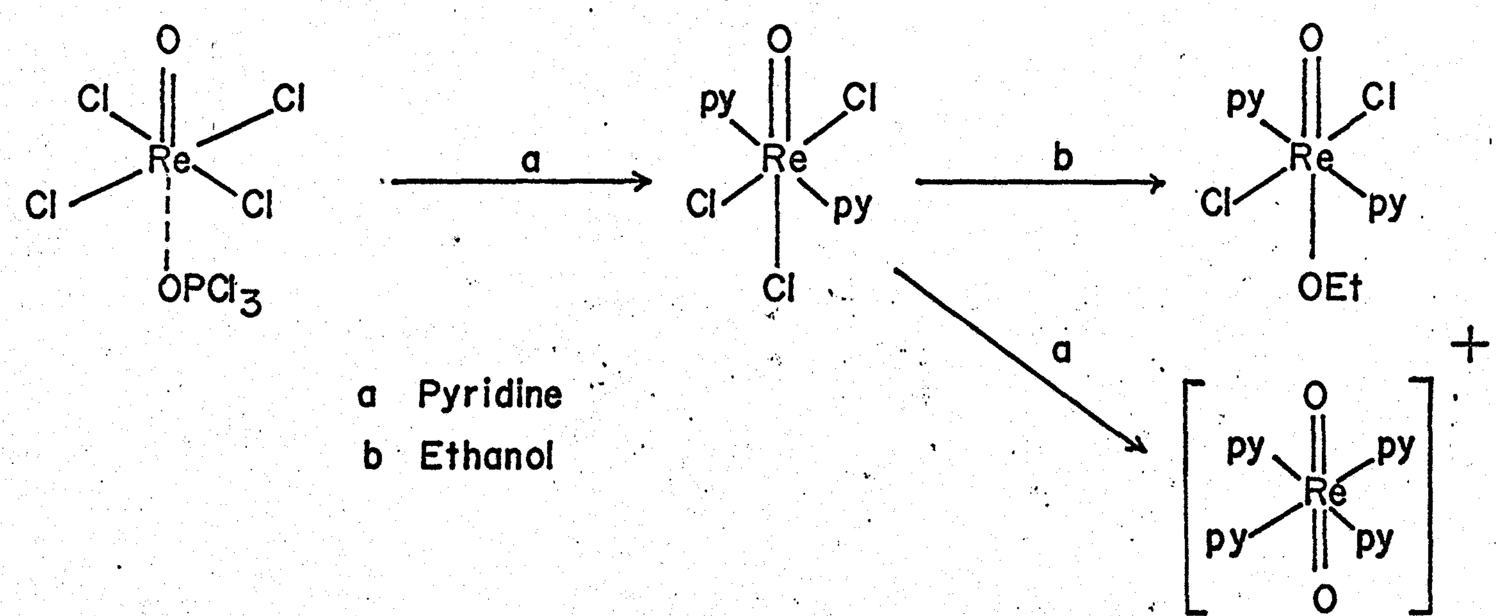


FIGURE 24a· Proposed reaction scheme of the pyridine complexes investigated.

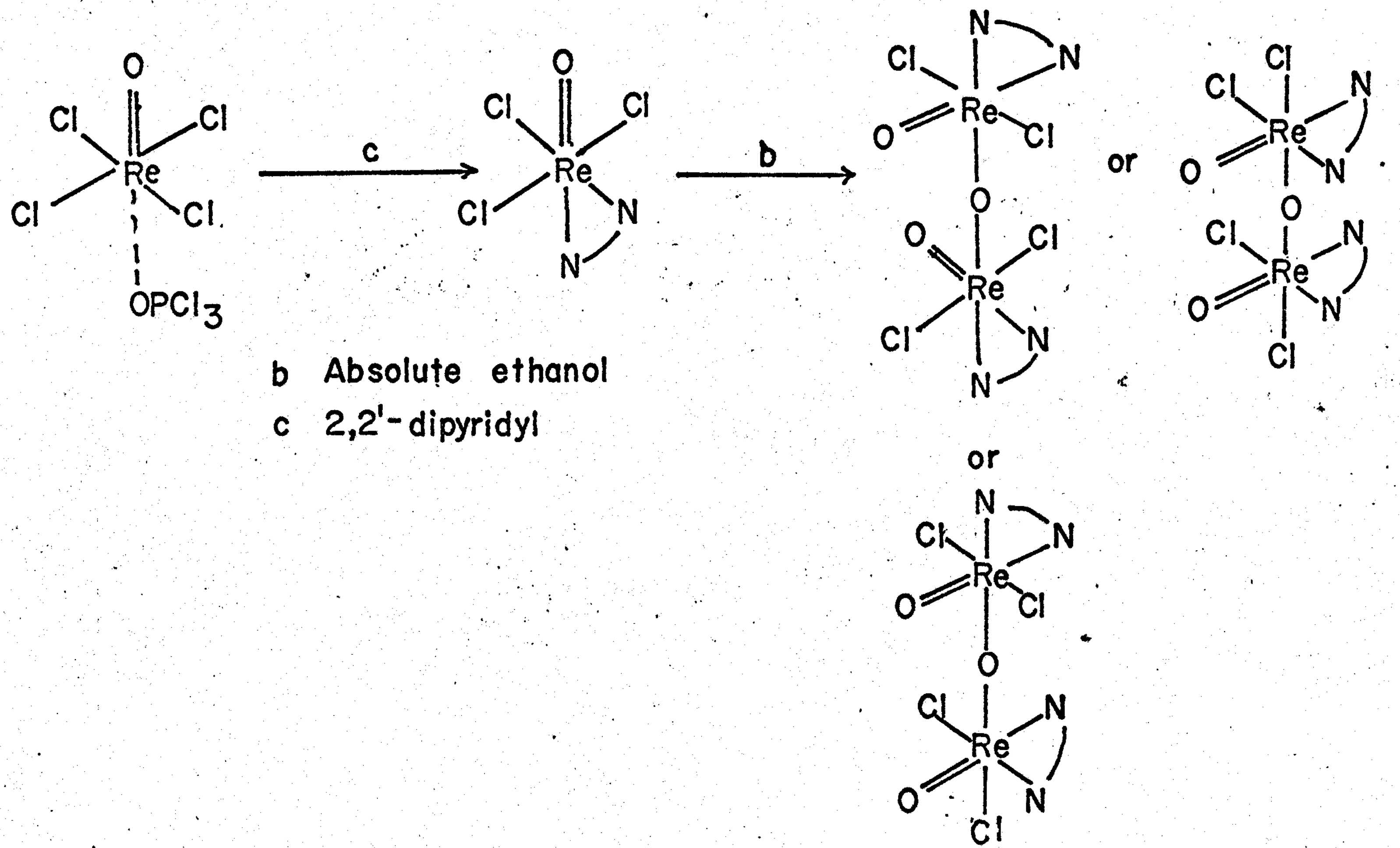
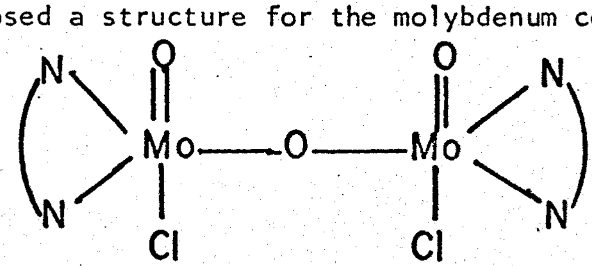


FIGURE 24b. Proposed reaction scheme of the 2,2'-dipyridyl complexes investigated.

has either chloride, or one of the nitrogen atoms of the organic group, trans to the oxygen bridge. The difference in the stabilities of the oxygen bridges towards ethanol may be used as an argument in favour of the proposed structures. The oxygen bridge of the pyridine compound was broken by refluxing in ethanol for three days (57). The oxygen bridge of the 2,2'-dipyridyl compound was formed in this medium under these conditions and no evidence for any cleavage has been observed. Multiply bonded oxygen atoms trans to the μ-oxo-linkage should weaken the oxygen bridge in the same way that a trans halide ion is made more labile.

Cotton et al. (50) have pointed out this "relative weakening of the bridging Re-O bonds" and presented infrared data to support it. They observed a "very strong broad band" at 710 - 675 cm^{-1} in the infrared spectrum of the oxygen-bridged pyridine compound. They compared the frequency of this absorption peak to that assigned to the assymmetric stretching mode in halo complexes, such as $(Ru_2OC\ell_{10})^{4-}$, which occur between 900 and 800 cm^{-1}. We were unable to pick out an absorption peak in the infrared spectrum of $ReOC\ell_2$dipy-O-$ReOC\ell_2$dipy which could be assigned to the bridging Re-O-Re bonds. Mitchell (137) has prepared the molybdenum analogue of this compound $MoOC\ell_2$dipy-O-$MoOC\ell_2$dipy, but he also was unable to assign an infrared absorption to the bridging Mo-O-Mo group. He proposed a structure for the molybdenum compound:



which suggests that he considers the oxygen bridge to be trans to a nitrogen atom of the 2,2-dipyridyl. However, although this supports our postulate, Mitchell offers no evidence for this structure.

It is realized that although the structures proposed above for the rhenium compounds fit the experimental observations, more work, preferably by single crystal x-ray diffraction, is required in proof.

(b) Rhenium(VII) Compounds

Re(VII) is a common, stable, formal oxidation state of rhenium, shown in the perrhenate ion (ReO_4^-) and perrhenyl chloride ($ReO_3C\ell$). However, only one co-ordination compound, μ-sulphuryl chloride bis(trioxochlororhenium(VII)) [$(ReO_3C\ell)_2SO_2C\ell_2$], containing Re(VII) has been claimed (70). As pyridine and 2,2'-dipyridyl gave clean reactions with rhenium oxytetrachloride, it was considered possible that these ligands might react with perrhenyl chloride to give Re(VII) containing complexes.

Trioxochlorobispyridinerhenium(VII) ($ReO_3C\ell py_2$) and trioxochloro 2,2'-dipyridylrhenium(VII) were obtained from the direct reaction of perrhenyl chloride and the corresponding ligand in carbon tetrachloride solution. The compounds were almost white and decomposed slowly in air. The compounds are interesting in that the central rhenium atom must have a co-ordiantion number of six. Rhenium(VII) normally has a co-ordination number of four, but it has been shown that in solid Re_2O_7 mixed six and four co-ordination is observed (138).

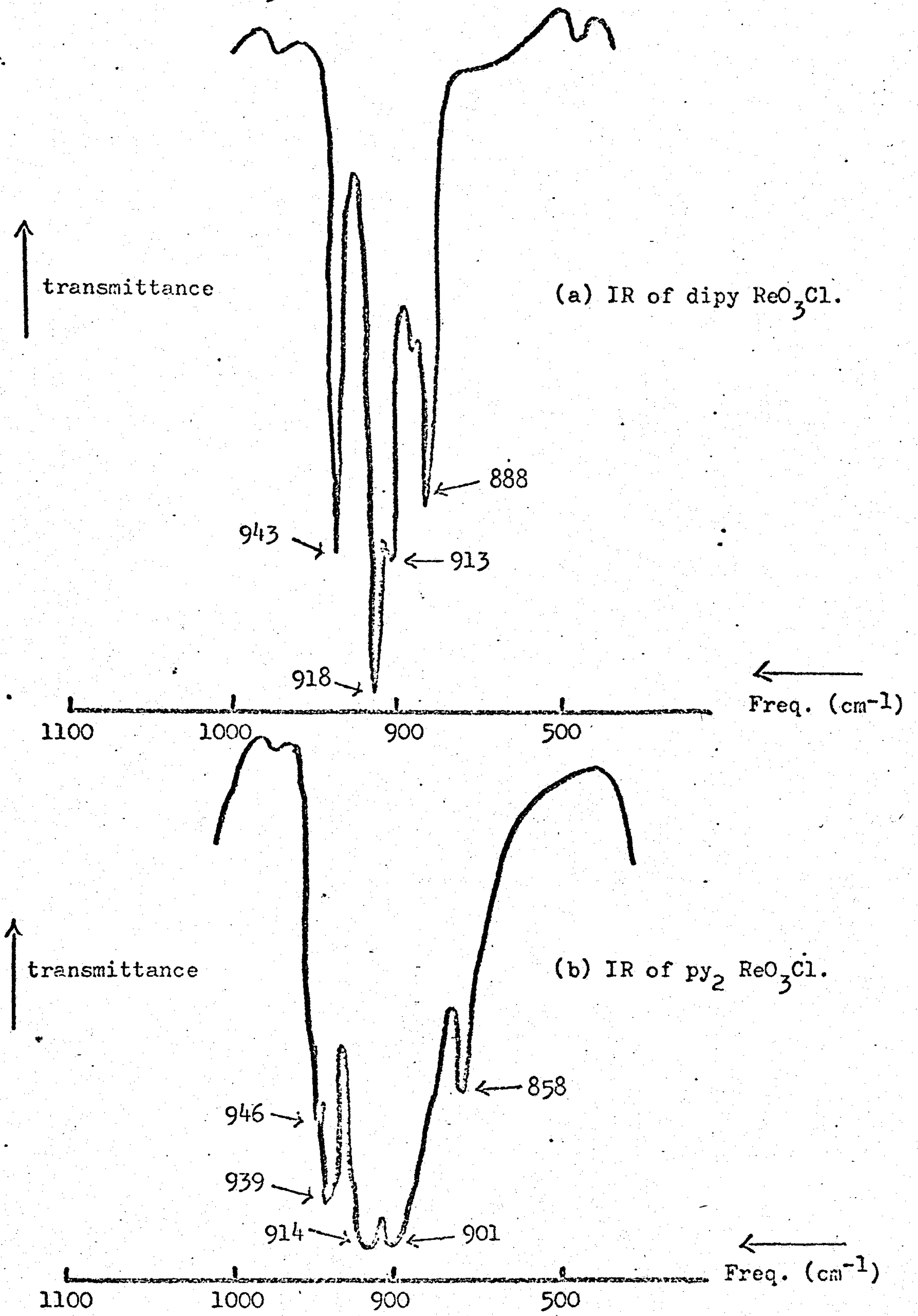
In addition to analytical results, evidence for the formulation as a Re(VII) compound was afforded by its reaction with water. The compound dissolved slowly at room temperature, but much more rapidly on boiling to give a clear colourless solution. A white precipitate was formed on addition of tetraphenyl arsonium chloride solution. This showed the presence of perrhenate ion and proved that hydrolysis accompanied dissolution. Rhenium in formal oxidation states lower than (VII) shows disproportionation on hydrolysis and deposits black hydrated rhenium dioxide (see Section II).

The infrared spectrum of $ReO_3C\ell dipy$ showed the absorptions associated with co-ordinated 2,2'-dipyridyl (135) and several absorption peaks in the region 800 - 1000cm^{-1}. The absorptions are not characteristic of co-ordinated 2,2'-dipyridyl (135) and may be assigned to rhenium oxygen vibrations. The spectrum for this region is shown in Fig. 25, (page 126).

$ReO_3C\ell py_2$ decomposed more rapidly in air than did $ReO_3C\ell dipy$, and was a pale yellow colour. $ReO_3C\ell dipy$ was involatile at 100°C, but the pyridine compound was sublimed at this temperature. A residue left on sublimation was shown by analysis and infrared spectroscopy to be pyridinium perrhenate.

In addition to analytical results, evidence for the formulation as a Re(VII) compound was again afforded by its reaction with water. $ReO_3C\ell py_2$ dissolved in cold water to give a perrhenate solution, and no rhenium dioxide was precipitated. The infrared spectrum of the solid showed absorptions normally associated with co-ordinated pyridine (134) and several absorptions in the range 800 - 1000 cm^{-1}, which may be assigned to rhenium-oxygen vibrations. The spectrum is presented in Fig. 25 (page 126).

Fig. 25. The infrared spectrum of (a) ReO_3Cl dipy and (b) $ReO_3Cl\ py_2$ in the range 800 - 1100 cm^{-1}.



The difference between the spectra of $ReO_3C\ell py_2$ and $ReO_3C\ell dipy$ in the 800 - 1000 cm^{-1} region may or may not indicate a difference in the geometries of the two compounds. More experimental work must be performed before any prediction of their geometries can be made.

Triphenylphosphine is the only other ligand which has been reacted with perrhenyl chloride. The method described in Section IV for pyridine and 2,2'-dipyridyl was used and a purple precipitate was formed. The product turned brown when vacuum was applied to remove excess solvent. Consistent analytical and spectral results have not been obtained, and the composition of this compound (or mixture of compounds) remains unknown.

To our knowledge, this is the first time rhenium oxychlorides have been used as starting materials for the preparation of co-ordination compounds. The number of ligands used, and the work performed on these reactions was necessarily limited, as this work was almost out of the original scope of this research. However, it has been shown that the preparation of co-ordination compounds from rhenium oxychlorides is possible and further investigations should prove a fruitful and interesting field of study.

VIII GENERAL CONCLUSIONS

In addition to increasing our knowledge of rhenium-chlorine chemistry, this research has provided techniques which should be useful in future investigations of sensitive compounds. The neutron activation method used for the determination of rhenium-chlorine ratios is potentially a rapid and accurate method for finding the stoichiometries of many systems where easily activated nuclei are present. The difficulty in obtaining vapour-phase infrared spectra, because of the lack of a suitable cell, was successfully overcome. The cell which was developed was extremely simple to construct, robust, and relatively cheap. This cell will find many applications and requests for reprints of a paper describing it (92) have been received from several countries.

Several old chemical problems, such as a reliable method of preparation of rhenium tetrachloride, have been solved, but many new questions have been raised. The compound thought to be rhenium hexachloride was shown to be rhenium oxytetrachloride. This leaves the anomaly of a second row metal, technetium, having a higher chloride than the third row metal, rhenium. The same workers that isolated "rhenium hexachloride" also isolated technetium hexachloride by a similar method. The chlorination product of a technetium mirror was to be re-investigated, but it has not yet been possible to obtain the metal.

The highest chloride formed for the group VI second row metal, molybdenum, is a pentachloride and by the group VIII metal, ruthenium, is a trichloride. The neighbouring third row metals, tungsten (group VI) and osmium (group VIII) form a hexachloride and a tetrachloride respectively. We failed to find a method of preparation of rhenium hexachloride. It may be possible to prepare hexachlorides of all these metals if a suitable method can be developed, but at the moment a re-examination of technetium hexachloride appears to be desirable.

It was not possible to identify with certainty the very volatile rhenium oxytetrachloride impurity (page 72) as rhenium oxytrichloride, but neutron activation analysis strongly indicated this formulation. A method of preparation of this compound in higher yields is required. Reactions which may produce rhenium oxytrichloride are the reactions of the known rhenium chlorides with rhenium oxides. Reaction of rhenium metals or rhenium oxides sealed in tubes with sulphur chlorides or phos--phorus chlorides may also prove fruitful.

As stated in Chapter V (c) (page 80), the preparation of rhenium tetrachloride is considered to be a reduction of rhenium pentachloride by antimony trichloride. It is possible that the reduction may be performed by other reagents. If so, the "accidental" preparation by the Shattuck Chemical Company may have resulted from reduction by impurities in their reaction vessel rather than the "thermal decomposition of rhenium pentachloride".

Only a few complexes were prepared using rhenium oxychlorides as starting materials. Reactions of these oxychlorides with other ligands will probably produce other new compounds, and these reactions are to be investigated in the near future.

This work has produced some new techniques, which are of wide application, some new rhenium compounds, and has introduced a little more order to the rhenium-chlorine system.

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