STUDIES IN THE STEREOCHEMISTRY OF RHENIUM

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by

W.T. ROBINSON

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PREFACE

The primary aim of this investigation was to determine the structure of the compound \( \text{CsReCl}_4 \) by X-ray methods. This led to the discovery of the \( [\text{Re}_3\text{Cl}_{12}]^{3-} \) anion and then, through another X-ray crystal structure analysis, to a determination of the structure of the \( [\text{Re}_3\text{Cl}_{11}]^{2-} \) anion in the compound \( (\text{Ph}_4\text{As})_2\text{Re}_3\text{Cl}_{11} \). Photographs of models of both anions are shown in the frontispiece.

As part of this work the author helped to establish a system of programs which enable the formidable calculations necessary for most crystal structure analyses to be carried out on an IBM 1620 computer. He also investigated certain aspects of the Buerger precession method and applied this photographic technique, with considerable success, to the complex problem of indexing Weissenberg photographs of a triclinic crystal.

In this thesis two chapters are devoted to each of the crystal structure analyses. They contain little rigorous theory and no mention of the methods used to calculate various results. The theory is adequately described in many textbooks, and the methods, which were common to both analyses, are described and criticised in the last chapter on the computing system. Similarly, well established experimental methods are not described at all, but a detailed discussion of new photographic techniques is given in chapter V.
Because some material has been referred to in several places in the text, it has been found useful to collect most diagrams, Fourier maps, structure factor listings and other tables in a separate volume of appendices.

It is hoped that separating the accounts of the crystal structure analyses from the detailed reports of experiments and computations has resulted in the reader being presented with a clear record of the steps taken in solving these structures. Throughout the text symbols have been used with the meanings ascribed in International Tables for X-ray Crystallography, Volume 1, p.xi.

The author gratefully acknowledges the interesting discussions and the facilities provided by many people in the University of Canterbury. In particular he thanks Dr. J.E. Fergusson, for his helpful supervision of chemical aspects of his work, and Dr. Bruce R. Penfold for introducing him to the intricacies of X-ray crystallography, and for suggesting logical methods for solving problems which failed to succumb to the onslaught of a beginner. Special thanks are also due to the New Zealand Universities Research Committee for the award of a Research Fund Fellowship.
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CHAPTER I  INTRODUCTION

A. LIGAND FIELD THEORY

In 1956 Orgel\(^1\) stated that the complex anion \([\text{ReCl}_4]^-\) should be a regular tetrahedron. His arguments were based on ligand-field theory and have since been presented in his book.\(^2\) They are summarized here to illustrate the main reasons for the present research.

Most problems of bonding in transition-metal chemistry are currently considered with reference to ligand-field theory. This can be regarded as a combination of a purely electrostatic crystal-field theory and molecular orbital theory. Both theories can be used to predict the energy levels of d-orbitals of a central metal atom or ion in the presence of variously distributed ligands. Many of the magnetic and spectral properties of transition-metal compounds can be explained by assigning available d electrons to these orbitals in special ways. Although this work was concerned with a possible tetrahedral ligand-field it is convenient to discuss the case of an octahedral field first.

Consider the complex \(\text{ML}_6\) which is to be formed by bringing six negatively charged ligands L up to a central metal ion M along the directions of octahedrally disposed axes (fig.1 page 101). The d-orbitals which lie along these axes (\(d_{x^2-y^2}, d_z^2\)) will be
affected more by the ligands than will the orbitals lying between these axes ($d_{xy}, d_{yz}, d_{zx}$). Thus the five degenerate $d$-orbitals of the free ion are rendered less stable in the complex. They are, in fact, split into two groups at different energy levels which are referred to as $e_g$ (doubly degenerate) and $t_{2g}$ (triply degenerate) orbitals respectively (fig. 2). The difference in energy between the two levels ($\Delta$) is used as a measure of the strength of the crystal field.

If the ligand field tetrahedral the $t_{2g}$ orbitals are destabilized more than the $e_g$ orbitals (fig. 2), but the energy of the crystal field is not as great as for the octahedral field when more ligands were present. For the same $M$ and $L$ species a tetrahedral field would have approximately $\frac{4}{9}$ the strength of an octahedral field.

Clearly the ground state of the central metal ion in a complex will depend on the way in which its $d$ electrons are distributed between the $e_g$ and $t_{2g}$ orbitals. The way in which these orbitals are occupied will depend on the relative magnitudes of the crystal field and the exchange energy. When $\Delta$ is less than the exchange energy Hund's rules are obeyed. When $\Delta$ is greater than the exchange energy the lower energy orbitals fill first and spin-pairing occurs.

General rules can sometimes be applied to predict likely conditions for spin-pairing in particular ligand-fields. The most pertinent of these, as far as the present argument is concerned, is that splitting increases from the first, through the second, to the third row transition series while the exchange
energy for d electrons decreases. In octahedral complexes spin-pairing occurs frequently in the first row transition series and is normal in the second and third rows. In the tetrahedral case, where the ligand-field is much smaller, there is little evidence for the existence of spin-paired complexes, though they could be expected to occur for the heavier metals.

Tetrahedral complexes are most likely to occur when highly polarizable ligands would lead to too great an accumulation of negative charge on the central metal ion if an octahedral complex was formed. The size of the ligand may also favour tetrahedral coordination. A symmetrical tetrahedron can only occur when the arrangement of electrons is symmetrical with respect to the ligands. Such arrangements are d⁰, e₂g, e₂g, 2e₂g, e₄g (spin-paired), e₄g, 2e₂g and d¹⁰. There are examples of spin-free tetrahedral complexes in the first transition series ([VCl₄]⁻, [FeCl₄]⁻, [MnCl₄]²⁻, [NiCl₄]²⁻), but there are no proved examples of spin-paired or spin-free tetrahedral complexes in the second and third rows.

Rhenium (III) has a d⁴ electron configuration, is a third row transition metal ion, and forms compounds of the type MReCl₄ where M is an alkali metal. These could be expected to be tetrahedral since chlorine is a highly polarizable ligand. The compounds are diamagnetic and therefore spin-paired. Earlier investigations³ failed to establish this stereochemistry, and the problem was considered suitable for single crystal X-ray structure
analysis. The results indicate that more is involved in the bonding than the simple crystal-field picture which has been outlined.

B. EARLIER WORK

The first investigation of this problem was undertaken by J.E. Fergusson at University College, London. In the course of this work he prepared two compounds of rhenium which subsequently assumed considerable significance in the present investigation. They were ReCl$_3$.Ph$_2$P and (Ph$_4$As)$_2$.Re$_2$.Cl$_{11}^{-}$.

The first of these compounds was prepared by heating under reflux a solution of rhenium trichloride and triphenylphosphine in acetone. Isopiestic molecular weight determination indicated a monomer. Other properties were a low conductivity (non-electrolyte) and a low magnetic moment (0.5 Bohr magnetons). This suggested a spin-paired tetrahedral complex, although such a tetrahedron would be distorted on account of the inequality of the ligands.

The second compound was prepared by adding tetr phenyl arsonium chloride to a solution of rhenium trichloride in alcohol saturated with hydrogen chloride. Red crystals were recrystallised from alcohol and analyses indicated the composition (Ph$_4$As)$_2$.Re$_2$.Cl$_{11}^{-}$. The molecular weight indicated dissociation into three particles and the conductivity was consistent with a 2:1 electrolyte. As before a low magnetic moment (0.4 B.M.) indicated the absence of unpaired
electrons. It was suggested that this was a spin-paired compound in which the rhenium atom was five-coordinate. Other work on this compound involved comparison of its X-ray powder diffraction pattern with those obtained from the compounds (Ph₄As) TlCl₄, (Ph₄As)InCl₄ and (Ph₄As) AuCl₄. The thallium and indium compounds were isomorphous with the corresponding vanadium and iron complex chlorides of which the iron anion was known to be a regular tetrahedron. No satisfactory conclusions were reached concerning the rhenium compound.

Fergusson did notice that the visible absorption spectra of solutions of the compounds ReCl₃·Ph₃P and (Ph₄As)₂ReCl₁₁, were similar to the spectra of ReCl₃ and also of ReCl₅ dissolved in hydrochloric acid where the complex anion [ReCl₄]⁻ was supposed to exist. In each case peaks occurred near 750 and 510 m\(\mu\). It was also suggested that since polymeric anions were formed by metals near rhenium in the periodic table, the tetraphenyl arsonium cation may cause such an anion to form in the case of rhenium. These observations are discussed further in chapter four in the light of the present work.

C. COORDINATION ABOUT RHENIUM (III)

Important compounds discussed by Fergusson are listed in the first half of table 1 (page 103). Little was then known of their structures, but some inferences had been made on the basis of physical measurements. Other compounds reported recently are
listed in the second half of the table. This section summarizes points which have been made by various authors concerning the stereochemistry of rhenium (III) compounds.

1. Three-coordinate compounds

The rhenium trihalides are the only known examples of apparently three-coordinate compounds. Of these ReCl$_3$ has been said to be dimeric from cryoscopic measurements in glacial acetic acid. A halogen bridged structure was proposed (similar to Al$_2$Cl$_6$). However the possibility of a metal-metal bond was not excluded.$^5$

2. Four-coordinate compounds

Four-coordinate halide complexes have already been dealt with. Recently, Colton, Levitus and Wilkinson$^6$ have reiterated the view that they are tetrahedral with d$^3$ type orbital hybridisation involved in the bonding, and suggest that the same scheme is applicable to the complex ReCl$_3$.Ph$_2$P. They have also prepared highly insoluble, diamagnetic complexes of stoichiometry Re$_2$Cl$_4$L where L is a bidentate ligand (1,10-phenanthroline; 2,2'-bipyridyl or 3,4-dimethylthiotoluene). These are possibly polymers, but the basic structural unit is said to contain both tetrahedrally coordinated Re(III) and octahedrally coordinated Re(I) if the diamagnetism is to be explained. A complex of quinaldine which is paramagnetic, probably with one unpaired electron, is also claimed to have a mixed valency state structure
All of these complexes have a deep purple colour.

In a further note the same authors report the preparation of diamagnetic complexes of general formula ReCl₂(NR₂·CS₂) where R = CH₃, C₂H₅ or C₃H₇. They claim that these complexes are best formulated as monomeric tetrahedral complexes of rhenium(III) with the same d⁵'s hybridisation.

3. Phosphorus ligands

The phosphine addition compounds ReCl₃·Ph₃P and ReCl₃(Ph₃P)₂ were first mentioned by Freni and Valenti and have subsequently been reported several times. Malatesta has prepared bromide and iodide complexes corresponding to ReCl₃·Ph₃P. Freni and Valenti report bromides and iodides corresponding to ReCl₃·(Ph₃P)₂. Colton et al. proposed structures for both chlorides which they claimed were diamagnetic monomers. The first has been dealt with and the second was presumed to be a trigonal bipyramidal structure involving five-coordinate rhenium (III). Recently, Lock and Wilkinson and Chatt and Rowe have detected oxygen in infra-red spectra of these supposedly five-coordinate compounds which have now been
reformulated \( \text{Re}^\text{V} \text{OX}_2 \left( \text{P PH}_3 \right)_2 \).

Other phosphine complexes, listed in table 1, were reported by Chatt and Rowe.\(^{13}\) They claim that their work confirms the existence of at least three classes of tertiary monophosphines with rhenium halides, namely, \( [\text{ReX}_2 \text{PR}_3]_n \), \( [\text{ReX}_3 \text{(PR})_2] \), and \( [\text{Re}^\text{II} \text{X}_2 \text{(PR})_2] \). The Re (II) series is significant to the present work in that Chatt and Rowe suggest the possibility of polymeric structures with Re-Re bonds in the solid state, thus accounting for the observed diamagnetism and low solubility in organic solvents.

Examples of the first series, including \( \text{ReCl}_3 \text{.PH}_3 \text{P} \), were poorly soluble in all solvents and presumed to be polymers linked through chlorine bridges. This is the first suggestion in the literature that Colton, Levitus and Wilkinson may not be correct in assuming that the complex \( \text{ReCl}_3 \text{.PH}_3 \text{P} \) is a monomer exhibiting tetrahedral stereochemistry.

Chatt and Rowe have ascribed essentially distorted octahedral configurations to their other complexes but do not give a satisfactory explanation of their observed diamagnetism.

4. **Five-coordinate compounds**

Colton et al.\(^6\) oxidized their bidentate complexes and obtained compounds which they claimed were clearly five-coordinate with the same structure as \( \text{ReCl}_3 \left( \text{PH}_3 \text{P} \right)_2 \). They also stated that
the band at 750 \( \mu \) in the visible absorption spectra of all these compounds appeared to be characteristic of five-coordinate rhenium (III). Since \( \text{ReCl}_3(\text{Ph}_3\text{P})_2 \) has been reformulated,\(^{11,12}\) as \( \text{ReOCl}_3(\text{Ph}_3\text{P})_2 \) any conclusions concerning the existence and structure of five-coordinate compounds of rhenium (III) must be treated cautiously.

6. **Higher coordination numbers**

Apart from \( \text{K}_2[\text{Re(CH}_3)_6] \), which has not been obtained in pure form\(^{14}\), and \( \text{K}_2\text{ReCl}_6 \), for which measurements are not available, the listed complexes are all paramagnetic and can be interpreted as having two unpaired electrons, as would be expected for \( t^4_{2g} \) octahedral complexes. Six-coordinate complexes with phosphorus ligands have already been mentioned.

Higher coordination numbers have not been reported, but Ferguson did point out that a seven-coordinate complex should be obtainable, probably involving \( d^3\text{sp}^3 \) hybridisation.

Many of these conclusions are re-examined in chapter IV in the light of the discovery of metal-metal bonds between rhenium atoms both in the present work and in the recently reported structure of the \( [\text{Re}_2\text{Cl}_8]^{4-} \) anion.\(^{15}\)
CHAPTER II THE X-RAY CRYSTAL STRUCTURE ANALYSIS OF CsReCl₄.

A. EXPERIMENTAL

1. Crystals

The first crystals used in this study were kindly supplied by Dr. J.E. Fergusson. A powder diffraction photograph, (fig. 3) obtained from a random sample of these crystals, using a Philips Powder camera (radius 57.3 mm) was identical to a photograph obtained by him in an earlier study of a compound which had analysed as having a composition corresponding to the empirical formula CsReCl₄.

Further crystals were prepared from a sample of ReCl₅, also supplied by Dr. Fergusson, using an extension of an established method for preparing ReCl₃ by thermal decomposition of ReCl₅ in an atmosphere of nitrogen. The apparatus used for the present work is shown in figure 4. Care was taken to keep the system free from oxygen and water which will readily react with ReCl₅ to form oxychlorides. Steps in the preparation of CsReCl₄ are outlined below. The reaction products for steps 1 and 2 have been established and their stabilities discussed by various workers.
1. \[ \text{ReCl}_5 \xrightarrow{\text{heat at } 300^\circ C} \text{ReCl}_3 + \text{Cl}_2 \]

2. \[ \text{ReCl}_3 + (\text{conc.}) \text{ HCl} \longrightarrow \text{HReCl}_4 \]

3. \[ \text{CsCl} + \text{HReCl}_4 \longrightarrow \text{CsReCl}_4 \downarrow + \text{HCl.} \]

4. \( \text{CsReCl}_4 \) precipitate recrystallized from A.R. grade conc. HCl.

A powder photograph of these crystals was identical with the photographs obtained from the other two samples.

Regular and complete extinction of most crystals examined under the crossed polaroids of a polarizing microscope suggested that they were not twinned. A large number of crystals was inspected but no common shape was found. Indeed the dark red coloured crystals seemed to be fairly poorly formed.

Several attempts to determine the density of the crystals failed. They sank rapidly in methylene iodide \((3.32 \text{ gm cm}^{-3})\)\(^{17}\) and there were too few of them to obtain an accurate result using a microvolumenometer \(^{18}\) or a Berman density balance. \(^{19}\) The latter apparatus is specially designed to facilitate the weighing of small samples in air and then in a liquid (in this case toluene). Calculations using these weights and Archimedes principle yield the density. In this case it was possible to set the lower limit for the density at \(3.82 \text{ gm cm}^{-3}\) using the balance. A similar lower limit \((3.85 \text{ gm cm}^{-3})\) was obtained by measuring the dimensions of two large, regularly shaped, weighed crystals, although this method is recognised as being very inaccurate.\(^{20}\)
In view of difficulties subsequently encountered in the analysis, it was unfortunate that the density could not be determined accurately by available experimental methods.

2. **Photography**

Two crystals were used for all of the photographic work.

The first crystal, used to check earlier work\(^1\) concerning the space group and the axial identity periods, and to provide the main part of the three dimensional X-ray diffraction data, was very roughly cubic in shape with an average dimension of 0.1 mm. Using a Unicam single crystal rotation camera and the method of Weiss and Cole\(^2\) the crystal was set from zero layer line photographs. From layer line spacings the identity period along the axis of rotation was approximately 14.05 Å. When the goniometer head was transferred, in the same setting, to a Unicam Weissenberg camera, a Weissenberg photograph, taken with 190° oscillation, showed the other two axes to be orthogonal with approximate identity periods of 14.00 Å and 10.65 Å. The experimental derivation of more accurate values for these parameters is discussed fully in chapter V. Final values used in all calculations were \(a = 10.66\) Å, \(b = 14.02\) Å and \(c = 14.08\) Å.

Initially it was assumed there were 16 molecules in the unit cell and the calculated density of 6.1 gm cm\(^{-3}\) (cf. correct value of 4.36 gm cm\(^{-3}\)) was used to derive linear absorption coefficients\(^2\)
of 1240 cm$^{-2}$ and 362 cm$^{-2}$ for CuK$\alpha$ and MoK$\alpha$ radiations respectively. To minimize absorption effects the three-dimensional intensity data were therefore recorded using MoK$\alpha$ X-radiation. Six equi-inclination Weissenberg photographs were taken of each of the reciprocal lattice layers $l = 0$ to $l = 8$. The only material available to absorb X-radiation between two films in a pack was aluminium foil of such thickness that nineteen sheets were required to reduce the intensity of the recorded spots by a factor of two. Thus it was only possible to expose two films at a time, and each layer line required three exposures of 96, 17 and 3 hours respectively.

The X-ray source for the photographs detailed so far was a Philips generator Type PW 1009. Further photographs were obtained by transferring the crystal, in the same setting, to a Buerger precession camera mounted on a Philips generator Type PW 1010 which has a current and voltage stabilized output. Three separate exposures, of 72, 24 and 8 hours respectively, were obtained of each of the reciprocal lattice layers $h0l$, $hk0$, $h2l$ and $h3l$. The first crystal was then lost, and a second crystal with the same average dimension and roughly the same shape was mounted about the same axis and used to obtain precession photographs of the $0kl$ and $1kl$ reciprocal lattice layers.
3. **Space group and indexing**

Tracings

Figure 5 shows tracings of three Weissenberg photographs used to derive a space group. Axes were arbitrarily labelled as indicated and C centring established from the complete absence of reflections of the type \( h+k \) odd. Examination of reflections of the type \( 0k\ell \) (absent for \( \ell \) odd) and \( h0\ell \) (not absent for \( \ell \) odd) indicated only one glide plane perpendicular to the x-axis with translation \( \ell/2 \). Space groups with these symmetry elements are tabulated with their standard settings and reference numbers.  

<table>
<thead>
<tr>
<th>Space group</th>
<th>Standard setting</th>
<th>Reference number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cmcm</td>
<td>Cmcm</td>
<td>63</td>
</tr>
<tr>
<td>Cm2_1</td>
<td>Cm2_1</td>
<td>36</td>
</tr>
<tr>
<td>Cc2m</td>
<td>Ama2</td>
<td>40</td>
</tr>
</tbody>
</table>

Of these three, number 63 (Cmcm) was the only space group with sixteen general equivalent positions. As this structure analysis was expected to demonstrate the existence of discrete, tetrahedral \([\text{ReCl}_4]^-\) anions, and as it was still assumed there were sixteen \(\text{CsReCl}_4\) molecules in the unit cell (page 12), the three-dimensional data were indexed on the basis of this space group in its standard setting.

This choice proved incorrect and section 3 of this chapter contains a description of the way in which the correct space group (Ama2) was deduced. To avoid unnecessary confusion, the photographic data are referred to their correct indices, based on space group Ama2, in all other parts of this thesis.
4. **Measurement of relative intensities**

Relative intensities of photographic spots were estimated by visual comparison with standard scales made by successively exposing one selected spot on adjacent parts of a film for steadily increasing intervals of time. In Weissenberg photography selection of a suitable spot is readily effected by combining a small oscillation with suitable screen setting. No similar, simple procedure is available in precession photography, and the method employed is discussed in chapter V.

Relative intensities of the extreme spots used on the intensity scales were in the ratio 1:20, the most accurate comparisons being obtained in the middle part of the scales. Correlation of the various films forming one layer line set, was achieved by using data measured in this part of the scale. In some sets of precession photographs of one reciprocal lattice layer, there were no spots of sufficient intensity to permit accurate correlation, and it became necessary to use relative exposure times for this purpose. This procedure is very approximate on account of varying developing conditions so that low intensity precession data, presented in the final structure factors listing, must be expected to be correspondingly inaccurate.

B. **CORRELATION OF EXPERIMENTAL DATA.**

It is convenient to discuss the correlation of independent sets of photographs, which go to make up a three-dimensional data
collection, in terms of the reciprocal lattice. Any two non-
parallel layers (planes) of this lattice intersect in a row (line)
of common points. Thus the h00 reciprocal lattice layer has the
point rows h00, h01 •••• h08 in common with the reciprocal
lattice layers h00, h01 •••• h08. If one set of intensities with
indices h00 is self-consistent (i.e. has been recorded on one film)
these common point rows can be used to correlate the intensities
of the independently recorded reciprocal lattice layers h00, h01,
••••• h08. Similarly a self-consistent h10 set can be used to
correlate the other sets as can any other reciprocal lattice
layer with point rows in common with the layers to be correlated.

It is important to note that this method for correlating
different sets of intensities is applicable when data is recorded
by different techniques and using different crystals, provided
corrections are made for the geometry of the recording method
(Lorentz effect) and for polarization and absorption effects,
before the correlation is attempted. In the case of CsK3dCl4
the h00 layer was recorded by the precession method and the
h00, ••••• h08 layers by the Weissenberg method. The crystal
was assumed spherical (radius 0.05mm.) and the necessary corrections
applied. All the Weissenberg data was then correlated with the
h00 precession data and then the rest of the precession data was
correlated with this data. Wherever a particular reflection
had been recorded by both techniques the correlated Weissenberg
data was accepted as being more accurate. In this way all of the Weissenberg data was included in the three-dimensional set together with precession data $hk\ell$ for $\ell>8$. The total number of independent X-ray reflections whose correlated intensities were used in all subsequent calculations was 501.

C. THE THREE-DIMENSIONAL PATTERSON FUNCTION.

1. Introduction

Using the expression

$$P(U,V,W) = \frac{1}{V} \sum_{hk\ell} \sum |F(hk\ell)|^2 \cos \left\{ 2\pi (hU + kV + \ell W) \right\}$$

the Patterson function $P(u,v,w)$ can be evaluated at a series of points $U,V,W$ filling the unit cell at regular intervals. In a continuous Patterson synthesis, peaks occur at the ends of vectors from the origin which also represent interatomic vectors in the crystal structure. Such peaks can be located by plotting, on a sufficiently fine grid, values of $P(U,V,W)$ calculated using the absolute values of the observed intensities $I(hk\ell)$ in place of the coefficients $F(hk\ell)$

By converting the experimental intensities $I(hk\ell)$ to values which would be obtained from a crystal composed of point atoms, and then applying an artificial temperature factor to the point atom coefficients (a procedure known as sharpening the Patterson function), it is possible to improve the resolution of peaks in a Patterson synthesis. Resolution is also improved by partly
or completely removing the large origin peak which dominates all Patterson syntheses, and corresponds to the sum of the peaks at the ends of $N$ interatomic vectors of zero length, where there are $N$ atoms in the unit cell.

The complete correlated data were used and both these procedures were adopted in producing the sections of the three-dimensional Patterson map for CsReCl$_4$ shown in figure 6. The function was evaluated at intervals of 0.02 of unit cell edges, over ranges sufficient to show its symmetry and deduce its complete form.

$$U \ 0.00 \text{ to } 0.52 \ \text{in intervals of } 0.21 \ \text{Å}.$$  
$$V \ 0.00 \text{ to } 0.52 \ \text{in intervals of } 0.28 \ \text{Å}.$$  
$$W \ 0.00 \text{ to } 0.26 \ \text{in intervals of } 0.28 \ \text{Å}.$$  

Points nearest peaks mentioned in the next sections have been marked with rings.

2. **The vector map and the space group.**

All attempts to derive rhenium atom positions from the vector map on the basis of space group Cmcm failed. The reason for this, and the reasoning which led to the correct space group, is conveniently demonstrated if the reference axes of the vector map are interchanged, so that the section coordinate is $U$ and the vertical coordinate is $W$. This corresponds to treating the lattice as $C$ centred instead of $A$ centred.
One approach to the analysis of a Patterson function derived from a centrosymmetric crystal, is to locate peaks which correspond to vectors between centrosymmetrically related atoms. Such peaks have coordinates \( U = 2x \), \( V = 2y \) and \( W = 2z \) which lead directly to atomic positions. This approach, based on a systematic examination of the relative weights of Patterson peaks, is discussed in the next chapter.

In the present case no useful information was gained from an examination of the relative weights of peaks and so each of the six non-origin peaks, at a level greater than \( J \) on the alphabetic scale, was tested to see if it could represent a vector between centrosymmetrically related atoms. These peaks all occur on the first three sections and therefore have \( U (= 2x) \) coordinates of 0.04 or less. In space group \( \text{Cmcm} \), \( 2x \) is the length of the vector between an atom in position \( x, y, z \) and an atom in the equivalent position \( x, y, z \), generated by the mirror plane perpendicular to the \( x \)-axis of the crystal lattice. The interatomic distance between these two atoms cannot, therefore, be greater than \((0.04 \times 14.08) \) Å. Such a situation is clearly impossible, and this result strongly suggests that the correct space group must have no mirror plane perpendicular to the \( x \)-axis. Of the three space groups (p. 17) determined from systematic absences of X-ray reflections, number 40 (\( \text{Cc} \_2 \_m \)) fulfilled this condition, and was used in determining heavy atom positions from the vector map.
Buerger has shown\textsuperscript{25} that most space groups can be determined from vector maps by examination of the concentration of peaks on various lines or planes. In particular, the three possible space groups for CsReCl\textsubscript{4}, treated as C centred, should show the following concentration of peaks in the vector map.

<table>
<thead>
<tr>
<th>Space group</th>
<th>Number</th>
<th>Linear concentrations</th>
<th>Planar concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cmc\textsubscript{2} \textsubscript{1}</td>
<td>36</td>
<td>uoc ov\textsubscript{1} \textsuperscript{1}</td>
<td>uv\textsubscript{2} \textsubscript{1}</td>
</tr>
<tr>
<td>C2cm</td>
<td>40</td>
<td>ov\textsubscript{1} \textsuperscript{1}, ow\textsubscript{2}</td>
<td>ovw\textsubscript{1},\textsubscript{2}</td>
</tr>
<tr>
<td>Cmcm</td>
<td>63</td>
<td>uoc ov\textsubscript{2},\textsubscript{3}, ow\textsubscript{4},\textsubscript{5}</td>
<td>ovw\textsubscript{2},\textsubscript{4}, uow\textsubscript{1},\textsubscript{5}, uv\textsubscript{2} \textsuperscript{3}</td>
</tr>
</tbody>
</table>

Subscripts indicate that particular linear concentrations are embedded in similarly subscripted planar concentrations. The underlined concentrations do not occur on the CsReCl\textsubscript{4} vector map unless peaks below the level of $K$ are considered. When this analysis was carried out, it was not considered that six prominent peaks were sufficient in number to conclusively establish the concentrations for any particular space group. In retrospect, it is easy to see that there is no planar concentration of the type $uv$ even if peaks of level $I\cdot J$ (which occur quite frequently in the vector map) are included in the analysis. These facts taken together could have been regarded as strong evidence for space group C2cm.
It is also worthwhile pointing out that the statistical tests devised by Wilson\textsuperscript{26} and by Howells, Phillips and Rogers\textsuperscript{27} could have been carried out using the observed intensities. Einstein\textsuperscript{28} has recently shown that such tests would have indicated the absence of a centre of symmetry. In a recent paper describing an independent analysis of this same crystal structure, Bertrand Cotton and Dollase\textsuperscript{29} state that statistical treatment of the distribution of intensities in the principal zones unambiguously indicated space group \textit{C2\textit{cm}}.

Presumably this space group was distinguished from \textit{Cmc\textit{2\textit{1}}} by identifying the centrosymmetric projection; a rather more elegant approach than that described in the present work although statistical tests can be unreliable when applied to some heavy atom structures\textsuperscript{30}.

Once space group \textit{C2\textit{cm}} was suspected, it was not difficult to analyse the vector map, and determine approximate heavy atom positions which led to complete elucidation of the structure.

3. \textbf{Interpretation of the vector map.}

Axes were first assigned to the map to correspond with the space group \textit{C2\textit{cm}} in its standard setting \textit{Ama\textit{2}}. These are the axes indicated on the map.

All special and general equivalent positions of this space group were analysed to yield the exhaustive list of possible

Fractional coordinates of equivalent positions \((0,0,0; \frac{1}{2}, \frac{1}{2}; \frac{1}{2})\):

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>c</td>
<td>1</td>
<td>(x,y,z; \bar{x},\bar{y},z; \frac{1}{2}-x,y,z; \frac{1}{2}+x,\bar{y},z).</td>
</tr>
<tr>
<td>4</td>
<td>b</td>
<td>(\frac{1}{2},y,z; \frac{1}{2},\bar{y},z).</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>a</td>
<td>2</td>
<td>(0,0,z; \frac{1}{2},0,z).</td>
</tr>
</tbody>
</table>

Coordinates of possible peaks in the Patterson synthesis:

(i) **between atoms of the same set of equivalent positions**:

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3 c</td>
<td>1</td>
<td>(\frac{1}{2} \quad 2y \quad 0 \quad a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2x</td>
<td>2y</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2}-2x)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4 b</td>
<td>m</td>
<td>(\frac{1}{2} \quad 2y \quad 0 \quad d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2} \quad 0 \quad 0 \quad e)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(ii) **between atoms of two different sets** \(x,y,z\) and \(x',y',z'\), where \(\Sigma = x+x'\) or \(y+y'\) or \(z+z'\) and \(\Delta = x-x'\) or \(y-y'\) or \(z-z'\):

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3 c</td>
<td>-3 c</td>
<td>(\Delta \quad \Delta \quad \Delta \quad \Sigma)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\Sigma \quad \Sigma \quad \Delta \quad \Delta)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2}-\Delta \quad \Sigma \quad \Delta \quad \Delta)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2}-\Sigma \quad \Delta \quad \Delta \quad \Delta)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 b</td>
<td>-4 b</td>
<td>(0 \quad \Delta \quad \Delta \quad i)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2} \quad \Sigma \quad \Delta \quad \Delta)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 a</td>
<td>-4 a</td>
<td>(0 \quad 0 \quad \Delta \quad l)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2} \quad 0 \quad \Delta \quad m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 c</td>
<td>-4 b</td>
<td>(\frac{1}{2}-x \quad \Delta \quad \Delta \quad u)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2}+x \quad \Sigma \quad \Delta \quad \Delta)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 c</td>
<td>-4 a</td>
<td>(x \quad y \quad \Delta \quad n)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2}-x \quad y \quad \Delta \quad n)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 b</td>
<td>-4 a</td>
<td>(\frac{1}{2} \quad y \quad \Delta \quad r)</td>
<td></td>
</tr>
</tbody>
</table>
Patterson peaks shown on the opposite page.

In this table each type of peak is labelled by an alphabetic vector. The remaining notation follows directly from that used in International Tables for X-ray Crystallography, and the list of equivalent positions has been extracted from these tables.

The prominent peak at $U = 0.22, V = W = 0.00$ was most probably type $c$. This was confirmed by locating the corresponding type $b$ peak at position $U = 0.28, V = 0.44$ or $0.56, W = 0.00$ and then the type $a$ peak at position $U = 0.50, V = 0.44$ or $0.56, W = 0.00$. The position $x_1 = 0.14, y_1 = 0.22$ or $0.28, z_1$ was therefore established as a likely rhenium atom site.

There being no other type $c$ peak, the only other prominent peak on the $W = 0.00$ section (at position $U = 0.50, V = 0.28$, or $0.72, W = 0.00$) was possibly type $d$ derived from an atom in position $x_2 = 0.25, y_2 = 0.14$ or $0.36, z_2$. This position was checked by examining the vector map for prominent type $n$ and type $o$ peaks corresponding to vectors between atoms of eightfold and fourfold sets. Such peaks were found at positions $U = 0.11, V = 0.14, W = 0.04$ and $U = 0.39, V = 0.42, W = 0.04$. Rhenium atoms were therefore expected in the following positions, where acceptable combinations of $y_1$ and $y_2$ are listed in column and where $z_1 < z_2 = 0.04$.

$$x_1 = 0.14, y_1 = 0.28 \text{ or } 0.22, z_1$$

$$x_2 = 0.25, y_2 = 0.14 \text{ or } 0.36, z_2.$$ 

Since all peaks of level $L$ and above were accounted for as representing vectors between these two sets of rhenium atoms, the
next highest peaks were examined in an endeavour to establish
positions for cesium atoms.

The peak at \( U = 0.50, V = W = 0.00 \) was possibly type \( q \)
corresponding to an atomic position \( x_3 = y_3 = 0.00, z_3 \). As
before, this position was checked by searching the map for type
\( p, q \) and \( r \) peaks corresponding to vectors between the established
rhenium atoms and this possible cesium atom. Such peaks, or
their symmetry equivalents, were found and are tabulated below.

<table>
<thead>
<tr>
<th>Type</th>
<th>U</th>
<th>V</th>
<th>W</th>
<th>Derivation of W</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p )</td>
<td>0.14</td>
<td>0.28 or 0.22</td>
<td>0.28 or 0.22</td>
<td>( z_1 - z_3 )</td>
</tr>
<tr>
<td>( q )</td>
<td>0.36</td>
<td>0.28 or 0.22</td>
<td>0.28 or 0.22</td>
<td>( z_1 - z_3 )</td>
</tr>
<tr>
<td>( r )</td>
<td>0.25</td>
<td>0.14 or 0.36</td>
<td>0.22 or 0.28</td>
<td>( z_2 - z_3 )</td>
</tr>
</tbody>
</table>

Arbitrarily choosing \( z_2 = 0.00 \) the following atomic positions were
therefore considered established:

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x_r )</th>
<th>( y_r )</th>
<th>( z_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>0.14</td>
<td>0.28 or 0.22</td>
<td>0.06 or -0.06</td>
</tr>
<tr>
<td>Re</td>
<td>0.25</td>
<td>0.14 or 0.36</td>
<td>0.00</td>
</tr>
<tr>
<td>Cs</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.22 or -0.28</td>
</tr>
</tbody>
</table>

Examination of the space group revealed that the alternative
combinations of atomic coordinates defined the same structure.
One combination could be derived from the other by transferring
the origin a distance \( \frac{b}{2} \) along the \( y \)-axis and reversing the
directions of this axis and the \( z \)-axis. These operations
retained a conventional right-handed system of axes and the
origin was still on a twofold axis of rotation. The analysis
proceeded using the first acceptable combination of atomic coordinates.

There being no other obvious type o or d peaks, unused peaks at the level I were examined as possibly defining vectors between established atoms and undiscovered cesium atoms. This analysis led to location of a cesium atom in position \( x_4 = 0.25, y_4 = -0.175, z_4 = 0.14 \). Corresponding peaks \( j, k, n, o, \) and \( x \) can be found (but are not marked) on the vector map. The type d peak should occur at position \( U = 0.50, V = 0.35, W = 0.00 \) but has disappeared in the process of sharpening the adjacent heavy peaks.

The remaining cesium atom position could not be established from the Patterson synthesis, but a careful check of the work outlined did lead to slight shifts in some of the trial coordinates. The set finally accepted for use in trial structure factor calculations is tabulated below.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x_r )</th>
<th>( y_r )</th>
<th>( z_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>0.135</td>
<td>0.280</td>
<td>0.040</td>
</tr>
<tr>
<td>Re</td>
<td>0.250</td>
<td>0.140</td>
<td>0.000</td>
</tr>
<tr>
<td>Cs</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.220</td>
</tr>
<tr>
<td>Cs</td>
<td>0.250</td>
<td>-0.175</td>
<td>0.140</td>
</tr>
</tbody>
</table>

D. **REFINEMENT OF THREE-DIMENSIONAL DATA**

1. **Structure factor calculations**

The structure factor \( F(hk\ell) \) can be calculated for any reflection \( hkl \) from a knowledge of the position and nature of the
scattering material in the unit cell.\textsuperscript{24}

\[ F(hkl) = \sum_{r} f_{r}(hkl) \exp \left[ 2\pi i(hx_{r} + ky_{r} + lz_{r}) \right] \]

In this expression \( f_{r}(hkl) = f_{o} \exp \left( \frac{-B_{r} \sin^{2} \theta}{\lambda^{2}} \right) \) where \( f_{o} \) is the atomic scattering factor of atom \( r \) and is dependent on the electronic structure of this atom and on the direction of scattering. \( B_{r} \) is the empirical constant known as the temperature factor and is used in the fashion indicated to modify \( f_{o} \) to account for isotropic thermal vibration of the atom \( r \).

\( F(hkl) \) is a complex quantity whose conjugate is \( \bar{F}(hkl) \).

If \( F(hkl) = A^{i} + i B^{i} \)
and \( \bar{F}(hkl) = A^{i'} - i B^{i'} \)
then \( |F(hkl)|^{2} = A^{i2} + B^{i2} \) (Friedel's law)
\[ |F(hkl)| = (A^{i2} + B^{i2})^{1/2} \]

where \( A^{i} = \sum_{r} f_{r}(hkl) \cos 2\pi (hx_{r} + ky_{r} + lz_{r}) \)
and \( B^{i} = \sum_{r} f_{r}(hkl) \sin 2\pi (hx_{r} + ky_{r} + lz_{r}) \)
and the summations include every atom \( r \) in the unit cell.

also \( A^{i} = |F(hkl)| \cos \lambda(hkl) \)
and \( B^{i} = |F(hkl)| \sin \lambda(hkl) \)
\[ \therefore \lambda(hkl) = \tan^{-1} \frac{B^{i}}{A^{i}} \]

where \( \lambda(hkl) \) is the phase angle associated with the complex quantity \( F(hkl) \). In acentric structures, such as CsReCl\textsubscript{4}, \( \lambda(hkl) \) can take any value between 0 and \( \pi \) but in centrosymmetric structures \( B^{i} = 0 \) and \( \lambda(hkl) \) must take one or other of these extreme values. Although \( \lambda(hkl) \) can be calculated by
the methods outlined it cannot be determined experimentally. \( |F(hk\ell)| \) can both be calculated \( (F_c) \) and determined experimentally \( (F_o) \) from the observed intensities of X-ray reflections. For a particular reflection

\[
|F_o| = k\sqrt{I(hk\ell)}
\]

where \( k \) is a constant scale factor used to put all \( F_o \) values on the same scale as \( F_c \).

In an accurately determined structure \( F_o \) would ideally be equal to \( F_c \). Such equality is only achieved by chance for odd X-ray reflections. The degree of agreement is limited by the accuracy with which X-ray reflection intensities can be determined, and also by the accuracy with which individual atomic scattering factors are known.

In an incompletely determined structure agreement is also limited by the use of rough atomic parameters \( (x_r, y_r, z_r, B_r) \) or by completely omitting the contribution of some atoms in calculating \( F_c \). Obviously agreement can be improved in such cases by refining the values of atomic parameters and the scale factor \( k \), and also by locating further atoms and using their atomic parameters in subsequent structure factor calculations. New atoms may be located by using electron density difference maps. Atomic parameters may be refined from these same maps or by the method of least-squares discussed in a later section.

In the present work one cycle of refinement is taken to mean the complete process of deriving new and improved atomic parameters
2. Electron density maps.

Values of \( F(hk\ell) \) and \( \alpha(hk\ell) \) can be used to calculate the electron density \( \rho(xyz) \) at any point \( X,Y,Z \) in a unit cell of volume \( V_c \):

\[
\rho(XYZ) = \frac{1}{V_c} \sum_{h} \sum_{k} \sum_{\ell} |F(hk\ell)| \cos \left[ \frac{2\pi}{V_c} (hX+kY+\ell Z) - \alpha(hk\ell) \right]
\]

The points \( X,Y,Z \), can be chosen to fill the cell at regular intervals, and, in a similar fashion to that described for a Patterson synthesis, peaks of maximum electron density located from an examination of \( \rho(XYZ) \) at these points.

Clearly no useful information is obtained if values \( F_0 \) are substituted for \( F(hk\ell) \) in deriving electron density maps. Peaks will simply occur in positions corresponding closely to the atomic coordinates used in the structure factor calculation.

If \( F_0 \) is used together with values for \( \alpha(hk\ell) \) calculated for the trial structure, the maps represent the approximate distribution of electron density in a unit cell of the structure. Such maps are usually approximate because the trial structure does not correspond exactly to the real structure and therefore values of
\( \lambda (hkl) \) are incorrectly determined. Also reflections from all possible \((hkl)\) planes can never be recorded experimentally and so series termination errors occur in the electron density calculations.

Although errors due to an inaccurate trial structure decrease as refinement proceeds, series termination errors do not. To minimize these errors, and also because heavy atom peaks may dominate an \( F_o \) synthesis so that nearby light atoms are obscured or unresolved, electron density difference maps were used in the present work. Such maps are produced by using values of \((F_o - F_c)\) as coefficients in the Fourier summation used to calculate electron densities. They represent closely the difference in electron density between the observed structure and the trial structure, and can be used to locate new atoms from peak positions and also to adjust the positions of established atoms.

Cochran has given an excellent account\(^3^1\) of the important properties of \((F_o - F_c)\) syntheses. In particular he demonstrates that the quantity \( \Phi = \Sigma \frac{w}{n} (F_o - F_c)^2 \) (\( n \) observations each of weight \( w \)) is minimized with respect to atomic coordinates when the electron density difference map has zero slope at atomic centres. Under these conditions the atomic coordinates are free from series termination errors, except in so far as the scattering factors used to calculate the \( F_c \)'s may be incorrect. Errors in atomic coordinates can be detected and corrected by means of slopes occurring at atomic centres on the difference map. The rate at which this type of refinement converges to minimize \( \Phi \) is said to be
approximately the same as that of the method of least-squares.

In this description of refinement technique the author has endeavoured to collect together only those general expressions and methods which were useful in solving the noncentric crystal structure of CsReCl₄. Simpler expressions and methods are applicable when solving centrosymmetric structures in projection. These are described in the next chapter.

3. CsReCl₄

In the initial stages of this refinement atomic scattering factors for the Cs⁺ and Re³⁺ species were obtained from the tables published by Thomas and Umeda⁴ while values for Cl⁻ were from tables published by Berguis et al.⁵

Wilson's method⁶ was used to derive an overall temperature factor of 0.8 and also an absolute scale factor k for the complete correlated data. This temperature factor was applied to each of the four atoms located from the Patterson synthesis, and Fₒ was calculated for some of the reflections (hkℓ). It was immediately obvious that these values of Fₒ were not on the same scale as corresponding values k/Fₒ. When the scale factor was adjusted and the calculation repeated better agreement was obtained. R-factors for all three sets of reflections (hk0),(0kℓ),(h0ℓ) were 0.36, 0.29 and 0.26 respectively. Lipson and Cochran⁷ suggest that values of R which are less than 0.40 are significant when examining the correctness of an acentric trial structure.
Accordingly, it was decided to construct electron density difference projections of the unit cell contents on to each of its three orthogonal faces. These maps were no use as atoms were not unambiguously resolved in them. The reasons for this emerged as the analysis proceeded.

The R-factor for all 501 recorded (hkℓ) reflections was 0.34, and this complete set was used to calculate the three-dimensional difference map of an asymmetric part of the unit cell. One section of this map (x = 0.25) is presented as it was used, together with a contoured key, in figure 7. This section is the mirror plane of the space group and has been selected for discussion as it demonstrates the main features of the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ anion and its elucidation from these difference maps.

(i) The rhenium atom included in the $F_0$ calculation with coordinates $x = 0.25, y = 0.14, z = 0.00$ appeared near the centre of a high peak in the difference map.

(ii) Since the $b$ and $c$ axes were nearly equal the square grid of this section was to scale. It appeared, therefore, that this rhenium atom was surrounded by three equidistant chlorine atoms at the centres of three intermediate height peaks.

(iii) A fourth peak of similar height appeared to bridge positions on both sides of the mirror plane occupied by the other rhenium atom included in the $F_0$ calculation.
(iv) The highest peak on this section undoubtedly located a fourfold cesium atom position.

(v) One peak could not be accounted for as it was very close to an established cesium atom position.

The same configuration of chlorine atoms was found around the other rhenium atom on general sections of this map. No other high peak occurred on these sections except in this rhenium atom position. It was considered unsatisfactory to interpret these high peaks as indicating that the temperature factors used in $F_c$ calculations were not low enough. They persisted in difference maps produced during three cycles of refinement, in the course of which all atoms were included in $F_c$ calculations and the R-factor dropped from 0.34 to 0.24.

During these cycles it was considered desirable to shift the origin to coincide with the cesium atom located on the fourfold special equivalent position $x = y = 0.00, z = -0.22$. Coordinates of atoms were improved by shifting them up lines of steepest gradient in electron density difference maps. The magnitudes of these shifts were first determined by trial and error, and ultimately by experience, since accurate calculations for acentric crystals are somewhat difficult. Attempts at temperature parameter refinement were unsuccessful, and this was assumed to be connected with the problem of high peaks occurring on rhenium atom sites. This assumption subsequently proved to be correct, but the state of temperature factor refinement is still far from satisfactory.
Throughout this work time was saved by calculating the difference maps only in regions known to contain atoms. When further progress from these maps seemed unlikely an electron density map was constructed for the entire asymmetric unit using \( F_o \) and \( \langle hkl \rangle \) values in the calculations. This synthesis showed no spurious peaks and confirmed that there were no other atoms in parts of the unit cell which had not been examined during the refinement. The entire \( x = 0.25 \) section of this map is reproduced in alphabetic form together with a contoured key in figure 8. By suppressing the background, the alphabetic plot has been made to show the arrangement of the two \( [\text{Re}_3\text{Cl}_{12}]^{3-} \) anions about this section. The other two anions in the unit cell are on the \( x = 0.75 \) section which is the mirror image of this one. Thus this section demonstrates the distribution of the complete contents of the unit cell, except for the face centred equivalent positions of the cesium atom on the origin.

At this stage of the analysis a further structure factor calculation using scattering factors corrected for anomalous dispersion\(^{17}\) showed no improvement in the \( R \)-factor which was 0.21 for 453 reflections excluding those recorded as unobserved. Bond lengths and angles were calculated and a model of the \( [\text{Re}_3\text{Cl}_{12}]^{3-} \) anion was constructed (frontispiece). These results were published\(^{36}\) (reprint pocket) and the data sent away for least-squares refinement.
4. **Least-squares refinement.**

In this method a set of observational equations relating changes in $F_c$ to changes in all the variable parameters, give rise to a set of normal equations which can be solved to give values for these changes which minimize the function.

$$\phi = \sum \frac{w_n}{r} (F_o - F_c)^2$$

where $w_n$ is the weight assigned to each of the $n$ observations. The best solution is obtained by inverting the full matrix of the normal equations. This process necessarily entails formidable calculations, and various time-saving methods of approximation have been fully discussed by Sparks.\(^{37}\) In the present work a program written by Busing, Martin and Levy,\(^{38}\) which utilizes the full matrix, was run on the IBM 7090 computer at the Weapons Research Establishment in Adelaide, South Australia.

In a first cycle shifts were derived for an overall scale factor, all variable atomic coordinates and all temperature factors. When these shifts were applied some temperature factors were not positive-definitive and so could not be used in new structure factor calculations. The new coordinates did lead to an improvement in $R$ (0.19 for 453 observed reflections) when used in conjunction with the more reasonable temperature factors. A careful examination of $R$-factors for data derived from different sets of films revealed very poor correlation between the sets. In these $F_c$ was generally less than $F_o$.
and this was presumed to explain the peaks occurring on difference maps in positions from which rhenium atoms were supposedly subtracted. The data were rescaled in sets and the R-factor dropped to 0.15 for 453 observed reflections. A second cycle of least-squares refinement was attempted with no further success. Some temperature factors shifted negative while the maximum shift and mean standard error in chlorine atom coordinates were 0.017 Å and 0.007 Å respectively.

The correlation matrix from the refinement indicated serious interaction between the z coordinates of the various heavy atoms. Further work was clearly needed to investigate the effect this interaction was having on the refinement. Also the refinement program itself required investigation to see whether it was able to handle this whole problem correctly. Since a paper describing a parallel, but highly refined, analysis of this same structure had by this time been published, it was not considered worthwhile pursuing these expensive and time consuming investigations.

The appendix contains a list of structure factors $F_o$ and $F_c$ (page 110) calculated using atomic parameters listed in the next section. When the 453 observed reflections were sorted into four equal groups increasing in $\sin \theta/\lambda$, relative R-factors gave some evidence of extinction on the innermost intense reflections.
Median value of \( \sin \frac{\theta}{\lambda} \)  
\[0.213 \quad 0.321 \quad 0.407 \quad 0.494\]

R-factor  
\[0.16 \quad 0.14 \quad 0.14 \quad 0.16\]

No. reflections in group  
\[113 \quad 113 \quad 113 \quad 114\]

\( F_0 \) values affected in this way are marked † in the structure factor listing.

This listing is followed by all sections of a three-dimensional electron density difference map (pages 111 to 125) calculated using these structure factors and corresponding calculated values of \( \varphi(hk\ell) \). It has been included as evidence for the present state of the structure analysis. Using the final atomic coordinates it is possible to ascertain the following facts from it.

(i) Considering the high detail of the alphanemic scale, rhenium atoms now appear in flat positions on the map.

(ii) The three cesium atoms lie in holes at the bottom end of the scale (\( -9.8e/\AA^3 \)). This situation would undoubtedly improve with satisfactory temperature factor refinement.

(iii) All chlorine atoms occupy flat positions on the map.

(iv) There is no peak exceeding the upper end of the alphanemic scale (\( 5.8e/\AA^3 \)) which could correspond to an unlocated atom.

5. Final atomic parameters

This list sets out fractional coordinates obtained from the second cycle of least-squares refinement together with temperature
factors from the first cycle \((B_1)\), the second cycle \((B_2)\), and the values used in the final structure factor and Fourier calculations \((B_3)\).

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(B_1)</th>
<th>(B_2)</th>
<th>(B_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs 1</td>
<td>0.0000*</td>
<td>0.0000*</td>
<td>0.0000*</td>
<td>1.36</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>Cs 2</td>
<td>0.2500*</td>
<td>0.3218</td>
<td>0.8782</td>
<td>1.80</td>
<td>2.09</td>
<td>2.09</td>
</tr>
<tr>
<td>Cs 3</td>
<td>0.2500*</td>
<td>0.0936</td>
<td>0.6061</td>
<td>2.92</td>
<td>2.81</td>
<td>2.81</td>
</tr>
<tr>
<td>Re 4</td>
<td>0.2500*</td>
<td>0.1415</td>
<td>0.2224</td>
<td>0.01</td>
<td>-0.20</td>
<td>1.00</td>
</tr>
<tr>
<td>Re 5</td>
<td>0.1540</td>
<td>0.2850</td>
<td>0.2710</td>
<td>0.71</td>
<td>0.69</td>
<td>1.00</td>
</tr>
<tr>
<td>Cl 6</td>
<td>0.2500*</td>
<td>0.1612</td>
<td>0.0533</td>
<td>1.86</td>
<td>1.54</td>
<td>1.54</td>
</tr>
<tr>
<td>Cl 7</td>
<td>0.2500*</td>
<td>0.4579</td>
<td>0.6590</td>
<td>-0.68</td>
<td>0.96</td>
<td>3.50</td>
</tr>
<tr>
<td>Cl 8</td>
<td>0.2500*</td>
<td>0.0674</td>
<td>0.3605</td>
<td>0.61</td>
<td>1.14</td>
<td>1.14</td>
</tr>
<tr>
<td>Cl 9</td>
<td>0.1027</td>
<td>0.3490</td>
<td>0.1137</td>
<td>2.41</td>
<td>2.02</td>
<td>2.02</td>
</tr>
<tr>
<td>Cl 10</td>
<td>0.0764</td>
<td>0.1279</td>
<td>0.7855</td>
<td>2.83</td>
<td>3.52</td>
<td>3.50</td>
</tr>
<tr>
<td>Cl 11</td>
<td>0.1079</td>
<td>0.2562</td>
<td>0.4284</td>
<td>2.30</td>
<td>2.62</td>
<td>2.60</td>
</tr>
<tr>
<td>Cl 12</td>
<td>0.2500*</td>
<td>0.4322</td>
<td>0.3117</td>
<td>0.01</td>
<td>-0.93</td>
<td>3.66</td>
</tr>
<tr>
<td>Cl 13</td>
<td>0.0254</td>
<td>0.1469</td>
<td>0.2198</td>
<td>3.77</td>
<td>3.66</td>
<td>3.66</td>
</tr>
</tbody>
</table>

Coordinates marked with an asterisk cannot be refined as they are determined exactly by the choice of origin and by space group symmetry.

E. DETAILS OF THE STRUCTURE.

Calculations of interatomic distances and angles established the trimeric configuration of the \([\text{Re}_3\text{Cl}_{12}]^{3-}\) anion before least-squares refinement.
### Table of Least-squares Planes in the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ Anion

All distances are given in angstroms.

#### Plane of the triangle of rhenium atoms.

Equation $0.00000 x - 4.17369 y + 13.44018 z + 2.35542 = 0$

<table>
<thead>
<tr>
<th>Distance from plane of atoms forming plane</th>
<th>Distance from plane of other atoms in the anion.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>6 -2.230</td>
</tr>
<tr>
<td>5 = 5'</td>
<td>9 -2.277</td>
</tr>
<tr>
<td>7</td>
<td>9' -2.277</td>
</tr>
<tr>
<td>10 = 10'</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
</tr>
<tr>
<td>13 = 13'</td>
<td></td>
</tr>
</tbody>
</table>

#### Plane through atoms (5, 9, 10, 11, 13):

Equation $5.24007 x + 11.74525 y + 3.34545 z + 4.97189 = 0$

<table>
<thead>
<tr>
<th>Distance from plane of atoms forming plane</th>
<th>Distance from plane of other atoms in the anion.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4 -1.256</td>
</tr>
<tr>
<td>9</td>
<td>6 -1.572</td>
</tr>
<tr>
<td>10</td>
<td>8 -1.664</td>
</tr>
<tr>
<td>11</td>
<td>7 -3.624</td>
</tr>
<tr>
<td>13</td>
<td>12 2.457</td>
</tr>
</tbody>
</table>

...
In figure 9a the anion is numbered to demonstrate which atoms are related by the crystallographic mirror plane. The numbers used are those assigned to each atom in the previous section. Figure 9b contains a plan of the plane of the triangle of rhenium atoms. It shows quite clearly two other related mirror planes in the anion, and is labelled with some important bond lengths and bond angles calculated using final atomic coordinates.

The distances of closest approach of cesium atoms to atoms of the anion are listed below.

1 7 3.330 Å
2 6 3.396 Å
3 10 3.146 Å

The full symmetry of D_{3h} was proved by calculating the best least-squares planes through the nine atoms apparently in the plane of the triangle of rhenium atoms (7, 3, 5, 10, 12, 13, 5', 10', 13') and through the five atoms (5, 9, 10, 11, 13) in an environment similar to (4, 6, 7, 8, 12) on the crystallographic mirror plane. These results are set out on the facing page. In every case atoms lie within 0.10 Å of least-squares planes to which they contribute. Distances of other atoms in the anion to these planes demonstrate that they closely approximate to mirror planes of the anion. Atoms related across the first plane lie within 0.05 Å of mirror image positions. The corresponding figure for the second plane is 0.26 Å, omitting
the poor result for the 8,11' pair. This is due partly to
the plane being defined by fewer atoms, and partly to
uncertainties in the coordinates of the light chlorine atoms.

A description of the trimeric anion is best referred to
the plane through the triangle of bonded rhenium atoms. Each
rhenium atom is bonded to two bridging chlorine atoms and one
terminal chlorine atom in this plane and also to two chlorine
atoms on either side of it. Rhenium atoms are therefore
seven-coordinate, each being at the centre of a distorted
pentagonal bipyramid which has as its apices two chlorine
atoms.

Discussion of these results is deferred until chapter 4.
CHAPTER III  THE CRYSTAL STRUCTURE ANALYSIS
OF (Ph₄As)₂Re₃Cl₁₇⁻

A. INTRODUCTION.

As soon as the configuration of the [Re₃Cl₁₂]³⁻ anion was established, Dr. Fergusson directed the author's attention to the compound (Ph₄As)₂Re₃Cl₁₇⁻, which he had isolated in earlier studies on the effects of various cations on the 
"[ReCl₄]⁻" anion. It seemed likely that this compound contained an [Re₃Cl₁₁]²⁻ anion with a configuration closely related to that of the [Re₃Cl₁₂]³⁻ anion. The main questions posed by this hypothesis were, which chlorine atom was removed from the [Re₃Cl₁₂]³⁻ anion, and what alteration in the stereochemistry of the rhenium atoms resulted from its removal? Answers were provided by the partial crystal structure analysis which is described in this chapter.

All of the equipment and many of the experimental methods used in determining the CsReCl₄ structure were also used in this work. The analysis was carried out using Patterson and Fourier projection methods followed by three-dimensional electron density difference maps. Calculations in projection and for centro-symmetric crystals were necessarily simpler than those already outlined. Wherever applicable, steps in this analysis have been described with reference to the earlier work.
b. Experimental

1. Crystals

Several samples of crystals were supplied by Dr. Fergusson. One batch seemed to consist of particularly well-formed single crystals as shown by regular and complete extinction under crossed polaroids of the polarizing microscope. The best crystals in this batch appeared to have a habit identical to that illustrated in Bunn for 1,4 dinitro 2,5 dibromo-benzene of crystal class 1. A random sample of these crystals gave a powder diffraction photograph (fig. 10) indistinguishable from that obtained from the compound \([ (\text{C}_6\text{H}_5)_4\text{As} ]_2\text{Re}_2\text{Cl}_{11}\) isolated and analysed during the earlier work. Another small sample was used to measure a lower limit for the density \((D_m = 1.95 \text{ gm cm}^{-3})\) using the Berman density balance.

2. Unit cell dimensions

One well-formed crystal of average dimension 0.12 mm was selected for single crystal diffraction studies. It was set on the Weissenberg camera from zero layer line rotation photographs. The identity period along the axis of rotation was approximately 9.8 Å. Zero and first layer Weissenberg photographs revealed no systematic absences and no orthogonal central point rows. Rotation and Weissenberg photographs taken about another axis with approximate identity period 12.0 Å confirmed a triclinic unit cell with a long third axis. Both
Weissenberg zero layer photographs were calibrated with NaCl powder lines (fig. 16a) and used to determine five accurate reciprocal lattice parameters. The sixth accurate reciprocal lattice parameter was determined from precession photographs. Parameters ultimately used in all calculations are tabulated below. Problems encountered in these determinations are discussed in chapter V.

### Lattice parameters

<table>
<thead>
<tr>
<th>Real unit cell</th>
<th>Reciprocal unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 12.01 Å</td>
<td>a* 0.0954 Å</td>
</tr>
<tr>
<td>b 26.22 Å</td>
<td>b* 0.0400 Å</td>
</tr>
<tr>
<td>c 9.87 Å</td>
<td>c* 0.1120 Å</td>
</tr>
<tr>
<td>( \alpha ) 88.5°</td>
<td>( \alpha^* ) 98.6°</td>
</tr>
<tr>
<td>( \beta ) 66.2°</td>
<td>( \beta^* ) 115.2°</td>
</tr>
<tr>
<td>( \gamma ) 105.4°</td>
<td>( \gamma^* ) 72.5°</td>
</tr>
<tr>
<td>V₀ 2712 Å³</td>
<td>V* 0.000368 Å⁻³</td>
</tr>
</tbody>
</table>

3. *Density and absorption*

If there are \( n \) molecules in the unit cell of a crystal its density can be calculated by the formula

\[
D_x = \frac{nM}{NV_0}
\]

where \( N \) is the Avogadro number and \( M \) the molecular weight. If \( D_m \) is substituted for \( D_x \) the equation can be solved to give a near integral value for \( n \). The correct integral value can be deduced and used to calculate an accurate value for \( D_x \). For \((\text{Ph}_4\text{As})_2\text{Re}_3\text{Cl}_{11}\)
the value of \(\alpha\) obtained from \(\frac{D_m}{m}\) was 1.85, indicating that there were two molecules in the unit cell. This led to a calculated density of 2.10 gm cm\(^{-3}\). The agreement between \(\frac{D_m}{m}\) and \(\frac{D_o}{o}\) was considered adequate to establish that there were two molecules in the unit cell, and no attempts were made to determine \(\frac{D_m}{m}\) more accurately, although this could doubtless be done (e.g. by flotation).

The calculated density was used to derive a linear absorption coefficient (\(\mu\)) of 185 cm\(^{-1}\) for CuK\(\alpha\) radiation.\(^{37}\) Assuming the mounted crystal was a sphere of radius \(R\) the value of \(\mu R\) was approximately 1.1 and absorption correction factors for \(\theta = 0^\circ\) and \(\theta = 90^\circ\) were 4.70 and 3.25 respectively. As these factors were not too different, CuK\(\alpha\) radiation was used to collect three-dimensional diffraction data. Even if absorption had been unfavourably high it would have been necessary to use CuK\(\alpha\) radiation to obtain Weissenberg photographs which it was practical to index. In the precession method it was possible to index the compressed reciprocal lattice pattern obtained from MoK\(\alpha\) radiation which was used for all precession photographs. Using the calculated density \(\mu R\) was equal to 0.55 and the difference between extreme absorption factors was less than 10\%. Any errors incurred by failing to make absorption corrections would therefore be much less than those inherent in the visual estimation of intensities.
4. **Photography**

Equi-inclination Weissenberg photographs were then taken of each of the reciprocal lattice layers $l = 0$ to $l = 5$ using five films in a pack and exposure times of five days. The full traverse of the Unicam instrument left part of the triclinic reciprocal lattice unphotographed, and so further sets of photographs were obtained using a small traverse after the crystal had been rotated through 90°. It was not found necessary to use this extra data during the analysis, but it was recorded while the crystal was mounted in case it should be needed in the future.

After the crystal was reset on the precession camera photographs were obtained of the $0k\ell$, $1k\ell$, $2k\ell$, $3k\ell$ and $h0\ell$ reciprocal lattice levels using Mo radiation. The $0k\ell$ photograph shown in figure 18c was taken within unfiltered radiation. The $1k\ell$ layer (fig. 18d) was recorded using filtered radiation and four separate exposures of 230, 105, 68 and 21 hours respectively. This data was intended to provide a means of correlating the three-dimensional Weissenberg layers. All other photographs were used extensively to assist with indexing the Weissenberg data.

5. **Indexing and intensity measurement**

Unit cell parameters listed in section 3 do not describe the reduced cell in this structure. They do describe the only cell on which it was convenient to base the indexing of
Weissenberg photographs. In this work the cell was treated as all-obtuse; \( \alpha \) and \( \beta \) were changed to be acute (as listed) at a later stage of the analysis.

As each reflection was indexed, its relative intensity was estimated by visual comparison with a standard scale. The five films from each layer line set were correlated in the same way as has already been described for CsReCl\(_4\). After the necessary corrections had been applied to both Weissenberg and 1kl precession data, reflections common to both these sets were compared to permit correlation of the six different reciprocal lattice layers.

All these matters are discussed in detail elsewhere in this thesis.

Most reflections for which \( \sin \theta/\lambda < 0.4 \) were estimated in this way, the data within this sphere being incomplete only on account of the reflections not recorded on the main set of films. Some data outside this sphere were measured so that the final correlated set contained 3,186 independent reflections. At least another 3,000 reflections occur at higher angles where indexing would be a long and difficult job.

C. OUTLINE OF METHODS

1. Procedure

Locating the contents of a unit cell of this size would normally entail complete three-dimensional analysis. In this
case it was hoped to use a combination of Patterson and Fourier projections to obtain the positions of three rhenium and also two arsenic atoms. These atoms would then be used to locate as many light atoms as possible by three-dimensional electron density difference maps. Before describing the application of these methods it is necessary to summarize some theory relevant to the calculations.

2. Patterson projections

The expression for the value of the Patterson function at any point \( U,V,W \) in vector space has been given on page 17.

\[
P(U,V,W) = \frac{1}{V} \sum_{h \neq 0} \sum_{k \neq 0} \sum_{l \neq 0} |P(hk\ell)|^2 \cos \left( \frac{2\pi}{\ell} (hU+kV+lW) \right)
\]

If the summation is carried out using only those reflections with a zero \( \ell \) index, the resulting map is a projection of the three-dimensional Patterson function down the \( w \)-axis. Although this map contains no information about \( w \) coordinates of Patterson peaks, it can sometimes be combined with a projection down one of the other axes to give these coordinates, and hence to give \( x,y \) and \( z \) coordinates for heavy atoms in the unit cell.

If there are \( n \) atoms in the unit cell there can be \( n(n-1) \) peaks in the complete Patterson synthesis. When these are projected on to one face of the cell only the largest peaks, corresponding to vectors between the heaviest atoms, are very likely to be resolved. The disadvantages of poor resolution are frequently outweighed by the much shorter and simpler calculations required to produce two Patterson projections instead
of a full three-dimensional synthesis. This was particularly so in the present work.

The Patterson function is always centrosymmetric at the origin, and so half of the \( n(n-1) \) possible peaks are related by this centre to the other half. If the crystal structure is also centrosymmetric the \( \frac{n(n-1)}{2} \) independent Patterson peaks can be divided into two groups; (i) \( \frac{n}{2} \) single weight peaks representing single vectors between centrosymmetrically related atoms \((x,y,z; -x,-y,-z)\) (ii) \( \frac{n(n-2)}{4} \) double weight peaks defining centrosymmetrically related vectors between atoms not related by the centre of symmetry.

If single weight peaks can be identified in the Patterson function they have coordinates \( u = 2x, v = 2y, w = 2z \), and can give values for the atomic coordinates \( x,y,z \). Unfortunately double weight peaks between a heavy atom and one which is not so heavy may be equivalent to single weight peaks between heavy atoms. In such cases the analysis can become confused. In Patterson projections interpretations based on weights of peaks may be further confused by poor resolution and overlap among the projected peaks.

3. **Structure factor calculations and electron density maps**

The general expression for the structure factor was given on page 25.
\[ F(hk\ell) = \sum_r f_r (hk\ell) \exp \left\{ 2\pi i (hx_r + ky_r + \ell z_r) \right\} \]

Space group \( \bar{P} \) provides the simplest special case of this expression. For every atom in position \( x_r, y_r, z_r \) there is a centrosymmetrically related one in position \( \bar{x}_r, \bar{y}_r, \bar{z}_r \).

\[ F(hk\ell) = 2 \sum_{r=1}^{n} f_r \cos \left\{ 2\pi (hx_r + ky_r + \ell z_r) \right\} \]

where the summation is carried out over only half the atoms in the unit cell. The expression for calculating electron density at a point \( x,y,z \) (page 27) is also simplified since the phase angle \( \varphi(hk\ell) \) is 0 or \( \pi \), and is included in the sign of the structure factor \( F(hk\ell) \).

\[ \rho(XYZ) = \frac{1}{V} \left[ F_{000} + 2 \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} F(hk\ell) \cos 2\pi (hx_r + ky_r + \ell z_r) \right] \]

Heavy atoms, which generally make the largest contributions to \( F(hk\ell) \), can determine the exact signs of a sufficiently large number of observed structure factors to make electron density maps useful at an early stage in the analysis of a centrosymmetric structure.

As with the Patterson synthesis, electron density calculations carried out using all the reflections with one index zero result in a map of the contents of the unit cell projected down the corresponding axis. There are far fewer atoms in a unit cell of real space than there are vector peaks in a corresponding unit cell of vector space. It is often possible to resolve
atoms and solve structures completely from electron density projections down short axes. In the present work electron density difference projections were used only to verify the coordinates of heavy atoms, as the unit cell had no particularly short axis and no light atoms were resolved in the projections.

All projections and sections of the unit cell discussed subsequently were obtained by evaluating the appropriate Patterson or electron density difference function at fractions of 0.03 of the unit cell edges a and c and 0.01 of the unit cell edge b. The grid interval was therefore 0.36 Å parallel to the x-axis, 0.26 Å parallel to the y-axis and 0.30 Å parallel to the z-axis.

D. ANALYSIS OF PROJECTIONS.

1. The (001) Patterson projection

All 393 (hk0) reflections were used to construct a sharpened projection of the Patterson function on the (001) face of the unit cell. Background was suppressed and 90% of the origin peak was removed. The remaining peaks are shown in contoured form in figure 11.

The analysis proceeded on the assumption that there were six rhenium atoms in a centrosymmetric unit cell. Six independent double weight peaks were easily located, and three
of these were close enough to the origin to represent
centrosymmetrically related vectors between bonded atoms in
a rhenium triangle. Corresponding single weight peaks were
not easy to locate, as there were more than three obvious
possibilities, some of which must have represented double
weight rhenium-arsenic vectors. Eventually the three
independent peaks marked with crosses were chosen and atomic
coordinates derived by halving those of the Patterson peaks.

<table>
<thead>
<tr>
<th>Atom</th>
<th>u</th>
<th>v</th>
<th>x_r</th>
<th>y_r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re (1)</td>
<td>.210</td>
<td>.400</td>
<td>.105</td>
<td>.200</td>
</tr>
<tr>
<td>Re (2)</td>
<td>.470</td>
<td>.600</td>
<td>.235</td>
<td>.300</td>
</tr>
<tr>
<td>Re (3)</td>
<td>.210</td>
<td>.500</td>
<td>.105</td>
<td>.250</td>
</tr>
</tbody>
</table>

In the vector convergence method as described by Lipscomb, a single weight peak is located on the vector map and a second
map superimposed with its origin on this peak. When the two
maps are added the highest peaks give the structure relative
to an origin half way between the separate origins of the
contributing maps. Although this projection was ultimately
solved by inspection, superpositions were tried. The results
would have been obtained rapidly if the single weight Re(1)
peak had been used as a superposition point. Unfortunately it,
and the Re(3) single weight peak, were obscured by the double
weight peak in position u = 0.210, v = 0.445.

2. The (001) electron density difference projection

Rhenium atom coordinates derived from the (001) Patterson
projection were used to calculate structure factors for all 393 (hk0) reflections. Scattering factors used in these calculations were those listed in International Tables for X-ray Crystallography. No corrections were made for anomalous dispersion at this stage. Temperature factors were assigned to the atoms on the basis of the low (and possibly incorrect) values obtained in the CsReCl₄ analysis. With obviously poor scaling between k/F₀ and F₀, the R-factor from this calculation was 0.45. An asymmetric unit of the electron density difference projection calculated using these structure factors is shown in figure 12.

High peaks occurred around positions from which rhenium/had been subtracted. This was not considered serious since the same effect had been noticed in the CsReCl₄ analysis as a result of poor scaling. Also the chlorine atoms of an [Re₃Cl₁₁]^{2-} anion could be expected to overlap in this general area. Arsenic atoms were assigned to the two highest peaks remote from this area and a second structure factor calculation revealed a drop in the R-factor to 0.39. The resulting difference map (not shown) showed no residual high peaks, but did suggest slight shifts in some of the coordinates. Coordinates derived for later refinement are listed below, together with values obtained from a very recent cycle of least-squares refinement.
Comparison of the two sets of figures shows that heavy atom coordinates derived from the (001) Patterson and electron density difference projections were not very different from the present refined values. Unfortunately similar success did not attend the analysis of the (100) projection.

3. The (100) Patterson projection

Two hundred and sixteen (0kℓ) reflections were selected from the correlated data and used to construct a sharpened (100) Patterson projection with the origin peak 90% removed. The background was severely suppressed leaving only the heavy peaks shown in contoured form in figure 13.

As before six independent double weight peaks were easily located, three of these being near enough to the origin to confirm the existence of another triangle of bonded rhenium atoms. There remained only two obvious single weight peaks with the V coordinates 0.40, 0.59 and 0.50 obtained from the (001) projections. It was therefore assumed that the peak at V = 0.40, W = 0.00 was actually
two unresolved peaks with V coordinates 0.40 and 0.59 respectively. The three peaks marked with crosses were selected as actual single weight rhenium-rhenium peaks and z coordinates were derived for atoms accordingly. The values given in brackets have been derived from the refined structure.

<table>
<thead>
<tr>
<th>Atom</th>
<th>v</th>
<th>w</th>
<th>y₀</th>
<th>z₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re (1)</td>
<td>.400</td>
<td>.000 (0.002)</td>
<td>.200</td>
<td>.000 (0.001)</td>
</tr>
<tr>
<td>Re (2)</td>
<td>.600</td>
<td>.000 (0.068)</td>
<td>.300</td>
<td>.000 (0.039)</td>
</tr>
<tr>
<td>Re (3)</td>
<td>.500</td>
<td>.380 (0.580)</td>
<td>.250</td>
<td>.190 (0.790)</td>
</tr>
</tbody>
</table>

At the time the alternative (and correct) set of single weight peaks (marked with squares) was completely overlooked. The best R-factor obtained from these coordinates in structure factor calculations was 0.48. Electron density difference maps were unsatisfactory and are not reproduced. Attempts at (h0L) structure factor calculations indicated an incorrect structure. Eventually some measure of agreement was obtained in (0kL), (h0L) and (hkL) structure factor calculations when the signs of all h and k indices were reversed.

It is instructive to examine why this should have been so. The z coordinates of Re(1) and Re(2) were nearly zero, and that of Re(3) was 0.19, which was quite close to the negative of the final refined value (0.19 ± [-0.21] = 0.79). If the final correct arguments in the cosine terms of the structure factor calculation were \( \{hx + ky + Lz\} \), it is clear that structure factors calculated with arguments \( \{-h)x + (-k)y + (-L)z\} \) would have a
correct modulus. In this case initial calculations involved
an incorrect argument of the type \( \{hx + ky + (-z)z\} \). When the
signs of \( h \) and \( k \) were reversed a correct modulus was obtained, but
only because the \( (z) \) terms for two atoms were zero and the third
symmetry was fortuitously close to the required correct value.
If either other symmetry had been finite agreement would have
been random, and the author would have been forced to discover
his error in interpreting the (100) Patterson. As it was, three-
dimensional refinement commenced using only the rhenium coordinates
which had given the best agreement in various trial structure
factor calculations.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( X_\text{R} )</th>
<th>( Y_\text{R} )</th>
<th>( Z_\text{R} )</th>
<th>( B_\text{R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re (1)</td>
<td>.105</td>
<td>.200</td>
<td>.956</td>
<td>1.0</td>
</tr>
<tr>
<td>Re (2)</td>
<td>.230</td>
<td>.295</td>
<td>.010</td>
<td>1.0</td>
</tr>
<tr>
<td>Re (3)</td>
<td>.110</td>
<td>.250</td>
<td>.190</td>
<td>1.0</td>
</tr>
</tbody>
</table>

E. THREE-DIMENSIONAL REFINEMENT

1. Electron density difference maps

Structure factor calculations including the complete data
showed a rapid fall off in agreement with increasing \( \ell \). This
could not be explained at the time, but is consistent with the
argument developed in the last section. The first three-dimensional
difference map was constructed using an "inner sphere" of
reflections for which the values of \( \sin \theta/\ell \) did not exceed 0.1.
The R-factor for these 1,355 reflections was 0.49. This was not considered excessive since many unobserved reflections were entered with $F_0$ zero. The asymmetric unit was covered by taking complete sections parallel to the (001) face of the unit cell with the $z$ fractional coordinate increasing in intervals of 0.03 from 0.00 to 0.48. The resulting maps each contained 3,434 values of the difference function $D$ plotted on an alphabetic scale.

As they occupy thirty-four quarto pages, it is clearly impossible to present them and discuss in detail the elucidation and refinement of the structure through all six cycles which were completed before least-squares refinement was undertaken. One complete set of maps is presented in the appendix as final evidence for the structure (page 442) and will be discussed in later sections.

Progress through each of the six cycles is summarized below.

Cycle 1:

Rhenium atoms were shifted and two arsenic atoms assigned to the two highest peaks remote from the anion. These had $x$ and $y$ coordinates consistent with those derived from the (001) projection. With an enlarged "inner sphere" (1,660 reflections) the R-factor still dropped to 0.44.

Cycle 2:

Atoms appeared in holes indicating that $F_0$ was too large. Real dispersion corrections were applied by subtracting five electrons from all rhenium scattering factors and 1.2 electrons from the arsenic scattering factors. Temperature factors
were increased arbitrarily to 1.5 Å and 2.5 Å for these atoms respectively. Chlorine atoms were assigned to the eleven highest peaks near the rhenium atoms with arbitrary temperature factors of 3.5 Å. The R-factor for the same 1,660 reflections dropped to 0.42.

Cycle 3:

Some chlorine atoms put in to the difference map appeared in holes and were rejected in favour of new high peaks near the rhenium atoms. In all 15 chlorine atoms and 3,186 reflections were included in a structure factor calculation which gave an R-factor of 0.44. From this point on the progress of the refinement was followed by means of the R-factor calculated without reflections observed as having zero intensity. At this stage this figure was 0.35 for 2,558 observed reflections.

Cycle 4:

Five of the fifteen chlorine atoms derived from the previous difference map had to be rejected. The R-factor dropped to 0.31.

Cycle 5:

An eleventh chlorine atom stood out from a map which was, by this time, showing fewer confusing spurious peaks in the neighbourhood of the anion than had been the case in previous cycles. The origin was shifted to bring the anion into the centre of the asymmetric unit by adding 0.50 to all x and z coordinates. The new R-factor was 0.29.
Cycle 6:

No peaks appeared at the level of the sole chlorine atom in cycle 5 and no obvious shifts could be made in any atomic coordinates. Agreement between observed and calculated structure factors now seemed to improve with increases in the $l$ index, or more specifically, with increasing $\sin \theta / \lambda$. This was consistent with the possibility of extinction on the innermost reflections, and also undoubtedly reflected the contributions which the 48 carbon atoms in the asymmetric unit should have been making to the $F_o$ calculations. Accordingly the 2,495 outermost reflections were selected for least-squares refinement, there being an upper limit of 2,499 on the number acceptable to the refinement program.

An attempt to produce an $F_o$ Fourier synthesis was unsuccessful on account of errors in the computer program.

2. Least-squares refinement

One cycle of this type of refinement was undertaken varying all atomic parameters and also scale factors for each block of data derived from separate halves of Weissenberg films. This procedure was adopted to permit crude corrections for extension and contraction of spots on higher layers as it was considered that visual estimations of integrated intensities were insufficiently accurate. Unobserved reflections were included with structure factors corresponding to one-half the minimum observable intensity on Weissenberg films. Apart from
a few of the most intense reflections all the data were weighted equally. The R-factor for 2,495 reflections dropped from 0.30 to 0.24 as a result of the refinement. A correlation matrix showed that the only serious interactions were between the temperature factors of the rhenium atoms and the various scale factors being refined. Final atomic parameters are listed below. The maximum shift and mean standard error in chlorine atom coordinates were 0.168 A and 0.029 A respectively. For rhenium atoms corresponding figures were 0.030 A and 0.004 A.

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re 1</td>
<td>0.6003</td>
<td>0.2035</td>
<td>0.4982</td>
<td>2.738</td>
</tr>
<tr>
<td>Re 2</td>
<td>0.7334</td>
<td>0.2982</td>
<td>0.4606</td>
<td>2.741</td>
</tr>
<tr>
<td>Re 3</td>
<td>0.6110</td>
<td>0.2465</td>
<td>0.7101</td>
<td>2.836</td>
</tr>
<tr>
<td>Cl 4</td>
<td>0.7524</td>
<td>0.1597</td>
<td>0.4638</td>
<td>5.014</td>
</tr>
<tr>
<td>Cl 5</td>
<td>0.4134</td>
<td>0.2161</td>
<td>0.5066</td>
<td>4.877</td>
</tr>
<tr>
<td>Cl 6</td>
<td>0.9251</td>
<td>0.2834</td>
<td>0.4152</td>
<td>5.170</td>
</tr>
<tr>
<td>Cl 7</td>
<td>0.5934</td>
<td>0.3382</td>
<td>0.4477</td>
<td>3.945</td>
</tr>
<tr>
<td>Cl 8</td>
<td>0.7623</td>
<td>0.2221</td>
<td>0.7347</td>
<td>4.772</td>
</tr>
<tr>
<td>Cl 9</td>
<td>0.4504</td>
<td>0.2806</td>
<td>0.7724</td>
<td>6.824</td>
</tr>
<tr>
<td>Cl 10</td>
<td>0.7284</td>
<td>0.3378</td>
<td>0.6937</td>
<td>6.983</td>
</tr>
<tr>
<td>Cl 11</td>
<td>0.4897</td>
<td>0.1629</td>
<td>0.7369</td>
<td>5.896</td>
</tr>
<tr>
<td>Cl 12</td>
<td>0.7063</td>
<td>0.2600</td>
<td>0.2395</td>
<td>6.552</td>
</tr>
<tr>
<td>Cl 13</td>
<td>0.5240</td>
<td>0.1215</td>
<td>0.3802</td>
<td>4.430</td>
</tr>
<tr>
<td>Cl 14</td>
<td>0.8691</td>
<td>0.3837</td>
<td>0.2977</td>
<td>5.439</td>
</tr>
<tr>
<td>As 15</td>
<td>0.0104</td>
<td>0.0802</td>
<td>0.7037</td>
<td>3.406</td>
</tr>
<tr>
<td>As 16</td>
<td>0.3223</td>
<td>0.4253</td>
<td>0.9089</td>
<td>3.680</td>
</tr>
</tbody>
</table>
These parameters were used to calculate the list of 3,086 structure factors given in the appendix (page 133). Innermost reflections, possibly suffering from extinction, are given at the end of this list. A further one hundred outer reflections were obviously incorrectly indexed, and are not listed. The R-factor for the remaining 2,503 reflections excluding those observed as zero was 0.24. As before, R-factors were obtained for groups of data arranged in increasing order according to \( \sin \theta / \lambda \).

| Median value of \( \sin \theta / \lambda \) | 0.171 | 0.249 | 0.295 | 0.341 | 0.387 | 0.438 |
| R-factor | 0.45 | 0.23 | 0.19 | 0.20 | 0.20 | 0.20 |
| No. reflections in group | 423 | 423 | 423 | 423 | 422 | 422 |

The trend towards better agreement at higher angles was still evident. Improvement can be expected at lower angles when carbon atoms are included in these structure factor calculations. On the average these atoms contribute 8% to the intensities of the innermost reflections but only 2% to reflections at \( \sin \theta / \lambda = 0.3 \) and 1% at \( \sin \theta / \lambda = 0.5 \). The corresponding contributions to structure factors are not greater than 28%, 15% and 11%.

Inclusion of these atoms in further refinement may result in slight shifts in some of the established atomic coordinates.

3. Final difference map

Using the structure factors given in the appendix electron density difference maps were constructed for the entire asymmetric
unit. These maps are presented in the appendix (page 142) and are plotted on the same alphabetic scale as the five sections from the cycle 5 difference map which precede them (page 141). The cycle 5 sections are contoured to show the only chlorine atom not put into the calculations at that stage. No other peak of similar height, and certainly no peak of sufficient height to represent an arsenic atom, could be found in the asymmetric unit.

Chlorine and arsenic atoms put into these calculations appear in flat positions on the map. Rhenium atoms lie in troughs which are less deep than a chlorine atom is high. There are many peaks left at about two-thirds the height of a chlorine peak which must be spurious or represent the carbon atoms of the tetraphenyl groups. The whole map will assume a much flatter aspect when these atoms are included in subsequent refinement.

F. DETAILS OF THE STRUCTURE

During the structural analysis of CsReCl\(_4\) three-dimensional difference maps were produced on a grid which closely represented a scaled model of the asymmetric unit in shape and in size. It was a simple matter to picture the \([\text{Re}_3\text{Cl}_{12}]^{3-}\) anion, particularly by looking at the section \(x = 0.25\) (fig. 7 page 103), and also to measure some typical bond lengths and draw conclusions about
Table of Least-squares Planes in the $[\text{Re}_3\text{Cl}_{11}]^{2-}$ Anion (i).

All distances are given in Angstroms.

Mirror plane through the triangle of rhenium atoms.

Equation 11.31782x - 14.44542y + 2.24338z + 4.93419 = 0

<table>
<thead>
<tr>
<th>Distance from plane of atoms forming plane</th>
<th>Distance from plane of other atoms in the anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 .038</td>
<td>4 2.315 5 -2.241</td>
</tr>
<tr>
<td>2 .092</td>
<td>6 2.374 7 -2.099</td>
</tr>
<tr>
<td>3 .013</td>
<td>8 2.133 9 -2.157</td>
</tr>
<tr>
<td>10 -.014</td>
<td></td>
</tr>
<tr>
<td>11 -.092</td>
<td></td>
</tr>
<tr>
<td>12 -.159</td>
<td></td>
</tr>
<tr>
<td>13 .094</td>
<td></td>
</tr>
<tr>
<td>14 .027</td>
<td></td>
</tr>
</tbody>
</table>

Mirror plane normal to the triangle of rhenium atoms.

Equation 4.10377x + 21.06035y + 1.21912z + 8.65792 = 0

<table>
<thead>
<tr>
<th>Distance from plane of atoms forming plane</th>
<th>Distance from plane of other atoms in the anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 -.093</td>
<td>1 -1.301 2 1.194</td>
</tr>
<tr>
<td>8 .044</td>
<td>4 -1.641 6 1.613</td>
</tr>
<tr>
<td>9 .042</td>
<td>5 -1.793 7 1.446</td>
</tr>
<tr>
<td>12 .008</td>
<td>11 -2.319 10 2.291</td>
</tr>
<tr>
<td></td>
<td>13 -3.485 14 3.352</td>
</tr>
</tbody>
</table>
symmetry which were subsequently verified by calculation. No such deductions could be made from the various maps produced during the analysis of \((\text{Ph}_4\text{As})_2\text{Re}_3\text{Cl}_{11}\). The grid intervals were coarse and not proportional to the sides of the unit cell and the rectangular grid did not approximate to the triclinic angles. Although it was always obvious that there were three rhenium atoms and several chlorine atoms in close proximity in the asymmetric unit the actual structure could only be obtained by bond length and angle calculations and by determining some least-squares planes.

The structure of the \([\text{Re}_3\text{Cl}_{11}]^{2-}\) anion is shown in figure 14a (page 176) with the \([\text{Re}_3\text{Cl}_{12}]^{3-}\) anion for comparison. It is clear that the two anions are essentially the same except for the lack of one terminal chlorine atom in \([\text{Re}_3\text{Cl}_{11}]^{2-}\). This has resulted in a reduction of symmetry from \(D_{3h}\) to \(C_{2v}\). Figure 14b contains a plan of the triangle of rhenium atoms and is marked with all the important bond lengths and angles in the anion, calculated using the refined atomic coordinates. The distances of closest approach of arsenic atoms to atoms of the anion are listed below together with the shortest distance between atoms of two neighbouring anions:

\[
\begin{align*}
15 & \quad 5 \quad 4.777 \quad \text{Å} \\
16 & \quad 9 \quad 4.500 \quad \text{Å} \\
8 & \quad 12 \quad 4.915 \quad \text{Å}
\end{align*}
\]

Figure 15 is a projection of the structure down the \(z\)-axis showing both anions and the four arsenic atoms in the unit cell.
Table of Least-squares Planes in the $[\text{Re}_3\text{Cl}_{11}]^{2-}$ Anion. (ii).

All distances are given in Angstroms.

Plane through atoms 1, 4, 5, 10, 13

Equation $-0.71404x + 9.87946y + 7.35146z + 1.25498 = 0$

Distance from plane of atoms forming plane

|   |  
|---|---|
| 1 | -.032 |
| 4 | .040 |
| 5 | .039 |
| 10 | -.013 |
| 13 | -.034 |

Plane through atoms 2, 6, 7, 11, 14

Equation $2.93863x + 12.51479y + 8.78792z + 9.93700 = 0$

Distance from plane of atoms forming plane

|   |  
|---|---|
| 2 | -.002 |
| 6 | -.023 |
| 7 | -.026 |
| 11 | .017 |
| 14 | .035 |
Results of least-squares planes calculations which establish the symmetry mm are set out on the previous facing page. Examination of the angles between Re-Cl bonds in the plane of the triangle of rhenium atoms, and of lengths of bonds from these atoms to the bridging chlorine atoms, suggests that the atoms 1,4,5,10,13 and 2,6,7,11,14 may also lie on planes, although these would not be mirror planes of the anion. Least-squares planes calculations which show this to be true are set out on the facing page.

G. MEAN BOND LENGTHS AND ANGLES

Before these results can be compared with those obtained for \([\text{Re}_3\text{Cl}_{12}]^{3-}\) it is necessary to discuss the bond lengths found in this anion.

Since maximum shifts made in the least-squares refinement were about seven times the estimated mean standard errors in atomic coordinates, conclusions based on these errors must be treated with every caution. Until further refinement has been carried out, the considerable difference in lengths of bonds which are apparently chemically similar, cannot necessarily be regarded as significant. Statistically, the difference between two bond lengths is regarded as significant at the 99.9% confidence level if it exceeds three times the standard deviation of such differences. The standard error in a bond length is calculated from the standard errors in the coordinates of the bonded atoms.\(^{35}\)
<table>
<thead>
<tr>
<th>Bond Description</th>
<th>Value (Å) ± Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re (1) - Re (2)</td>
<td>2.50 ± 0.006</td>
</tr>
<tr>
<td>Re (3) - Re (1,2)</td>
<td>2.43 ± 0.006</td>
</tr>
<tr>
<td>Re (1,2) - Cl (bridging)</td>
<td>2.46 ± 0.03</td>
</tr>
<tr>
<td>Re (3) - Cl (bridging)</td>
<td>2.31 ± 0.03</td>
</tr>
<tr>
<td>Re - Cl (terminal in plane of Re atoms)</td>
<td>2.53 ± 0.03</td>
</tr>
<tr>
<td>Re (1,2) - Cl (terminal out of plane of Re atoms)</td>
<td>2.30 ± 0.03</td>
</tr>
<tr>
<td>Re (3) - Cl (terminal out of plane of Re atoms)</td>
<td>2.19 ± 0.03</td>
</tr>
<tr>
<td>Cl to Cl (non-bonded out of plane atoms)</td>
<td>3.19 ± 0.03</td>
</tr>
<tr>
<td>Cl to Cl (terminal out of plane to in plane)</td>
<td>3.09</td>
</tr>
</tbody>
</table>

Cl (bridging) - Re - Cl (bridging)

- On Re (1) and Re (2) | 183 |
- On Re (3) | 176 |

Cl (bridging) - Re - Cl (terminal in plane)

- To Cl (10) and Cl (11) | 94 |
- To Cl (12) | 89 |

Cl (terminal) - Re - Cl (terminal) | 158 |
In the \([\text{Re}_3\text{Cl}_{11}]^{2-}\) anion the standard error in an individual Re-Cl bond is 0.029 Å while that of an Re-Re bond is 0.006 Å. Differences between individual bonds which are greater than 0.123 Å and 0.025 Å respectively, are therefore significant. Such differences exist between the two chemically dissimilar Re-Re bonds; with one exception between the two dissimilar Re-Cl bridging bonds; and between the in plane and out of plane terminal bonds.

Mean lengths of bonds which are apparently chemically similar are given in the opposite table. It is recognised that further investigation, particularly location of the phenyl groups in the cations, may demonstrate that other differences in bond lengths are as significant as those pointed out in this section.

Values for chemically similar bond angles are also listed. Apart from the Cl (bridging) - Re-Cl (bridging) angles (which are fixed by bond lengths), it is not possible to assess the significance of various differences until atomic coordinates are more certain. Angles related by the twofold rotation axis of the anion have been grouped together and the angle between the terminal chlorine atoms on Re(3) grouped with similar angles on Re(1) and Re(2).
H. **FURTHER WORK.**

This investigation was primarily undertaken to determine the difference in structure between the \([\text{Re}_2\text{Cl}_{11}]^{2-}\) and the \([\text{Re}_2\text{Cl}_{12}]^{3-}\) anions. The composition of the \([\text{Re}_2\text{Cl}_{11}]^{2-}\) anion was previously established by analysis and from physical measurements. Its existence has been confirmed by this structure determination and its configuration shown to be similar to that of \([\text{Re}_2\text{Cl}_{12}]^{3-}\) with one terminal chlorine atom removed. The final difference map has been examined in the region where this chlorine atom would be located if this structure did contain an \([\text{Re}_2\text{Cl}_{12}]^{3-}\) anion. No peak above half the average level at which chlorine atoms appeared on previous maps can be found. There are many spurious peaks in other parts of the map at the same level as the two peaks which can be located. The largest spurious peak \(\left(\frac{3}{4}\right)\) height of Cl occurs at position \(x=0.51, y=0.23, z=0.66\) which is less than 2 Å from several atoms of the anion, including rhenium atoms, and hence is probably due to series termination effects.

Although evidence for the existence and configuration of this anion is considered conclusive, further refinement is essential to establish the significance of distortions apparent from the present work, and also to determine the positions of the phenyl groups and their effect on the structure.

The configuration of the tetraphenylarsonium cations may also
prove interesting in its own right. Mooney has shown that, in \((\text{Ph}_4\text{As})\,\text{I}\), this cation consists of a central arsenic atom to which four phenyl groups are connected at strictly tetrahedral angles. The apparent point group of this cation was \(D_{2d}\). Zaslow and Rundle have found this symmetry destroyed in the compound \((\text{Ph}_4\text{As})\text{FeCl}_4\) on account of a \(25^\circ\) rotation of the planes of the phenyl groups about the As-C bonds. They suggest this ability to rotate the planes of its phenyl groups may be one reason why this cation is such a good precipitating agent. This theory can certainly be investigated further in the \((\text{Ph}_4\text{As})_2\text{Re}_3\text{Cl}_{11}\) structure.
CHAPTER IV DISCUSSION

A. EXPLANATION AND ACKNOWLEDGEMENT

In the last few months there has been a considerable amount of research in this laboratory in examining various implications of these results. The author wishes to emphasize that his own work consisted entirely of solving the crystal structures. He is especially indebted to Mr. B.H. Robinson and to Miss J.H. Gainsford for permission to include results from some of their recent work in this discussion.

Most of the points of chemical and crystallographic interest were announced in a paper read at the 1963 Annual Conference of the New Zealand Institute of Chemistry and are contained in a letter to the editor of Nature.

Just before this chapter was written the author received pre-prints of two papers from Professor Cotton of the Massachusetts Institute of Technology. One of these gave full details of the independent crystal structure analysis of Cs$_3$Re$_3$Cl$_{12}$ mentioned earlier in this thesis. The other presented a molecular orbital approach to the bonding in this complex. Some of these results are compared with those obtained in the present work.
B. NOMENCLATURE

Throughout this work it has been found convenient to refer to these anions by their formulae. Bertrand et al. state that the proper name of Cs$_3$Re$_3$Cl$_{12}$ is cesium dodecachlorotrithenate (III). Rigorous application of the rules laid down by the Commission on the Nomenclature of Inorganic Chemistry$,^48$ however, leads to the more descriptive name cesium tri-$\mu$-chlorononochlorotrithenium (III). Similarly the compound (Ph$_4$As)$_2$Re$_3$Cl$_{11}$ is described by the systematic name tetraphenylarsonium tri-$\mu$-chlorooctachlorotrithenium (III).

C. CRYSTALLOGRAPHY

1. The two analyses of Cs$_3$Re$_3$Cl$_{12}$

Results obtained from this analysis of Cs$_3$Re$_3$Cl$_{12}$ are in good agreement with those obtained by Bertrand, Cotton and Dollase at M.I.T.$^46$ Unit cell dimensions are in accord within experimental error (all $\pm 0.02$ A).

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>10.66</td>
<td>14.02</td>
<td>14.08</td>
</tr>
<tr>
<td>M.I.T.</td>
<td>10.69</td>
<td>14.00</td>
<td>14.06</td>
</tr>
</tbody>
</table>

The M.I.T. workers report similar difficulties with the least-squares refinement of temperature factors and $z$ coordinates of the heavy atoms. After ten cycles of least-squares refinement, their R-factor for some 580 reflections dropped to 0.18.
(During each cycle, only those parameters which did not interact strongly were allowed to vary.) Chlorine atom positions were then obtained from a difference map and a further nine cycles of least-squares refinement caused the R-factor to drop to 0.073.

No useful comparisons can be made between the temperature factors obtained from the two analyses because of the unsatisfactory refinement already mentioned in the present work (page 34). It is worth noting, however, that the average values for refined rhenium and chlorine atom temperature factors for the \([\text{Re}_3\text{Cl}_{12}]^{3-}\) anion seem lower than those reported by Morrow\(^4^9\) for the anion \([\text{Re}_2\text{OCl}_{11}]^{4-}\) and lower than those obtained for the present partial analysis of the crystal structure containing the \([\text{Re}_3\text{Cl}_{11}]^{2-}\) anion.

\[
\begin{array}{ccc}
\text{Re} & 1.57 & 2.47 & 2.78 \\
\text{Cl} & 2.60 & 3.2 & 4.54
\end{array}
\]

In table 4 (page 178) average values for chemically similar interatomic distances and angles are compared for the \([\text{Re}_2\text{Cl}_{11}]^{2-}\) anion and for both studies of the \([\text{Re}_3\text{Cl}_{12}]^{3-}\) anion. Figures obtained from both studies of the latter anion are in close agreement, except for the Re-Cl (terminal in plane) bond lengths and the non-bonded Cl-Cl interatomic distances. Since the M.I.T. figures have been derived from more complete experimental data and refined further than the author's own results, they are used in the following comparison and discussion of determined rhenium-
Some transition-metal complexes containing metal-metal bonds \(^{46,50,51}\)

<table>
<thead>
<tr>
<th>Group No.</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st row</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>Compound</td>
<td>(\text{Mn}<em>2(\text{CO})</em>{10})</td>
<td>(\text{Fe}<em>3(\text{CO})</em>{12})</td>
<td>(\text{Co}<em>4(\text{CO})</em>{12})</td>
<td></td>
</tr>
<tr>
<td>M-M distance Å</td>
<td>2.93</td>
<td>2.8</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>2nd row</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
</tr>
<tr>
<td>Compound</td>
<td>([\text{Nb}<em>6\text{Cl}</em>{12}]^{2+})</td>
<td>([\text{Mo}<em>6\text{Cl}</em>{18}]^{4+})</td>
<td>(\text{Tc}<em>2(\text{CO})</em>{10})</td>
<td>(\text{Ru}<em>3(\text{CO})</em>{12})</td>
</tr>
<tr>
<td>M-M distance Å</td>
<td>2.85</td>
<td>2.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd row</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
</tr>
<tr>
<td>Compound</td>
<td>([\text{Ta}<em>6\text{Cl}</em>{12}]^{2+})</td>
<td>([\text{W}<em>2\text{Cl}</em>{9}]^{3-})</td>
<td>([\text{Re}<em>3\text{Cl}</em>{12}]^{3-})</td>
<td>(\text{Os}<em>3(\text{CO})</em>{12})</td>
</tr>
<tr>
<td>M-M distance Å</td>
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<td>2.88</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{Re}<em>2(\text{CO})</em>{10})</td>
</tr>
</tbody>
</table>
rhenium and rhenium-chlorine bond lengths. Figures given in parentheses in table 4 are standard deviations calculated from the standard errors in atomic coordinates estimated during the least-squares refinement.

2. Rhenium-rhenium bond lengths

The $[\text{Re}_3\text{Cl}_{12}]^{3-}$ anion provides the first confirmed example of a metal-metal bond between halogen bridged rhenium atoms. There are many examples of metal-metal bonds in the transition series. Some of these compounds and bond lengths are shown in the facing table. Two of these lengths are as short as the 2.48 Å bond found in $[\text{Re}_3\text{Cl}_{12}]^{3-}$. The 2.41 Å W-W bond in $[\text{W}_2\text{Cl}_9]^{3-}$ is particularly interesting since tungsten is an adjacent element to rhenium in the third row transition series, and it has been shown that this short length corresponds to a metal-metal multiple bond. The Re-Re bond is significantly shorter than the interatomic distance found in rhenium metal (2.74 Å) and also shorter than the distance Pauling has estimated for a Re-Re single bond (2.56 Å). A Re-Re double bond is included in the bonding scheme for these anions postulated in section E of this chapter.

The significant difference in length between the two Re-Re bonds found in $[\text{Re}_3\text{Cl}_{11}]^{2-}$ is assumed to be a consequence of there being no terminal in plane chlorine atom on Re(3).
Recently an even shorter Re-Re bond (2.22 Å) has been reported by some Russian workers\textsuperscript{15} who have elucidated the structure of the \([\text{Re}_2\text{Cl}_8]^{4-}\) anion in \((\text{C}_5\text{H}_5\text{NH})\text{HRe}^{\text{II}}\text{Cl}_4\). This work is in a preliminary stage so that this length must be regarded as very approximate.

Cotton and his co-workers have given a full discussion of "metal atom clusters" which occur in this part of the periodic table.\textsuperscript{46} It is worth observing that technetium is in such a position that its complex halides, like its carbonyl\textsuperscript{51}, could well be expected to provide further examples of direct metal-metal bonding.

3. Rhenium-chlorine bond lengths

From a consideration of covalent radii Pauling\textsuperscript{50} has estimated the length of a Re-Cl single bond to be about 2.35 Å. Values observed by other workers are 2.37 Å \((\text{K}_4\text{Re}^{\text{IV}}\text{OCl}_1)\text{\textsuperscript{49}}\), 2.38 Å \((\text{K}_2\text{Re}^{\text{IV}}\text{Cl}_6)\text{\textsuperscript{54}}\), and 2.43 Å \((\text{C}_{\text{PyH}}\text{HRe}^{\text{II}}\text{Cl}_4)\text{\textsuperscript{15}}\). In the \([\text{Re}_2\text{Cl}_6]^{3-}\) anion the Re-Cl (terminal in plane) bonds (2.52 Å) are significantly longer than the other terminal Re-Cl bonds (2.36 Å). The terminal in plane bonds for \([\text{Re}_3\text{Cl}_{11}]^{2-}\) (2.53 Å) are similarly significantly longer than the other Re-Cl bonds. In each anion this is ascribed to van der Waals repulsions between non-bonded chlorine atoms; an argument which is supported by other interatomic distances and angles listed in table 4.
It is also possible that shorter terminal out of plane bonds are observed in \( \text{[Re}_3\text{Cl}_{11}]^{2-} \) as a consequence of a reduction in van der Waals repulsions when there is one less atom in the anion. This argument is supported by a comparison of the non-bonded Cl-Cl distances of both anions, although it has already been pointed out that conclusions based on apparent distortions in \( \text{[Re}_2\text{Cl}_{11}]^{2-} \) must be treated cautiously until their significance can be properly estimated.

The main point of these differences in the present discussion is that the in plane terminal chlorine atoms are attached to their rhenium atoms by longer, and consequently weaker, bonds than the other singly bonded chlorine atoms.

**D. CHEMICAL IMPLICATIONS**

The long terminal in plane Re-Cl bonds, and the deviations of the angles they make with the out of plane bonds from 90°, imply that there is considerable strain in the \( \text{[Re}_3\text{Cl}_{12}]^{3-} \) anion. It might have been expected, therefore, that the loss of one chlorine would have been accompanied by a change to give a symmetrical anion with a consequent reduction in strain. That such a change has not occurred strongly suggests that the stability of both anions is due mainly to the bonding system within the Re₃ triangle which is strong enough to outweigh considerable strain in the bonds external to it. The loss of one terminal chlorine atom,
which apparently results in some significant distortions in the 
$[\text{Re}_2\text{Cl}_{11}]^{2-}$ anion, would seem to be a consequence of the packing 
requirements of the large $(\text{Ph}_4\text{As})^+$ cations in the crystal lattice. 
This latter point has been investigated by B.H. Robinson,$^{55}$ who 
has made the compound $(\text{Ph}_3\text{MeAs})_3\text{Re}_3\text{Cl}_{12}$. Apparently three of the 
smaller $(\text{Ph}_3\text{MeAs})^+$ cations can pack around an $[\text{Re}_2\text{Cl}_{12}]^{2-}$ anion. 
Further investigations, in which very large cations are being used 
in a endeavour to prepare compounds containing an $[\text{Re}_3\text{Cl}_{10}]^-$ anion, 
have so far been unsuccessful. One large cation has led to the 
isolation of another compound, $(\text{o-phen.H})_2\text{Re}_2\text{Cl}_{11}$, which presumably 
contains an $[\text{Re}_2\text{Cl}_{11}]^{2-}$ anion.

It is also obvious, from the results of these structure 
analyses, that all the complex halides of rhenium (III) for which 
spin-paired tetrahedral structures have been proposed may in fact 
be polymeric with metal-metal bonds. Following up Fergusson's 
observations on the similarity of the visible absorption spectra 
of solutions of the compounds $\text{ReCl}_3\cdot\text{Ph}_3\text{P}$, $(\text{Ph}_4\text{As})_2\text{Re}_2\text{Cl}_{11}$, $\text{ReCl}_3$ 
and $[\text{ReCl}_4]^-$, Gainsford$^{56}$ and Robinson$^{55}$ have prepared a range of 
complex chlorides of Re(III) which might be expected to contain 
triangles of bonded rhenium atoms. Peaks in the visible 
absorption spectra of these compounds in the solid state and in 
solution are listed in table 5 (page 179). The close similarity 
between these spectra is believed to indicate the persistence of 
the trinuclear bonded rhenium arrangement in both states. 
Variations in the number of bonded chlorine atoms, or replacement
of chlorine by triphenylphosphine in the anion, does not affect the spectra significantly.

These observations, together with the structural knowledge that the terminal in plane Re-Cl bonds are weak, suggest that the basic framework for all these structures is $\text{Re}_3\text{Cl}_9$ with three bridging chlorines and also three terminal chlorines on each side of the rhenium plane. The clearest test of these conclusions will undoubtedly lie in crystal structure analyses of the compounds $\text{ReCl}_3\cdot\text{Ph}_3\text{P}$ and $\text{ReCl}_3$.

E. BONDING

The bonding in both $[\text{Re}_2\text{Cl}_{12}]^{3-}$ and $[\text{Re}_3\text{Cl}_{11}]^{2-}$ and also in the hypothetical $[\text{Re}_2\text{Cl}_{10}]^{2-}$ and $\text{Re}_3\text{Cl}_9$ can be simply explained in terms of seven-fold coordination about Re. Each Re atom would direct seven $d^2sp^3$ hybrid orbitals to the corners of a pentagonal bipyramid*. Two of these orbitals would be singly occupied and would overlap with similar orbitals in the adjacent Re atoms to form $\sigma$-bonds. The remaining five vacant hybrid orbitals would be available for the formation of dative $\sigma$-bonds from Cl atoms.

* The maximum deviation from $D_{5h}$ symmetry about one Re atom is 19° for the bridging chlorine atoms and so this description does involve bent bonds. For Re(3) in $[\text{Re}_3\text{Cl}_{11}]^{3-}$ this deviation is reduced to 16° so that this hybridisation scheme provides some explanation of the distortions consequent on removing one Cl atom from the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ anion.
When there is a deficiency of chlorine one of the Re hybrid orbitals may remain vacant. This leaves two electrons on each Re atom in two orbitals which can form \( \Pi \) molecular orbitals and accommodate the total of six electrons, thus accounting for the short Re-Re distance. Since all electrons are paired this scheme also accounts for the experimentally observed diamagnetism in these compounds.

Bertrand et al.\(^{29}\) state that a satisfactory first-order treatment of the metal-metal bonding can be given using an LCAO-MO approach. Each rhenium atom is taken to form a set of hybrid, octahedrally directed \( \sigma \)-orbitals, of which five are used to bind chlorine atoms and the sixth points to the centre of the Re\(_3\) triangle. These combine to form a bonding and an antibonding molecular orbital. Similarly, the \( d_{xy}, d_{yz}, d_{zx} \) orbitals of each rhenium atom combine to give bonding and antibonding molecular orbitals. There are just six bonding orbitals which are filled by the twelve electrons, thus accounting for the experimentally observed diamagnetism. Hans and Cotton have found this approach has value in considering the bonding in other metal atom clusters.
CHAPTER V PHOTOGRAPHIC METHODS

A. WORK WITH WEISSENBERG FILMS

1. Introduction

Buerger\textsuperscript{57} has given a discussion of systematic sources of error encountered when determining lattice parameters from the positions of reflections on cylindrical films. These include eccentricity of the specimen with respect to the axis of the film cylinder, lack of knowledge of the film radius, change of film radius due to shrinkage in the developing process and absorption of X-rays. Each of these errors can be calculated or corrected for by various experimental methods. In this laboratory it has been standard practice to superimpose single crystal Weissenberg films with NaCl powder lines (fig. 16a) following calibration techniques developed by Christ\textsuperscript{58}, Pabst\textsuperscript{59} and Fridrichsons\textsuperscript{60}. From the accurately known cell dimensions of NaCl\textsuperscript{61} it was possible to estimate the $\theta$ angle, and consequently the effective film radius, for every pair of powder lines appearing on both sides of the film. The effective film radius for a pair of single crystal reflections was then calculated by linear interpolation of the radii of the adjacent powder lines. Finally this radius was used to determine the Bragg angle and hence the interplanar spacing for the reflection concerned.
\[ \theta = \frac{s}{4R} \] (where \( s \) is the distance between the reflections measured normal to the powder lines). Statistical accuracy of the order of 0.1% and better has been claimed \( ^{62,63} \) after averaging the results of several determinations of one lattice parameter using relatively few pairs of reflections on a central point row.

Four main criticisms of this method may be offered.

(i) Eccentricity and absorption errors may be different for the powder sample and the single crystal.

(ii) The film radius may vary along the length of the camera. This has been detected from a slight divergence in the supposedly parallel powder lines.

(iii) Reflections at higher angles give best results, but only those on central point rows have been used. Either general high angle reflections should be used, or else the final results for a single parameter should be the mean of individual determinations weighted in favour of the high angle reflections.

(iv) The method of calculation seems to be an unnecessarily complicated way of interpolating accurately known \( \theta \) values (for the powder lines) for unknown \( \theta \) values (for pairs of reflections).

Careful experimental work will reduce errors due to (i) and (ii).

Use of all available high angle reflections means simultaneously determining three reciprocal lattice parameters by solving a set of normal equations derived from the observational
equations for each reflection. This was not done in the present work because of computational difficulties.

Application of Newton's interpolation formula for divided differences reduces errors due to (ii) and avoids all determinations of effective film radii during the calculation of $\theta$.

2. The interpolation method

Consider $f(x)$ with values given for $x = x_0, x_1, x_2$ etc.
The differences $x_1 - x_0, x_2 - x_1$ etc., are not necessarily equal.
Divided differences of various orders are defined as follows where $f_n = f(x_n)$.

First order $\left[f_n f_{n+1}\right] = \frac{f_n - f_{n+1}}{x_n - x_{n+1}} \quad 1.$

Second order $\left[f_n f_{n+1} f_{n+2}\right] = \frac{\left[f_n f_{n+1}\right] - \left[f_{n+1} f_{n+2}\right]}{x_n - x_{n+2}} \quad 2.$

Third order $\left[f_n f_{n+1} f_{n+2} f_{n+3}\right] = \frac{\left[f_n f_{n+1} f_{n+2}\right] - \left[f_{n+1} f_{n+2} f_{n+3}\right]}{x_n - x_{n+3}} \quad 3.$

e tc.

From 1. $f_n = f_{n+1} + (x_n - x_{n+1}) \left[f_n f_{n+1}\right]$ 

From 2. $f_n = f_{n+1} + (x_n - x_{n+1}) \left[f_{n+1} f_{n+2}\right] + (x_n - x_{n+1}) \left(x_n - x_{n+2}\right) \left[f_n f_{n+1} f_{n+2}\right]$ 

From 3. $f_n = f_{n+1} + (x_n - x_{n+1}) \left[f_{n+1} f_{n+2}\right] + (x_n - x_{n+1}) (x_n - x_{n+2}) \left[f_{n+1} f_{n+2} f_{n+3}\right] + (x_n - x_{n+1}) (x_n - x_{n+2}) (x_n - x_{n+3}) \left[f_n f_{n+1} f_{n+2} f_{n+3}\right]$ 

e tc.
The Bragg angle of a pair of powder lines, or of a pair of single crystal reflections, on a Weissenberg film is a function of the separation distance ($x_n$ or $s$ fig. 16b) for the pair. Similarly any trigonometric function of this angle is also a function of the separation distance. In particular

$$\sin^2 \theta = f(x_n \text{ or } s),$$

and so the interpolation formula can be applied to determine an unknown $\sin^2 \theta$ value, for a pair of single crystal reflections with separation $s$, from the known $\sin^2 \theta$ values and separation distances of powder lines.

$$\sin^2 \theta = \sin^2 \theta_{x_1} + (s - x_1) \left[ \sin^2 \theta_{x_1} \frac{\sin^2 \theta_{x_2}}{\sin^2 \theta_{x_1}} \right] + (s - x_1) (s - x_2) \left[ \sin^2 \theta_{x_1} \frac{\sin^2 \theta_{x_2}}{\sin^2 \theta_{x_1}} \frac{\sin^2 \theta_{x_3}}{\sin^2 \theta_{x_1}} \right]$$

In practice it has not been found necessary to include higher order divided differences terms.

Since the accuracy of this calculation depends on the magnitude of the actual differences ($x_n - x_{n+1}$), and not on the form of the function involved, the distances can be measured along the line joining a pair of reflections, or indeed along any line which is convenient. If the line joining the pair of reflections marked with circles (fig. 16b) is chosen, errors due to a variable effective film radius will be reduced. Jameson has pointed out that a further consequence of the independence of the result from the form of the function is that distances can be measured in this same direction for reflections which occur on broken central point rows (e.g. the pair marked with
crosses in fig. 16b).

A computer program has been written to handle the interpolation calculations, and also to compute the reciprocal lattice parameter for pairs of reflections on a central point row. The limits of error in cell dimensions determined in this way for both crystals were of the order of 0.2%.

3. Angles and general methods

Reciprocal angles between central point rows on Weissenberg films of the triclinic crystal, were determined by direct proportion based on the self calibration imposed on these films by repetition of the pattern every 180°. With a good vernier rule such angles may be estimated accurately to within 0.1% of their correct value.

Recently Main and Woolfson have described an extremely elegant method for obtaining lattice parameters from Weissenberg photographs with an expected accuracy of 1 part in 1,000. The Bragg angle is determined for a number of high angle general reflections from a measure of the separation of resolved doublets. Cell parameters are refined by an iterative least-squares process in which normal equations are solved to determine corrections for approximate values. The calculation is then repeated using the corrected parameters.

This method seems to be superior to the work described with calibrated films. Even if general high angle reflections were used it is doubtful if comparable results could be obtained with
the facility claimed by Main and Woolfson.

4. **Indexing Weissenberg films**

In the Weissenberg method reciprocal lattice layers perpendicular to the oscillation axis are isolated by screens and recorded, in a distorted fashion, by moving the film cylinder parallel to this axis, so that different parts of the film are exposed to the different reflections produced by the oscillating crystal. Central point rows, which appear as straight lines on these photographs (fig. 16a), are easily indexed and can provide a starting point for indexing the remainder of the pattern. Unfortunately such rows do not generally occur on upper layer photographs of triclinic crystals, so that other methods of indexing must be employed.

The most common of these is to derive coordinates by constructing reciprocal lattice diagrams of the various levels to be indexed. Bunn has described a method for doing this in which all levels are represented at once by projecting one reversed reciprocal lattice axis onto the equatorial plane defined by the other two. The same coordinates can also be calculated by an available computer program, although this method is slow, and the listed results are less readily usable than the projection diagram. Both these methods presuppose a knowledge of all the parameters of the reciprocal unit cell. In the present work they were used as a helpful check on each other and on the indices.
assigned by intensity comparisons with undistorted photographs of the reciprocal lattice produced on a Buerger precession camera.

B. APPLICATIONS OF PRECESSION PHOTOGRAPHY

1. Precession photographs and indexing

In the Buerger precession camera (fig. 17) the crystal and the film are simultaneously oscillated about horizontal and vertical axes. The resultant complex motion causes reciprocal lattice layers which have been set normal to the incident X-ray beam, to be recorded in an undistorted fashion on the film. One particular layer can be isolated by suitable positioning of the film and of the annular screen which excludes unwanted cones of diffracted beams.

Four typical photographs obtained during the present work are shown in figure 18. In the zero layer photographs one reciprocal lattice axis is represented by the central horizontal axis of the film which was parallel to the horizontal spindle on which the crystal was oscillated while the photograph was taken. The other reciprocal axis intersects the horizontal axis at the centre of the film and at the appropriate reciprocal lattice angle. Because two zero level reciprocal lattice layers can be photographed by simply rotating the mounted crystal on the spindle axis, the most obvious application of the method is in the determination of the dimensions of the reciprocal unit cell. This will be discussed separately in a later section.
Indexing precession photographs is as simple as reading the coordinates of a point from a piece of graph paper. Even when the points are very close together, as may happen when a reciprocal lattice with a short axis is photographed with molybdenum radiation, the grid is readily discernible on both zero and higher level photographs. The upper level Weissenberg photographs of \((\text{Ph}_4\text{As})_2\text{Re}_2\text{Cl}_{11}\) (hkl, hk2, hk3, hk4, hk5) were all indexed by comparing intensities of the reciprocal lattice rows which they had in common with the 0kl, 1kl, 2kl and 3kl precession photos.

2. **Intensities from precession photographs**

In both crystal structure analyses intensities of reflections which were common to one precession and several Weissenberg films were used to correlate the latter data and produce one three-dimensional set (pages 16 and 42). The correlations were not good, and the data were ultimately rescaled in sets so as to make the sums of the observed and calculated structure factors equal for data derived from each set of films.

The author found that intensities measured from precession photographs were not as great, and consequently not as accurate, as those obtained under similar conditions by the Weissenberg method. This experience, though not uncommon, does not appear to have been fully explained. Accuracy would have improved with longer exposures, but this was impractical in the present work.
Similarly, larger crystals would have increased the recorded intensities but would also have increased problems associated with absorption.

Further comment on the use of precession photographs to obtain intensity data is concerned with the derivation of intensity scales. The circular area of the reciprocal lattice section which is recorded on the film is a function of the "precession angle", which is the angle of tilt set on an arc located behind the film. It is clear from the photographs of CsReCl$_4$ (fig. 18) that two intense reflections, on either side of the central backstop shadow can be isolated by reducing the radius of the recorded area on the h0l layer. They can then be exposed, for successively increasing intervals of time, on adjacent parts of the film by shifting the film cassette vertically between each exposure. In this way an intensity scale was produced for CsReCl$_4$ and subsequently used in intensity measurements on both crystals.

The scale was a good one in that there appeared to be definite changes in intensity in proceeding from any one reflection to its neighbours. It was, however, not very easy to use with the reciprocal lattice photographs which had been taken with a very much larger precession angle, as these reflections were more diffuse. Although this discrepancy may have contributed to the poor quality of the data derived from precession films, it is still considered that the low level at which these intensities were generally recorded was the major reason for their unreliability. The poor agreement for the outermost group of reflections in the
R-factor table for CsReCl$_4$ (page 35) can be attributed to precession data.

Further evidence of the poor quality of this data was the unreliable correlation initially achieved for the three-dimensional data sets. Because of this experience with CsReCl$_4$, a new intensity scale was not obtained for (Ph$_4$As)$_2$Re$_3$Cl$_{11}$. The correlation was checked and adjusted as soon as structure factor calculations became possible.

3. **Cell dimensions from precession photographs**

It has already been pointed out that the two zero level reciprocal lattice layers which intersect in the spindle axis of the precession camera can both be recorded from the same setting of the crystal relative to this spindle. The angle through which the spindle must be rotated between these planes, together with the reciprocal lengths and angles measured on the films, comprise all the data necessary to determine this lattice.

Dimensionless reciprocal lengths are simply determined by dividing lengths measured on the films by the film to crystal distance. When the two axes recorded on a film are orthogonal (CsReCl$_4$) the best estimates are obtained by measuring the distance between two parallel and well separated rows of points. The method is said to be usually accurate to 2.5 parts per 1,000 which is comparable with Weissenberg methods described elsewhere in this thesis (page 78).
Reciprocal angles measured with protractors are not as accurate as those determined from Weissenberg films, and so the two methods should be regarded as complementary in determining and checking unit cell parameters.

Transformations from the unit cell in reciprocal space to the unit cell in real space are effected by means of well established formulae.\textsuperscript{57,70}

4. \textit{Triclinic crystals and the precession method.}

It has been stated\textsuperscript{71} that since the Weissenberg camera photographs reciprocal lattice planes perpendicular to the spindle axis, and the precession method photographs planes parallel to this axis, the two instruments complement each other by allowing the three principal planes of the reciprocal lattice of a crystal, mounted on a universal head, to be recorded without disturbing the crystal itself. This is incorrect for any setting of a triclinic crystal, since the Weissenberg oscillation axis does not coincide with an axis of the reciprocal lattice. In such cases the crystal must always be reset when changing from one camera to the other. The information gained from precession photographs in the triclinic system, however, makes this effort well worthwhile. Some relevant observations and results for the triclinic system which do not appear in current manuals or instructions for use with the Buerger precession camera,\textsuperscript{23,71} are now outlined.
(i) Difficulties frequently encountered in studies of triclinic crystals include the choice of a suitable unit cell with a right handed system of axes and a consistent set of angles,\textsuperscript{23,28} and the assignment of correct indices to reflections recorded on a set of Weissenberg films. In the author's experience these problems are logically and unambiguously overcome with the aid of precession photographs of two intersecting zero level reciprocal lattice layers.

(ii) The angle through which the spindle axis of the precession camera must be turned to move from one zero level reciprocal lattice layer to another is not equal to the reciprocal lattice angle between these layers. This situation is illustrated in figure 19 (page 184) in which \( z^* \) is arbitrarily chosen as the spindle axis, and \( G \) is the rotation angle corresponding to the reciprocal lattice angle \( \gamma^* \). It can be shown from a consideration of the various triangles involved in the figure that

\[
\cos G = \frac{\cos \gamma^* - \cos \alpha^* \cos \beta^*}{\sin \alpha^* \sin \beta^*}
\]

a result which is necessarily symmetrical in \( \alpha^* \) and \( \beta^* \).

Similar results can be derived for the rotation angles \( \alpha \) and \( \beta \) corresponding to the reciprocal angles \( \omega^* \) and \( \phi^* \) respectively.

(iii) The perpendicular distance \( d^* \) between various reciprocal lattice layers (a quantity which is required when setting the camera to record upper levels of the reciprocal lattice) cannot be determined directly from measurements on either zero level film.
## Lattice Parameters

### Real

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<tr>
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<tr>
<td>C*</td>
<td>0.1120</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha</td>
<td>88.571 Sin .999689</td>
</tr>
<tr>
<td>CoS</td>
<td>.724920</td>
</tr>
<tr>
<td>Alpha*</td>
<td>98.600 Sin .988755</td>
</tr>
<tr>
<td>CoS</td>
<td>-149539</td>
</tr>
<tr>
<td>Beta</td>
<td>66.181 Sin .914830</td>
</tr>
<tr>
<td>CoS</td>
<td>.403837</td>
</tr>
<tr>
<td>Beta*</td>
<td>115.200 Sin .904825</td>
</tr>
<tr>
<td>CoS</td>
<td>-425783</td>
</tr>
<tr>
<td>Gamma</td>
<td>105.363 Sin .964264</td>
</tr>
<tr>
<td>CoS</td>
<td>-264943</td>
</tr>
<tr>
<td>Gamma*</td>
<td>72.500 Sin .953717</td>
</tr>
<tr>
<td>CoS</td>
<td>300703</td>
</tr>
</tbody>
</table>

### Precession Camera Setting Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reciprocal</td>
<td>91.428 113.818 74.636</td>
</tr>
<tr>
<td>Layer Index</td>
<td>H .08323 K .03813 L .10130</td>
</tr>
</tbody>
</table>

### Data for Equatorial Projections

<table>
<thead>
<tr>
<th>Projected Reciprocal Cell Edge</th>
<th>Equatorial Reference Cell Edge</th>
<th>First Alternative Angle Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>A*</td>
<td>B*</td>
<td>-52.019 0.04661</td>
</tr>
<tr>
<td>B*</td>
<td>C*</td>
<td>-60.280  0.01206</td>
</tr>
<tr>
<td>C*</td>
<td>A*</td>
<td>3.031   0.04775</td>
</tr>
</tbody>
</table>

Reciprocal distances are in reciprocal angstroms.
but can be calculated from formulae similar to that given below which determines the distance between the $h\ell$, $h'\ell$, $h2\ell$ etc., reciprocal lattice layers.

\[ d^* = b^* \sin \alpha^* \sin \vartheta = b^* \sin \varphi^* \sin \Lambda \]

5. **Manipulating triclinic parameters**

Haendler\(^{72}\) has written a program, for an IBM 1620 computer, which calculates the six real lattice parameters from those of the reciprocal triclinic lattice, and also calculates the real and reciprocal unit cell volumes. This has been considerably extended by the present author so that it also calculates the three possible rotation angles and the three principal interplanar distances in the reciprocal lattice, as well as all the information necessary to construct the three possible equatorial projection diagrams which may be useful in indexing Weissenberg photographs.\(^{73}\) Formulae used in these extensions have been given in the last section or are outlined in Bunn.\(^{40}\)

A sample output listing for $(\text{Ph}_4\text{As})_2\text{Re}_3\text{Cl}_{11}$ is presented on the facing page.
CHAPTER VI COMPUTING

A. INTRODUCTION

With the sole exception of the least-squares refinement, all calculations necessary to this work were carried out by the author at the Mobil Computer Laboratory of the University of Canterbury. The equipment and programs which were used are listed in tables 6a and 6b (page 185). Programs marked with an asterisk were written by the author and are listed in the appendix (pages 186 to 187). Other programs in the CAXR series were written by Dr. B.R. Penfold who also modified programs from other sources for use with the available equipment. These sources were the Institute for Cancer Research in Philadelphia (ICR programs), the University of Colorado in Denver (CUXR program), and the University of Pittsburgh in Pennsylvania, U.S.A. All programs are completely general and, where applicable, can be used in any X-ray crystal structure analysis.

The programs fall into three groups. At the top of the table CAXRO, CAXR12 and CUXR - WEISS 2 assist in the determination of unit cell parameters and in the indexing of Weissenberg films, particularly of triclinic crystals. The main series of programs, in the central portion of the table, processes the indices and intensities of X-ray reflections with the ultimate object of
producing a well resolved map of the Patterson function or of an electron density function. Unit cell parameters and atomic coordinates are used by the final group of three programs, to determine the spatial relationships between the atoms of the structure.

Arrows have been used in the table to indicate that the punched card output of one program forms the bulk of the input to the next program in the series. Plain line connections indicate that the output of one program provides information necessary to initialize one of the main programs. One of the most important features of the main series of programs is that intensity data are hand punched only once, one reflection per card, for input to the LP and absorption correction programs. This is clearly the only reasonable way to handle a large amount of data such as the 3,186 recorded reflections for \((\text{Ph}_4\text{As})_2\text{Re}_3\text{Cl}_{11}\).

In the next section each program is briefly described in the approximate order and in the mode in which it was used. References are given to detailed write-ups where these are available. Unless otherwise stated, programs have been written in the IBM FORTRAN programming language.

B. **PRINCIPAL FUNCTIONS OF PROGRAMS**

CAXRO: Reciprocal lattice parameters are calculated from pairs of reflections on central point rows of Weissenberg films (page 78).
Reciprocal lattice parameters for triclinic crystals are used to calculate real lattice parameters, data for setting the Buerger precession camera, and data to construct the reciprocal lattice projections used in indexing Weissenberg films.

Equi-inclination Weissenberg reflection coordinates are calculated for the general case.

LP and spherical absorption factors are applied to indexed X-ray reflection intensities. Output consists of one card for each reflection containing $h,k,l$, corrected intensity and $\sin \theta/\lambda$.

Two data decks, derived from different films, are searched to find common reflections from which correlation factors are derived. These factors may be applied to the different sets of data in programs CAXR5, CAXR7 or ICR4.

Data from CAXR2 and CAXR3 can be sorted into groups according to $\sin^2 \theta$ or $\sin^3 \theta$ and the average intensity in each group determined.

Intensities are placed on an absolute scale, using information from CAXR9, and are then modified (page 17) so that a sharpened Patterson function can be produced by programs CAXR 6 and ICR1.
CAXR6: Output from the FORTRAN program, CAXR5, is converted to a format which is acceptable to the SPS program ICR1. Reflections with the same \( |h|, |k|, |l| \) indices are combined and modified Fourier coefficients derived from their separate intensities. The positions of these indices and coefficients can be rearranged so that sections of the Patterson function produced by ICR1 have any desired horizontal and vertical crystallographic axes. This program is written entirely in the symbolic programming system (SPS).

CAXR7: This program is written in FORTRAN and SPS. \( |F_o| \) and \( \frac{\sin^2 \theta}{\lambda^2} \) are calculated for each reflection. The multiplicity of the reflection is determined and values of scattering factors, for the particular value of \( \frac{\sin \theta}{\lambda} \), are derived by linear interpolation of tables for up to eight different types of atom. All this information is punched on cards in a format acceptable to the SPS program ICR4. A code number on each card indicates whether or not the reflection was unobserved (entered CAXR7 with zero recorded intensity).

ICR4: On the basis of a trial structure \( F(hk\ell) \) and \( \chi(hk\ell) \) are calculated for each of the observed reflections. \( F_o \) is compared with \( F_c \) and the reflection coded as acceptable or unacceptable according to a logical routine which tests the relative and absolute magnitudes of these quantities for such effects as extinction. The routine may be varied by the user.
and this code may be used to reject logically unacceptable reflections from subsequent calculations. ICR4 is written in SPS.

CAXR11: This program, written in FORTRAN and SPS, can be used to determine R-factors for blocks of ICR4 output data both including and excluding unobserved reflections. Optional features include direct production of a structure factor listing or punching h,k,ℓ,F₀ and F₀, for each reflection, onto cards in a format suitable for listing through the IBM 870 data converting system.

ICR6: This program is written in SPS and performs a similar function to CAXR6 in modifying and arranging F₀ or (F₀ - F₀) coefficients, with the same |h|, |k|, |ℓ| indices, in preparation for the Fourier summation program ICR7.

ICR7: Output from CAXR6 or ICR6, sorted into a special order, is used to calculate two or three-dimensional Fourier summations for any portion of the unit cell at grid intervals which are multiples of \( \frac{1}{100} \) th. of unit cell edges. The resultant Patterson or electron density sections can be plotted numerically or alphabetically on the typewriter or punched alphabetically on cards, one line of a section per card, and then listed on the IBM 421 accounting machine.
Atomic coordinates and unit cell parameters are used to produce tables of increasing interatomic distances between a central target atom and its neighbours.

Tables of distances from the previous program are used to calculate angles subtended by bonds at the central target atom.

Least-squares plane \( ^{39} \) The best plane through a set of atoms is calculated and then the deviations of any atoms from this plane determined.

**C. ICR1 OUTPUT**

Full numeric output from ICR1 is impossibly slow for large jobs and so the author of this program has devised an extremely versatile alphanumeric plotting scheme. Answers which lie within a predetermined numeric range are transcribed as one of 39 available characters on the typewriter. Answers outside this range are transcribed as blanks. Careful selection of upper and lower limits for the numeric range will facilitate the production of a well resolved map such as that shown in fig. 8 (page 107).

Usually the scale chosen does not result in maps which are as easy to interpret as this one. This is particularly so in difference Fourier work where negative regions may be important. Several such maps have been presented in this thesis and many more were used during the analyses of these structures. Although they may
be more difficult to work with than the traditional contoured sections they represent the only practical way of applying Fourier methods on the large scale required by the present work.

If the alphabetic answers are punched on cards, instead of typed, computing time can be halved, and multiple copies of maps can be produced rapidly by the line printer which is part of the IBM 421 accounting machine. The author used two such copies (one on tracing paper) when trying superposition methods to analyse Patterson projections of \((\text{Ph}_4\text{As})_2\text{Re}_2\text{Cl}_{11}\).

D. CRITICISM

When the IBM 1620 computer became available, efforts were directed at building up the main series of programs in table 6b as quickly as possible, and then getting on with crystal structure analysis. Some of these programs are inefficient (e.g. GAXR7) and some others should be extended to do more useful work (e.g. GAXR4, GAXR9). One prominent omission from the system is a program for performing least-squares refinement. At the time of writing several other workers have these problems in hand.
REFERENCES

(2nd edition).
56. Gainsford, J.H., University of Canterbury, Private communication.
60. Fridrichson, J., Amer. Min., 44, 200.
63. Nobbs, C.L., University of Auckland, Private communication.
64. Jameson, M.B., University of Canterbury, Private communication.


71. "Manual for the use of the Buerger precession camera as manufactured by the Charles Supper Company."


* Detailed write-ups for these programs have not yet been prepared.