CRYSTAL STRUCTURE OF $[ReOOH(en)_2](ClO_4)_2$

AN X-RAY INVESTIGATION OF THE CRYSTAL

STRUCTURE OF $[ReOOH(en)_2](ClO_4)_2$

By

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SCOPE AND CONTENTS:

The structure of one of the complexes of rhenium (V)
is discussed in this work, namely, $[ReOOH(en)_2](ClO_4)_2$.
Chapter I, the Introduction, surveys some of the recent work
on rhenium complexes and introduces the basic problems.
Chapter II contains a summary of most of the relevant
theory for crystal structure determinations. The partial
solution of the structure is given in Chapter III entitled
Experimental. This section concludes with a discussion of
the ambiguity of the actual space group, the ambiguity
being whether the space group is $P\bar{1}$, or $P1$. Chapter IV
summarizes and discusses the results obtained and compares
them with other known results. Anomolous dispersion and
neutron diffraction are suggested as possible means for
complete solution.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

The crystal structure determination of $[Re(en)_2OOH]$ $(ClO_4)_2$ is part of a program of study carried on at this university. Its purpose is to gain a better understanding of the chemistry of rhenium, a member of the third transition metal series. Rhenium has as its most common oxidation states; III, IV, V and VII, with VI more difficult to obtain. Besides the large number of oxidation states, rhenium has coordination numbers ranging from 4 to 9, with 6 and 8 being the most common.

The present work describes the structure determination of a six coordinated complex of Re(V) containing two ethylenediamine rings and two oxygen atoms. This complex is one of a series of three which differ only in the number of hydrogen atoms attached to the oxygen atoms.

In complex A, in Figure I, one of the chlorine atoms can be replaced by an ethoxy group to give the complex B. When this is treated with ethylenediamine, the cation C is produced. This is the first member of the series. Upon treatment with a strong acid, for example, $HClO_4$, one of the oxygen atoms is protonated to give D. If this is treated with H_2PtCl_6, both oxygen atoms are protonated to produce E or possibly the cation F[1].

Figure I   2
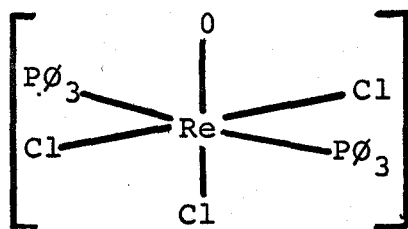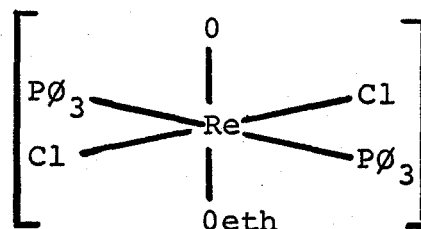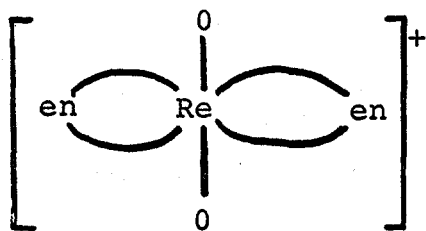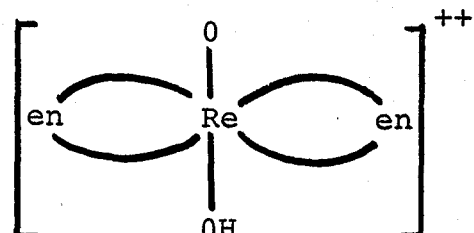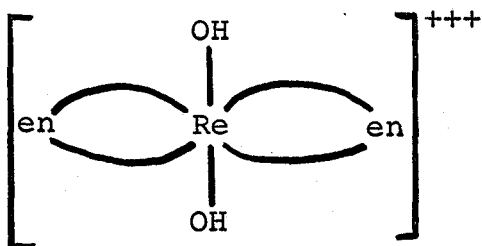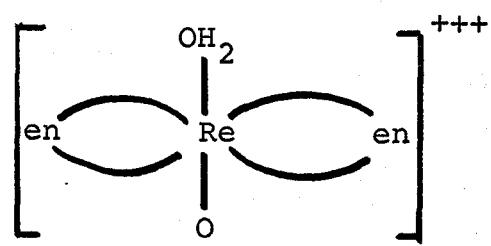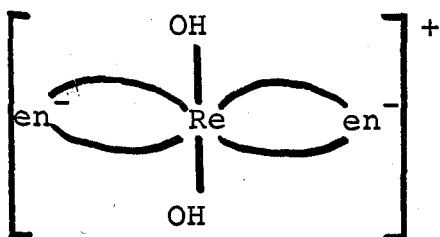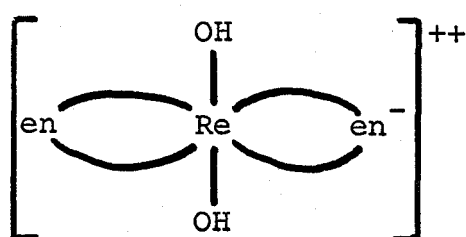
Complexes of Rhenium (V)

In the cation C, the trans-oxygen atoms will be competing for the d_{xz} and the d_{yz} orbitals of the rhenium atom. Johnson, Lock and Wilkinson[2] have suggested that a pi bond is formed between the p_x orbital of one of the oxygens and the d_{xz} orbital of the rhenium. A second pi bond will be formed between the p_y orbital of the other oxygen and the d_{yz} orbital of the rhenium. These, together with a sigma bond, would allow the rhenium and oxygen atoms to form at most a double bond.

Because of the competition for the orbitals and the lone pair of electrons on each of the oxygens, it might be expected that one of the oxygen atoms could be easily protonated to form the complex D. In this arrangement, the hydroxyl oxygen can be considered to form a single sigma bond with the rhenium. This frees the second d orbital on the rhenium atom to form a second pi bond with the other oxygen, giving rise to a triple bond between the rhenium and the oxygen. The overlap in this case could be considered as one sigma bond and two pi bonds, the first being the overlap of the Op_x with the $Re_{d_{xz}}$ and the second the overlap of the Op_y with the $Re_{d_{yz}}$. Further protonation is possible and has been reported[3] to produce one of the two species, E or F.

Evidence for the trans-arrangement of the oxygen atoms is two fold. First, infrared studies of the stretching frequencies of cation C show only one absorption peak

corresponding to a Re-O stretch in the neighbourhood 810 to 820 cm^{-1}. The Re-O stretch would occur at two points in the infrared spectrum for a cis-arrangement. The trans-arrangement stretch results from the asymmetric vibration, while the symmetric vibration, being a forbidden transition, products no dipole and thus is not observed. For a cis-arrangement both the symmetric and the asymmetric vibration produce absorption peaks in the infrared spectrum.

Secondly, Baldwin's criterion[4] can be used to interpret the infrared work of Johnson, Lock and Wilkinson. This criterion states that for ethylenediamine complexes, the infrared absorption spectra appears more complicated and extends, generally, over a larger region for a cis-arrangement than for a trans-arrangement. The trans-arrangement usually consists of a single relatively sharp band. In ethylenediamine complexes this is particularly evident for the CH_2 rocking mode in the region 870 to 900 cm^{-1}. This was found in the work of Johnson, Lock and Wilkinson.

Evidence has been given to indicate that there is a triple bond produced in the cation D. It would be expected that the oxygen forming this bond would not be easily protonated to produce the cation E. The association constants found by Murmann and Forrester[5] indicate this as follows:

for the reaction $[Re(en)_2O_2]^+ + H^+_{aq} \rightleftharpoons [Re(en)_2OOH]^+$
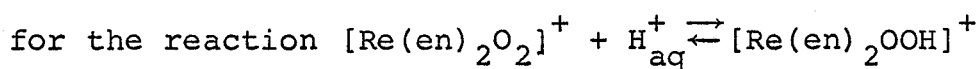
the association constant is given as

$logK_1 = 3.26 \pm 0.02$ for $\mu = 0.02$ and 25.3^o,

while for the second protonation reaction

$$[\text{Re(en)}_2\text{OOH}]^{++} + \text{H}^+_{aq} \rightleftarrows [\text{Re(en)}_2(\text{OH})_2]^{+++}$$
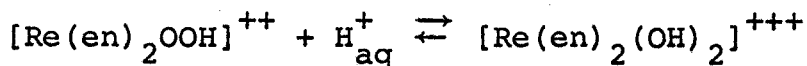
the association constant was found to be extremely small and was estimated to be $\log K_2 = -0.9 \pm 0.1$ at $\mu = 5$ and 25.3^o.

Alternative structures have been proposed by Evteev[6]. These differ from the above in the location of the hydrogen atoms. He proposed that complex C should be formulated as G with the oxygens protonated by the hydrogen atoms migrating from the nitrogen atoms of the ethylenediamine ring. The cation has the formula $[\text{Re(OH)}_2(\text{en}^-)_2]^+$ where $\text{en}^- = \text{NHCH}_2\text{CH}_2\text{NH}_2$. The cation D, then, takes the form H, $[\text{Re(OH)}_2(\text{en})(\text{en}^-)]^{++}$. E remains unchanged.

Evidence for the structure H is again found in the infrared spectrum of $[\text{Re(OH)}_2(\text{en})(\text{en}^-)]\text{Cl}_2$ where an absorption band was seen at 3470 cm^{-1} and was attributed to the hydroxyl group.

The complex, E, further appears to retain the two trans-hydroxyl groups as is indicated by the broad absorption band at 3350 cm^{-1} in $[\text{Re(OH)}_2(\text{en})_2]\text{Cl}_3$.

In the cation C, the Re-O bond length should be that corresponding to a double bond (1.8 Å), while cation D should have two different Re-O bond lengths, one corresponding to a single Re-OH distance (2.0Å), the other that of a single Re-O distance (1.8 Å) . For

the complex F, the bond lengths should be near those of complex D.

The determination of the crystal structure of $[ReOOH(en)_2](ClO_4)_2$ by x-ray diffraction was undertaken in order to differentiate between the structures D and H and to obtain accurate values for the Re-O and Re-N bond distances.

During the determination the question arose as to whether the hydrogen atom is present in the crystal at all. Neither x-ray measurements nor density measurements are able to detect its presence directly. The error in the chemical analysis is greater than one hydrogen per molecule. Nuclear magnetic resonance gives no evidence for the presence of this hydrogen atom because of the rapid exchange of the hydrogen atom. The most conclusive evidence is found in the diamagnetism of the complex[7]. If the hydrogen atom is not present the rhenium would have to be in the oxidation state Re(VI). This requires that there be only one electron in the d state and the resulting compound would be paramagnetic. Since the compound is diamagnetic it must be considered to be Re(V). The complex can thus only have an ionic charge of 2+ if an additional hydrogen atom is present.

CHAPTER II

THEORY

Diffraction by a Crystal

A crystal may be regarded as groups of atoms each
with the same orientation repeated at regular intervals
in all directions. When a beam of x-rays falls on a crystal,
the electrons of the atom are set into vibration and act
as secondary sources of radiation. This secondary radiation
will give a resultant amplitude in any direction which is
the sum of the radiation scattered from each electron. The
electrons can be considered to have a density distribution
$\rho(\underline{r})$ in the crystal, where

$$\underline{r} = (u + x)\underline{a} + (v + y)\underline{b} + (w + z)\underline{c} \qquad (1)$$

where u, v and w are integers, $0 \leqslant x,y,z \leqslant 1$, and $\underline{a}$, $\underline{b}$ and
$\underline{c}$ are the primitive lattice vectors of the crystal, thus,

$$\underline{r} = \underline{R} + \underline{R}_o \qquad (2)$$

where $\qquad\qquad \underline{R} = x\underline{a} + y\underline{b} + z\underline{c}$

and $\qquad\qquad \underline{R}_o = u\underline{a} + v\underline{b} + w\underline{c}.$

Because of the periodicity, $\underline{R}_o$, in the crystal
$\rho(\underline{r}) = \rho(\underline{R})$. The total scattered radiation from all the
electrons may be represented as

$$F(\underline{s}) = K\int_{crystal}\rho(\underline{r})\ \exp\ (2\pi i\underline{r}\cdot\underline{s})\,d\underline{r} \qquad (3)$$

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where $K\rho(\underline{r})$ is the magnitude of the wave scattered at a point $\underline{r}$, $\underline{s} = \underline{s}_o - \underline{s}_i$ with $\underline{s}_o$ = incident wave vector and $\underline{s}_i$ = the diffracted wave vector and $|\underline{s}_o| = |\underline{s}_i| = 1/\lambda$. Substituting in (3) from (1) and (2), the expression can be written as

$$F(\underline{s}) = \iint K\rho(\underline{R}) \exp 2\pi i(\underline{R}\cdot\underline{s}) \exp 2\pi i(\underline{R}_o\cdot\underline{s}) d\underline{R}d\underline{R}_o \quad (4)$$

Because $\underline{R}_o$ has the periodicity of the lattice, the integral over $d\underline{R}_o$ becomes the sum

$$\Sigma \exp(2\pi i\underline{R}_o\cdot\underline{s}) \quad (5)$$

This sum is zero unless $\underline{R}_o\cdot\underline{s}$ is an integer for all values of $\underline{R}_o$, in which case, it becomes N, the number of unit cells in the crystal. The structure factor is defined as the amplitude scattered corresponding to the vector $\underline{s}$ and takes the form

$$F(\underline{s}) = NK \int \rho(\underline{R}) \exp(2\pi i\underline{R}\cdot\underline{s}) dR \quad (6)$$

The condition $\underline{R}_o\cdot\underline{s}$ = integer is known as the Laue Equation[8]. Since $\underline{R}_o\cdot\underline{s} = u\underline{a}\cdot\underline{s} + v\underline{b}\cdot\underline{s} + w\underline{c}\cdot\underline{s}$ and since u, v and w can have any arbitrary integral value,

$$\underline{a}\cdot\underline{s}, \quad \underline{b}\cdot\underline{s} \text{ and } \underline{c}\cdot\underline{s} \text{ must separately be integers} \quad (7)$$

The Reciprocal Lattice

The reciprocal lattice may be defined in the following manner. Because of the requirement that $\underline{R}_o\cdot\underline{s}$ must be an integer, the vector, $\underline{s}$ may be defined in terms of a reciprocal lattice as follows:

$$\underline{s} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^* \qquad (8)$$

where h, k and l are the coordinates of any three non planar

vectors $\underline{a}^*$ $\underline{b}^*$ and $\underline{c}^*$. The product

$$\underline{R}_O \cdot \underline{s} = hu\underline{a} \cdot \underline{a}^* + kv\underline{b} \cdot \underline{b}^* + lw\underline{c} \cdot \underline{c}^* + hv\underline{a} \cdot \underline{b}^* + hw\underline{a} \cdot \underline{c}^*$$
$$+ ku\underline{b} \cdot \underline{a}^* + kw\underline{b} \cdot \underline{c}^* + lu\underline{c} \cdot \underline{a}^* + lv\underline{c} \cdot \underline{b}^* \qquad (9)$$

$$= \text{integer for a diffraction maximum}$$

By setting $\underline{a} \cdot \underline{b}^* = \underline{a} \cdot \underline{c}^* = \underline{b} \cdot \underline{a}^*$ etc. $= 0$ and $\underline{a} \cdot \underline{a}^* = \underline{b} \cdot \underline{b}^* = \underline{c} \cdot \underline{c}^* = 1$,

the vectors $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ are chosen such that $\underline{a}^*$ is per-

pendicular to $\underline{b}$ and $\underline{c}$, $\underline{b}^*$ is perpendicular to $\underline{a}$ and $\underline{c}$ and $\underline{c}^*$

is perpendicular to $\underline{a}$ and $\underline{b}$. Both the direction and magnitude

of these vectors have been defined.

The Laue equation reduces to $hu + kv + lw = n$, an

integer. Since u, v and w are integers, h, k and l must

also be integers.

In this way a reciprocal lattice has been defined

based on the vectors a^*, b^* and c^* where

$$\underline{a}^* = \frac{\underline{b} \times \underline{c}}{V}, \ b^* = \frac{\underline{c} \times \underline{a}}{V} \text{ and } c^* = \frac{\underline{a} \times \underline{b}}{V} \qquad (10)$$

Each reflection, then, corresponds to a point on the

reciprocal lattice and can be identified by the integral

indices h,k and l.

The Structure Factor

The electron density $\rho(\underline{R})$ of an atom referred to

the coordinates of the unit cell is given by the convolution

of the atomic electron density function $\rho_i(\nu)$ with the

delta function $\delta(R-R_i)$ giving the position (R_i) of the

centre of the atom with respect to the origin of the unit cell.

Then $\qquad \rho_i(\underline{R}) = \int \rho_i(\underline{v}) \ \delta(\underline{v} + \underline{R} - \underline{R}_i) dv.$

From equation (6)

$$F_i(\underline{s}) = N \int \rho_i(\underline{R}) \exp 2\pi i(\underline{R} \cdot \underline{S}) d\underline{R}$$

and from the convolution theorem,[9] the amplitude scattered by the atom at $\underline{R}_i$ is

$$F_i(\underline{s}) = f_i(s) \ G_i(s)$$

where

$$f_i(\underline{s}) = \int \rho(\underline{v}) \ \exp 2\pi i(\underline{v} \cdot \underline{s}) d\underline{v}$$

and

$$G_i(\underline{s}) = \int \rho(\underline{R} - \underline{R}_i) \exp(2\pi i \underline{R} \cdot \underline{s}) d\underline{R}.$$

$f_i(\underline{s})$ is called the scattering factor for the atom and $G_i(s) = \exp 2\pi i(\underline{R}_i \cdot \underline{s})$ gives the phase of the x-rays scattered from this atom. When there are several atoms present, the total structure factor is the sum of such contributions and is given as

$$F(\underline{s}) = \sum_i F_i(\underline{s}) = \sum_i f_i(\underline{s}) \exp 2\pi i(\underline{R}_i \cdot \underline{S}) \qquad (11)$$

A further application of the convolution theorem splits $f_i(\underline{s})$ into a stationary atomic scattering factor $f_i^0(\underline{s})$ and a temperature factor given by

$$\exp(-B_i \cdot s^2)$$

where the quantity B_i, the temperature coefficient, has the

value $8\pi^2 u^2$ where u is the mean square displacement of the atom from its mean position. For the case of anisotropic thermal vibrations, the simple form above cannot be used and the temperature factors must be written in dyadic form

$$\exp(-\vec{S}\cdot\overset{\leftrightarrow}{B}_i\cdot\vec{S})$$

where B_i represents the second order matrix

$$B_i = \begin{pmatrix} b_{11}a^2 & b_{21}b_9 & b_{31}ca \\ b_{22}ab & b_{22}b^2 & b_{32}cb \\ b_{13}ac & b_{23}bc & b_{33}c^2 \end{pmatrix}$$

The anisotropic temperature factor then takes the form

$$\exp[-b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{12}hk + b_{23}k\ell + b_{13}h\ell\,].$$

The Electron Density Distribution

Because a crystal is three dimensionally periodic with the period of the unit cell, the electron density of the unit cell must also be periodic. Any periodic function may be represented by a Fourier series, thus the electron density can be written

$$\rho(\underline{r}) = \sum_t C(t)\exp(2\pi i\ \underline{t}\cdot\underline{r}). \tag{12}$$

To determine the values of the constants C(t) the inverse transform may be taken

$$\int \sum_t C(\underline{t})\exp(2\pi i\underline{t}\cdot\underline{r})\exp(-2\pi i\underline{r}\cdot\underline{s})\,dr = \int \rho(\underline{r})\{\exp(-2\pi i\underline{r}\cdot\underline{s})\,dr\} \tag{13}$$

By orthogonality, the left hand side of (13) is zero,

unless $\underline{t} = \underline{s}$ in which case it becomes $C(\underline{s})$, thus

$$VC(\underline{s}) = \int \rho(\underline{r})\exp(-2\pi i\ \underline{r}\cdot\underline{s})d\underline{r}$$

$$= F^*(\underline{s})$$

Equation (12) may be written as

$$\rho(\underline{r}) = \sum_s F^*(\underline{s})\ \exp(2\pi i\underline{s}\cdot\underline{r}) \tag{14}$$

and because of the periodicity in $\underline{r}$ with the period of the

lattice

$$\rho(\underline{r}) = \rho(\underline{R})$$

and (14) reduces to

$$\rho(\underline{R}) = \sum_s F^*(\underline{s})\ \exp(2\pi i\ \underline{s}\cdot\underline{R}) \tag{15}$$

since $\underline{r}$ need only be calculated over the range of $\underline{R}$.

Since the electron density is a real function,

$$\rho^*(\underline{R}) = \rho(R)\ .$$

Taking the complex conjugate of (15) the electron density

can be expressed in the more usual form

$$\rho(\underline{R}) = \sum_s F(\underline{s})\exp(-2\pi i\ \underline{R}\cdot\underline{s})\ . \tag{16}$$

which is the Fourier transform of the structure factor.

The Phase Problem and Solutions

From equation (16), it appears that the electron

density distribution could be determined from a knowledge

of the structure factor. This, however, is not easily

accomplished in practice, since the structure factor is a complex quantity and only the intensity, related to $|F(hkl)|$, can be determined in any experiment.

Patterson in 1934 showed that one method of solution which is often helpful is to use the convolution of the electron density with itself displaced by a vector $\underline{u}$, then

$$P(\underline{u}) = \int_O^V \rho(\underline{R})\,\rho(\underline{R}+\underline{u})\,d\underline{R} \ .$$

From equation (16)

$$P(\underline{u}) = \frac{1}{V^2}\int \sum_{\underline{s}} \sum_{\underline{s}'} F(\underline{s})\exp(-2\pi i\ \underline{s}\cdot\underline{R})\ F(\underline{s}')\exp[-2\pi i\ \underline{s}'\cdot(\underline{R}+\underline{u})]\,d\underline{R}$$

again, because of orthogonality relationships, the only contribution is from terms for which $s = -s'$ thus,

$$P(\underline{u}) = \frac{1}{V^2}\int \sum_{s} F(\underline{s})\,F(-\underline{s})\exp(2\pi i\ \underline{s}.\underline{u})\,d\underline{R}.$$

$$= \frac{1}{V}\sum_{s} F(\underline{s})\,F^*(\underline{s})\ \exp(2\pi i\ \underline{s}.\underline{u})$$

This is obviously the Fourier transform of the intensity since $F(s)F^*(s)$ is proportional to the intensity, a measureable quantity.

The function can be interpreted as representing the sum of all the products of electron densities separated by a vector $\underline{u}$. If the vector corresponds to an interatomic vector, the function will have a large value, otherwise it will be zero or very small, determined by the spread of the atom. If there are n atoms in the unit cell, there will be

n^2 peaks in the Patterson function, n of which lie on the origin, being the product of an atom with itself. The remaining peaks are distributed over the Patterson unit cell, which is the same size as the crystal unit cell. The function has a centre of symmetry, since, for every vector $\overrightarrow{AB}$ between the atoms A and B there is a vector in the opposite direction $\overrightarrow{BA}$

For a large number of atoms, the Patterson function becomes complicated and the interpretation difficult. If, however, the molecule contains a few "heavy atoms", that is, atoms with many electrons, the interatomic vector between any two will be represented on the Patterson function as a large peak. This function is extremely useful in positioning heavy atoms relative to each other.

If the structure is triclinic, only two space groups are possible, P 1 and P $\bar{1}$. If also, there is only one heavy atom, it must lie on a special position in the space group P $\bar{1}$, which can be chosen as the origin. In the space group P 1, the heavy atom can lie anywhere, and without loss of generality, it can, too, be chosen to lie at the origin.

Interatomic vectors between the single heavy atom and medium sized atoms will show, in the Patterson function, as rather large peaks. With the heavy atom at the origin, the position of the medium sized atoms relative to the origin peak will be the same for both the Patterson function and the electron density function.

Since the scattering factor from the heavy atom will be larger than from the other atoms, the major part of the phase as well as the amplitude of the structure factor will be determined by the heavy atom.

With the heavier atoms approximately located, other atomic positions can often be found from the electron density map, calculated using the observed F, with the phase calculated using the positions of the heavier atoms only.

It is not possible to measure an infinite number of reflections to use in the Fourier series calculation. The result is that the series is finite and is not a true representation of the electron density. The electron density, therefore, shows ripples caused by the series termination and these limit the resolution in a way analagous to the limitation imposed in a microscope by the use of finite apertures.

One method of circumventing the above problem, after the majority, if not all, of the phases have been determined, is to use in place of $F(\underline{s})$ in equation (16) the quantity $F_o(\underline{s}) - F_c(\underline{s})$ where $F_o(\underline{s})$ is the observed structure factor and $F_c(\underline{s})$ is the calculated structure factor. The expression then becomes

$$\Delta(\underline{R}) = \sum_{\underline{s}} (F_o(\underline{s}) - F_c(\underline{s})) \exp -2\pi i \underline{s} \cdot \underline{R}.$$

This as can be easily seen, is the difference of two electron densities, the first that of the actual structure and the

second that of the assumed structure. If only some of the

atoms were used to prepare the calculated structure factors,

the difference synthesis will show peaks corresponding to

the remaining atoms in the real structure. Once all of

the atoms have been located exactly, the difference synthesis

will appear almost flat except for slight undulations re-

sulting from errors in observation.

Series termination is avoided in the difference

synthesis as a result of the subtraction of the two types

of electron densities. The ripples caused by series

termination in the actual structure will be cancelled by

those of the assumed structure.

The difference synthesis is useful, also, in indi-

cating the direction in which the atoms in the assumed

structure should be moved to attain their correct positions.

If two equal atoms, one in the assumed structure the other in

the real structure, are separated by a small amount, ϵ,

the difference of the electron densities will be such that

one atom lies on a hill while the other lies in a depression.

By moving the two atoms closer together, the slope of the

gradient between the depression and the hill becomes

shallower until, when the two are superimposed, the

resulting difference is zero. Considering that one of these

atoms is fixed by the actual crystal structure, and that

the other atom corresponds to the equivalent atom in the

proposed model, it is then necessary to shift the proposed

model atom up the gradient. The amount of the shift can be calculated in the following manner. Near the centre of an atom the electron density is given by $\rho(\underline{R} + \underline{r}) = \rho^O(\underline{R})\exp(-pr^2)$ where p is a constant approximately equal to 0.5 and $\rho^O(\underline{R})$ is the maximum density. For small distances the approximation can be made that

$$\rho(\underline{R}) = \rho^O(\underline{R})\ (1-pr^2)$$

The gradient in the difference synthesis $\frac{\partial}{\partial r}(\rho_O - \rho_c)$, may be written as $\frac{\partial}{\partial r}(\rho_O)$ since, at the point $\underline{R}$ the calculated electron density is maximum; that is, if the separation between the actual atomic position and the proposed atomic position is ε

then

$$\frac{\partial\rho_O}{\partial r} = 2\rho_O\ pr$$

and

$$r = \varepsilon = \frac{\partial(\rho_O - \rho_c)}{\partial r}\ /\ 2\rho_O p$$

which allows the error in the atomic positions to be calculated from the gradient of the difference synthesis.

Least Squares Refinement

Once a close approximation to the structure has been attained the various parameters can be refined further by the method of least squares. Assuming that the best values of the parameters p_k are in error from the actual values, p_k^O, by an amount ε, the calculated structure factor $F_j = F_j(p_k + \varepsilon)$ can be expanded in a Taylor series about p_k^O as

$$F_j^C(p_k) = F_j^C(p_k^O) + \frac{\partial F_j^C}{\partial p_k} \varepsilon_k \qquad (17)$$

to first order.

By minimizing the quantity

$$R = \sum_j W_j (F_j^O - F_j^C)^2 \qquad (18)$$

where W_j is the weighting factor and substituting (17) in (18) and writing

$$F_j^O - F_j^C(p_k^O) = D_j$$

(18) becomes

$$R = \sum_j W_j (D_j - \sum_k \frac{\partial F_j^C}{\partial p_k} \varepsilon_k)^2$$

The minimum value of R is obtained by setting

$$\frac{\partial R}{\partial p_\ell} = 0 = 2 \sum_j W_j (D_j - \sum_k \frac{\partial F_j^C}{\partial p_k} \varepsilon_k) \frac{\partial F_j^C}{\partial p_\ell}$$

This may be rewritten as

$$\sum_j W_j D_j \frac{\partial F_j^C}{\partial p_\ell} = \sum_j \sum_k W_j \frac{\partial F_j^C}{\partial p_\ell} \frac{\partial F_j^C}{\partial p_k} \varepsilon_k \qquad (19)$$

If the identification is made between terms of a matrix equation

$$[A_{\ell k}] [\varepsilon_k] = [B_\ell]$$

and equation (19) as

$$A_{\ell k} = \sum_j W_j \frac{\partial F_j^C}{\partial p_\ell} \frac{\partial F_j^C}{\partial p_k} \quad \text{and} \quad B_\ell = \sum_j W_j D_j \frac{\partial F_j^C}{\partial p_\ell}$$

the solution of the equation $[\varepsilon_\ell] = [A_{\ell k}]^{-1} [B_\ell]$ gives the corrections to the parameters p_k. The problem then is the

calculation of $[A_{\ell k}]$ and the subsequent inversion in order to determine ε_k.

A measure of the agreement between the proposed model and the true structure is given in terms of the R-factor defined by

$$R = \left[\frac{\sum\limits_{j} W_i (b|F_o| - |F_c|)^2}{\sum\limits_{i} W_i (b|F_o|)^2} \right]^{1/2}$$

where b is a scaling factor and is treated as a variable during refinement.

In choosing a suitable crystal and type of radiation to be used for intensity measurements, it is necessary to consider the total linear x-ray absorption coefficient μ. This depends strongly on the wavelength used and, for a given wave length, is characteristic of the absorbing material. The intensity, I, of the emergent beam depends on the thickness, R , of the material through which the beam has travelled and is given by $I = I_o \exp(-\mu R)$ where I_o is the incident intensity. A mass absorption coefficient is defined as μ/ρ where ρ is the density. It is found that μ/ρ is approximately additive with respect to the mass absorption coefficients of the constituent elements of the crystal, thus, $\mu/\rho = \sum\limits_{i} g_i (\mu/\rho)_i$ where the sum is over all the atomic species and g_i is the fractional mass of species i having a mass absorption $(\mu/\rho)_i$.

Having selected a crystal, it is mounted on a camera
and the diffraction pattern is recorded as a series of
spots on a film. If the density of the spots, measured by
the blackening of the film, is not too great, the density
is a linear function of exposure and, hence, of the
intensity. It is possible to estimate a value of the
intensity by measuring the relative blackness of spots on
a film. One method of estimation is to prepare a standard
scale and to compare the blackness of each spot with the
blackness of the standard scale, sometimes referred to as
a wedge. The graded series required is obtained by allowing
a relatively strong reflection to fall on the film and vary
the exposure time with the film displaced for each exposure.
This has the advantage that the spot shapes on the particular
layer photographed are the same as those of the standard
scale, making comparison easier.

By measuring the intensities in this manner, the
peak height is obtained. It is thus assumed that the
integrated intensity is proportional to the peak height.
This is not so, for several reasons, which are discussed in
Buerger[10]. The plateau method is one means of obtaining
values of the integrated intensities. The integrated
intensity is proportional to the number of photons in the
diffracted beam and is thus proportional to the area under
the profile of the diffraction spot. A method has been
developed whereby the profile is laid down at equally

spaced intervals on the film by moving the film uniformly during exposure. The sum of the heights of several curves along this profile is the sum of equally spaced heights in the single profile. Since the sum is a constant at the centre, thus producing a plateau, the height of the plateau is the integrated intensity.

One reason for the peak height not being proportional to the integrated intensity for higher layer Weissenberg photographs is that the spots on the upper and lower halves of the film are extended and contracted respectively. Phillips[11,12] and Singh[13] developed equations to account for the contraction. By considering the divergence of the incident radiation, two Ewald spheres can be drawn, one for the normal incoming beam, the other corresponding to maximum divergence. Two circles are produced by the intersection of the two Ewald spheres with the reciprocal lattice plane under consideration. The centres of these circles are defined at a distance r_o and r_1 respectively, from the origin of reciprocal space. The correction factor, then, is given as

$$\frac{L \pm \Delta L}{L} = 1 \pm \frac{180}{\pi} \left[\frac{\sin \nu \cos \nu \cos \theta}{(\cos^2 \nu - \cos^2 \theta)^{1/2} (r_1 + r_o \cos \nu)} \right]$$

where L is the length of the reflection spot, ΔL is the amount of contraction, ν is equal to the equi-inclination angle for which the above expression applies and θ is the

Bragg angle.

Before intensity measurements can be used, Lorentz[14] and polarization[15] factors must be applied. These are different for the Weissenberg and precession methods.

CHAPTER III

EXPERIMENTAL

Crystal Selection

Single crystals of the compound $[ReOOH(en)_2](ClO_4)_2$, where en = $(NH_2CH_2CH_2NH_2)$ were prepared by the method of Murmann[16]. They are reddish purple needles which show complete extinction every 90° when viewed under a polarizing microscope. The density of these crystals is 2.8 g/ml and was determined by noting that they just float in bromoform which has a density of 2.8 g/ml. A crystal was chosen which was small enough that the x-ray absorption correction could be ignored. The linear absorption coefficients for $MoK\bar{\alpha}$ and $CuK\bar{\alpha}$ radiation were calculated by the method of Chapter II to be 10.5 and 20.5 mm^{-1} respectively, using the mass absorption coefficients of International Tables[17].

The needle shaped crystals ranged in length from 0.2 mm to 1.0 mm with a base, roughly an equal sided parallelogram, with sides ranging from 0.05 to 0.5 mm. Since the crystals exploded when attempts were made to break them into fragments, the smallest crystal that could be chosen was 0.05 mm thick. This gives $\mu R = 0.5$ for $MoK\bar{\alpha}$ and 1.0 for $CuK\bar{\alpha}$ radiation. A crystal of dimensions 0.08 x 0.08 x 0.4 mm was chosen and $MoK\bar{\alpha}$ radiation was selected. This combination allows the

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absorption correction to be ignored.

Crystal Data

The selected crystal was mounted on a goniometer head in such a manner that the needle axis of the crystal was parallel to the axis of the goniometer head. A rotation photograph, taken with this setting, showed the needle axis, chosen as c, had a spacing of 9.0 $\overset{o}{A}$. A Weissenberg photograph of the hk0 plane taken in the same setting showed two axes, a^* and b^*, whose lengths were 0.188 and 0.133 $\overset{o-1}{A}$ respectively, with an angle of 84° between them.

The hk0 photograph showed that this layer had p2 symmetry. A first layer photograph, hkl, showed the crystal to be triclinic.

Accurate cell parameters were determined from precession photographs. The crystal data are shown in Tables I and II.

Intensity Data Collection and Correction

Intensity photographs were taken of the layers with $\ell = 0, 1, 2$ and 3 using a Weissenberg camera. Several photographs were taken of each layer having different exposure times as follows:

hk0 5/9, 5/3, 5, 15 and 45 hrs.

hkl 1, 3, 6 and 18 hrs.

hk2 1, 3, 6 and 18 hrs.

hk3 1, 3, 6 and 15 hrs.

The intensities of the reflections of the film were

Table I

Crystal Data

Formula $[ReOOH(NH_2CH_2CH_2NH_2)_2](ClO_4)_2$

System   Triclinic

Space Group $P1$ $(P\bar{1})$

Cell Constants $a = 5.701 \pm 0.006$ Å $\alpha = 114.12 \pm 0.05°$

$b = 8.214 \pm 0.008$ Å $\beta = 111.22 \pm 0.05°$

$c = 9.017 \pm 0.012$ Å $\gamma = 84.79 \pm 0.05°$

Volume of unit cell $= 368.4$ Å^3

Density Measured   2.8 g/mℓ.

Density Calculated 2.6 g/mℓ.

Z (No. of formula weights   1
   per unit cell)

Table II

Reciprocal Cell Parameters

	a^*	b^*	c^*	α^*	β^*	γ^*
hk0	0.1887 ± 0.0002	0.1339 ± 0.0002	–	–		86.15 ± 0.03
h0ℓ	0.1885 ± 0.0002	–	0.1302 ± 0.0002	–	$69.06 \pm 0.03°$	–
0kℓ	–	0.1336 ± 0.0002	0.1299 ± 0.0002	$66.12° \pm 0.03$	–	–
Best Value	0.1886 ± 0.0002	0.1337 ± 0.0002	0.1301 ± 0.0002	$66.12 \pm 0.03°$	$69.06 \pm 0.03°$	86.15 ± 0.03

Calibration crystal was rutile for which $a = 4.6937 \pm 0.00005$ Å $\underline{c} = 2.9581 \pm 0.00005$ Å [18]

estimated visually using a calibrated wedge as explained in Chapter II. Errors were assigned to the intensities and ranged from 20 to 30% depending upon the number of independent measurements of the reflection and where in the range of the calibrated wedge the intensity fell.

Late in the refinement, it became evident that there were systematic errors on the upper level Weissenberg data and these were traced to spot shape. A program was written to apply the correction developed by Phillips (Chapter II) to the intensity of the reflections.

Integrated precession photographs were also taken of the hk0 and 0kℓ planes using a Supper integrating precession camera. The exposure times, in multiples of the integration cycle, were, for 0kℓ, 1, 2 and 6 cycles, and for hk0, 1, 4, 16 and 48 cycles. One cycle requires 2 hrs. and 24 min. for completion. The intensity was measured from these films with a Leeds and Northrup microdensitometer. On the record a smooth background was seen and this was subtracted from the peak height to give a value of the integrated intensities. Errors were again assigned as for the Weissenberg data.

The Lorentz and polarization factors were applied to all of the intensities to give the square of the modulus of the structure factor.

Structure Determination and Refinement

From the density of the crystal and the volume of the unit cell, the number of formula units per unit cell was calculated to be one.

A triclinic crystal can have only one of two space groups P 1 and P $\bar{1}$. In $[ReOOH(en)_2](ClO_4)_2$, there are even numbers of atoms in the unit cell for all species except rhenium and hydrogen. If the space group is to be P $\bar{1}$ both the odd hydrogen and the rhenium atoms must lie on one of the eight special positions, namely, the corners, body centre, face centres or the edge centres of the unit cell[*], otherwise the space group must be P 1. Without loss of generality, the rhenium atom can be placed at the origin, the corner of the unit cell. If this is done, the odd hydrogen would necessarily lie on one of the seven other special positions if the space group is P $\bar{1}$.

A Patterson function was expected to show distinctly only the peaks corresponding to the Re-Re vector located at the origin and the Re-Cl vectors, since, because of the relatively large scattering factor of the rhenium and chlorine atoms, all the other interatomic vectors would not be distinguishable from the background fluctuations. If the structure is noncentrosymmetric four peaks are expected in the Patterson function corresponding to the two

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[*]these positions are 000, $00\frac{1}{2}$, $0\frac{1}{2}0$, $\frac{1}{2}00$, $0\frac{11}{22}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{11}{22}0$, $\frac{111}{222}$.

Re-Cl vectors and the two Cl-Re vectors. If the structure
is centrosymmetric the two Re-Cl peaks will coincide and,
likewise, the two Cl-Re peaks, thus, only two distinct
peaks will be observable - the Re-Cl and the Cl-Re.

A Patterson function was calculated and plotted
using the Okℓ data (Figure II). This showed only two large
peaks apart from the origin peak. Thus, it must be assumed
that the arrangement of the chlorine atoms is centrosymmetric
(or nearly so) around the rhenium atom. With the rhenium
placed at the origin of the unit cell, the positions of
the chlorine atoms can be taken directly from the Patterson
function.

Using again the Okℓ data, an electron density and
difference synthesis were calculated and plotted. Since
the space group chosen for these calculations is P $\bar{1}$ and
the heavy rhenium atom is placed at the origin, all the
signs of the structure factors are positive. In the
difference synthesis the contribution of the Re and Cl
atoms was removed. These functions are shown in Figures
III and IV.

Because of series termination, the electron density
shows ripples which are not present in the difference
syntheses (Chapter II),thus, the latter gives information
about the atomic positions of the cation which are hidden
by the ripples in the electron density. As can be seen
in the difference synthesis, the remaining members of the

Figure II   Patterson Function (0kℓ)

The full cell of the Patterson Function projected
onto the (0kℓ) plane. The contours are drawn at arbitrary
units. The shaded portions indicate that the contours
are too closely spaced to be drawn.

Figure II 31

(010)

(000)

(001)
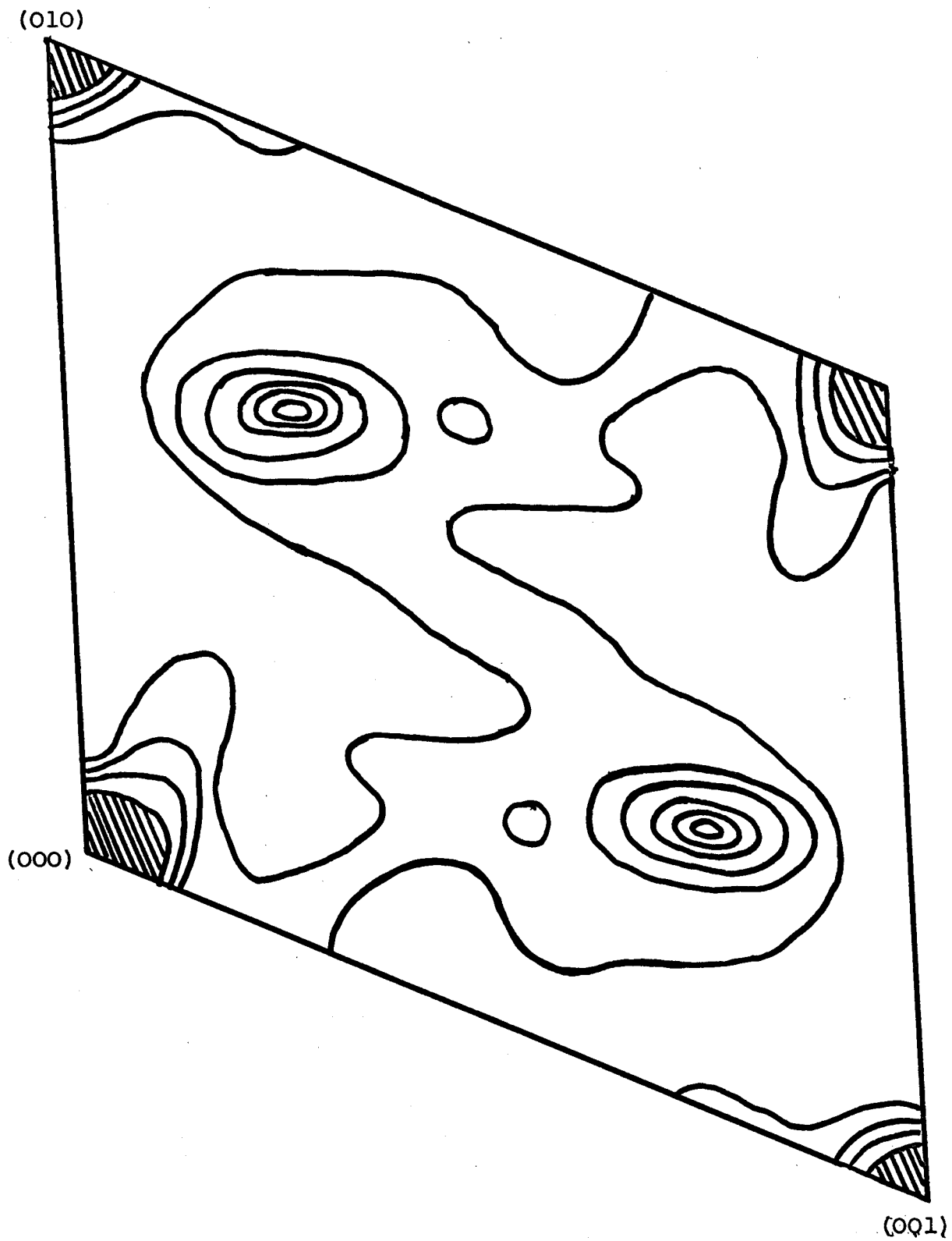
Patterson Function (0kℓ)

Figure III   Electron Density (0kℓ)

One half cell of the centrosymmetric electron density function projected onto the (0kℓ) plane . The contours are drawn at intervals of 1.7 electrons/$\overset{\circ}{A}^2$. The dashed lines represent the cation group with the rhenium atom at the origin. The position of the chlorine atom is indicated by the symbol X. Where the contours are too closely spaced the area is shaded. The zero contour is drawn at 4.0 electrons/$\overset{\circ}{A}^2$.

Figure III

33

(010)

(000)

$(00\frac{1}{2})$

X

Electron Density (0kℓ)
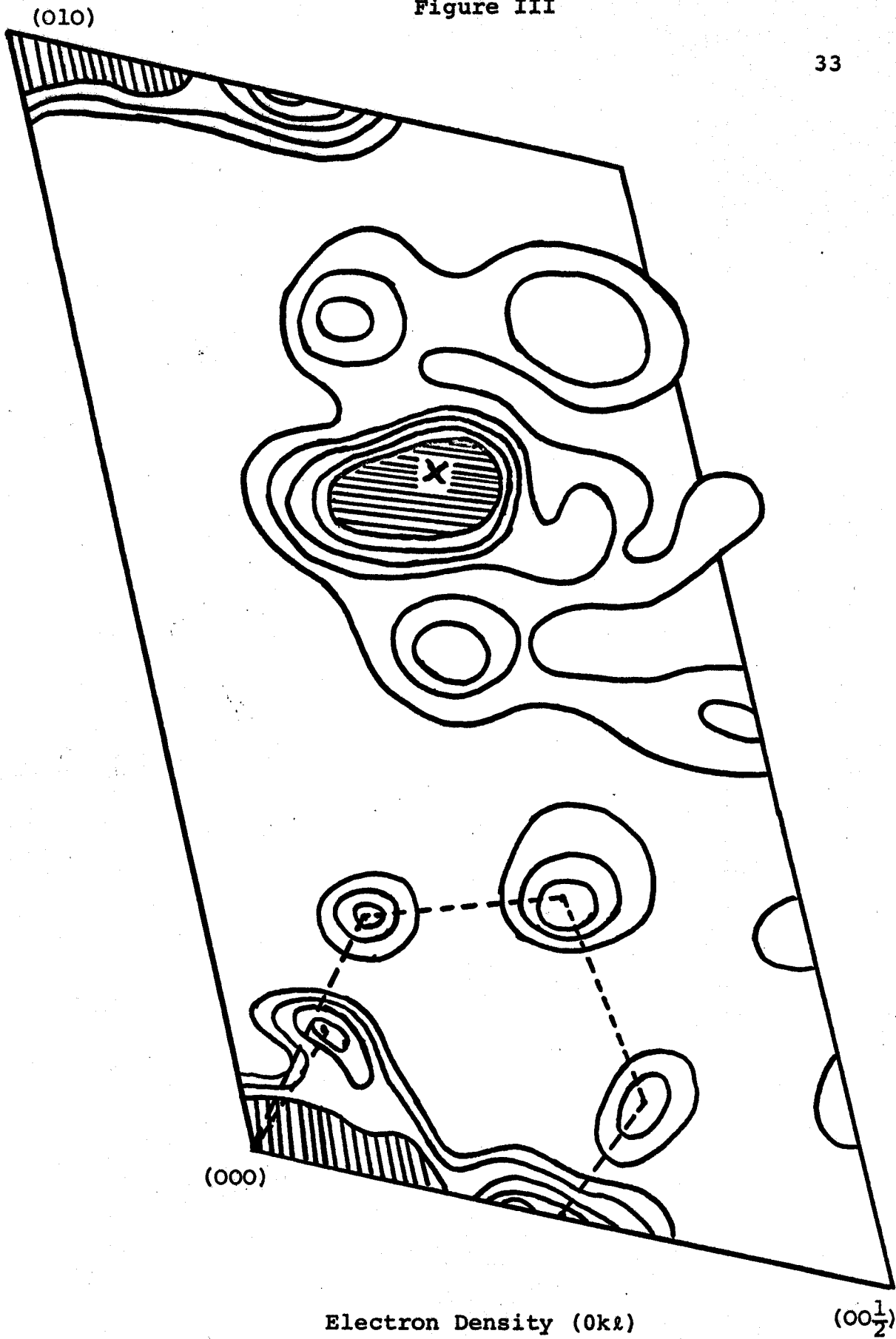
Figure IV Difference Synthesis (0kℓ)

One half cell of the centrosymmetric difference synthesis projected onto the (0kℓ) plane. The rhenium atoms located at the origin and the chlorine atom located by the symbol + have been removed in the calculation.

Figure IV

35

(010)

(000)
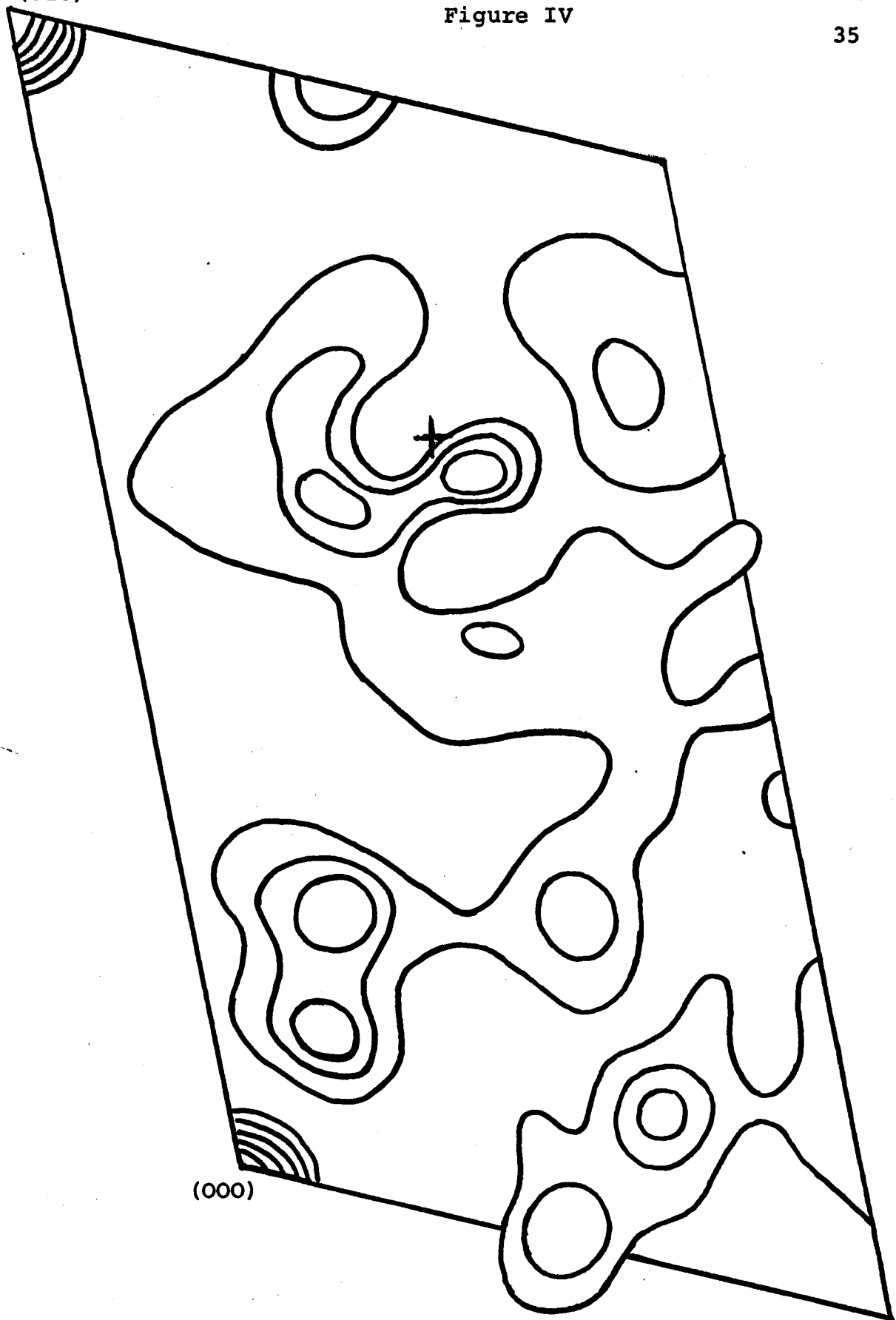
$(0\frac{1}{2}0)$

Difference Synthesis (0kℓ)

cation are represented by 10 peaks rather than 20. This again suggests that the ligands are placed centrosymetrically about the Re atom. The positions of the carbon, oxygen and nitrogen atoms were taken from the difference synthesis.

A least squares program, which minimized the sum of the squares of the difference between the observed and calculated structure factors, was used to refine the positions of the atoms in the cation and the chlorine atoms, together with the isotropic thermal vibration parameters (temperature factors) in the space group P $\bar{1}$. This reduced the R-factor (Chapter II) from 0.39 to 0.12.

A Patterson function was then calculated using hk0 data. From this function the x coordinate of the chlorine atoms could be found, the y coordinate having already been determined above.

The Patterson function again showed the chlorine atoms arranged centrosymmetrically about the rhenium atom (Figure V). The electron density was calculated in the space group P $\bar{1}$ using the hk0 data with the rhenium at the origin, the signs of the structure factors again all being positive. The plot of the electron density is shown in Figure VI. With the y coordinate from the 0kℓ refinement, the x coordinate of the atoms in the cation could be found. The x and y coordinates and the temperature factors were refined by least squares and the R-factor for

Figure V Patterson Function (hk0)

One half cell of the Patterson function projected onto the (hk0) plane. The contours are drawn at arbitrary units.

Figure V
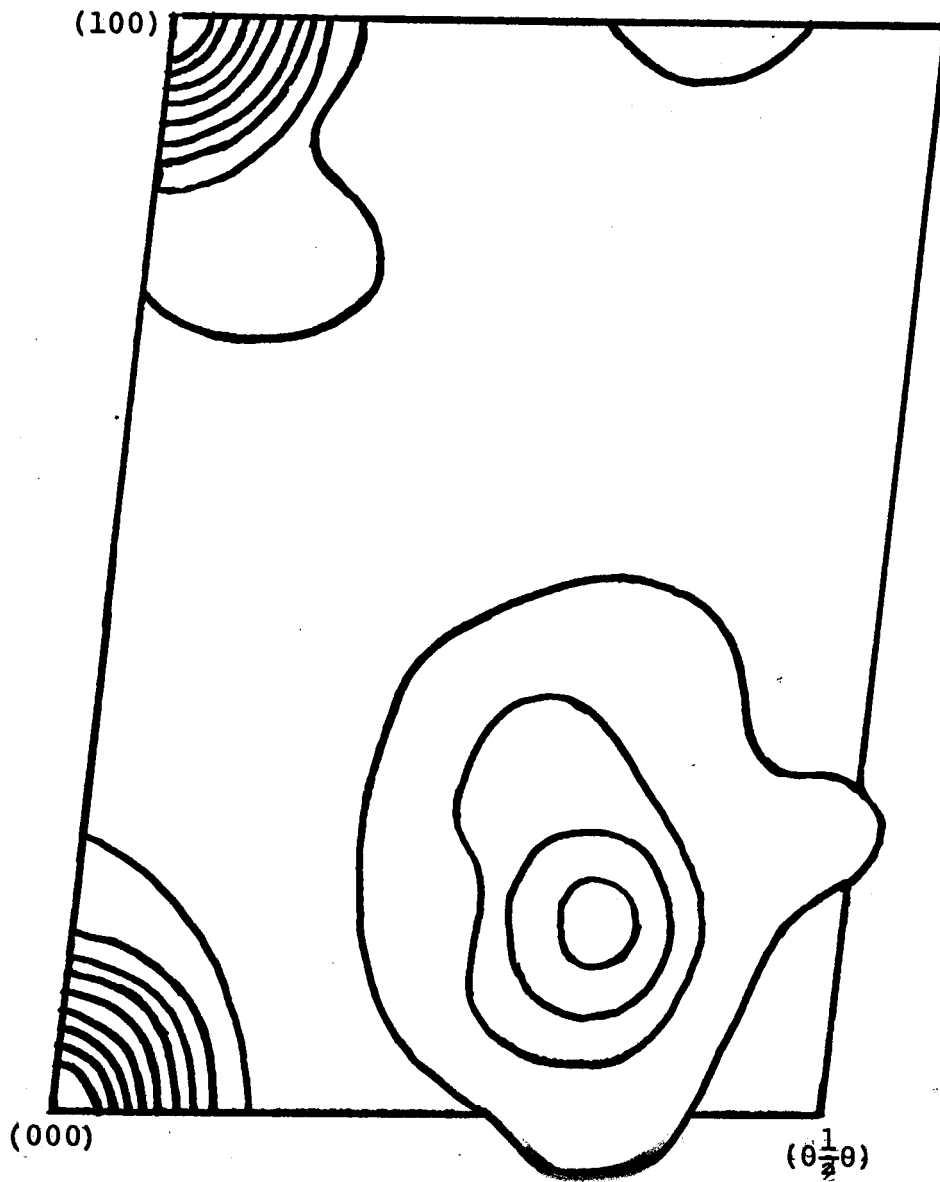
Patterson Function (hk0)

Figure VI   Electron Density (hk0)

One half of the centrosymmetric electron density function projected onto the (hk0) plane. The contours are drawn at intervals of 1.5 electrons/$\overset{\circ}{A}^2$. The rhenium atom is at the origin and the position of the chlorine atom is given by the symbol X. Where the contours are too closely spaced to be drawn the area is shaded. The zero contour is drawn at 3.5 electrons/$\overset{\circ}{A}^2$.

Figure VI
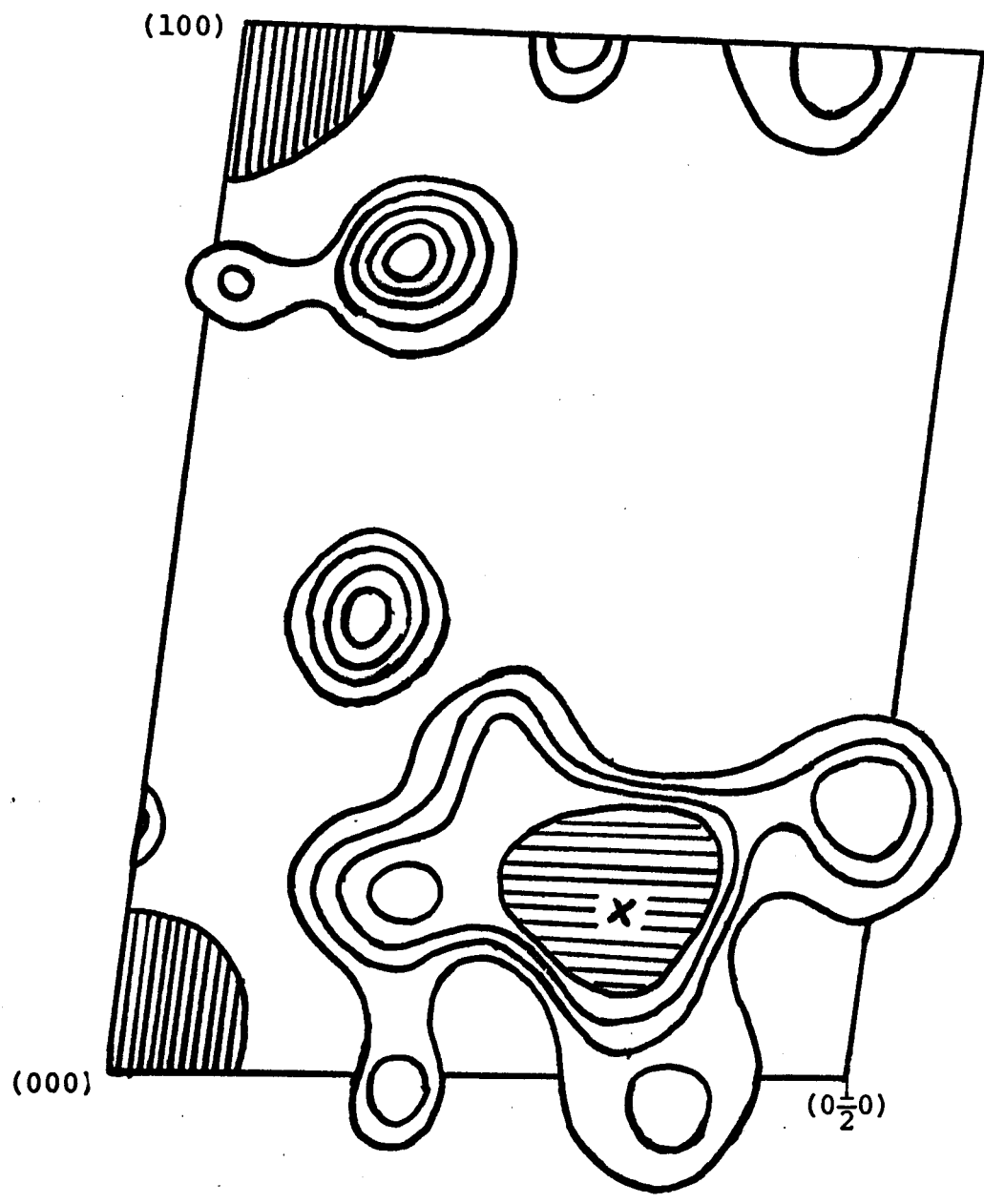
Electron Density (hk0)

this projection dropped from 0.19 to 0.12.

Difference syntheses using the Okℓ and hk0 data with the cation and the chlorine atoms removed, showed a large smearing of electron density around the chlorine atom in the position where the oxygen atoms of the perchlorate groups were expected. It was, thus, difficult to assign coordinates to these atoms. Two peaks, however, were sufficiently resolved that they were assumed to be two atoms. By placing an atom at the centre of each of the peaks, the position of the other two oxygen atoms was calculated, assuming that the anion would be tetrahedral.

Using all of the three dimensional data, further refinement was carried out in the space group P $\bar{1}$. All of the atoms except the hydrogen atoms were   included in the model of the structure. R dropped from 0.29 to 0.13 when the anisotropic temperature factors and atomic positions of all these atoms were varied. A table of the coordinates at the end of this refinement is given in Table III and a list of observed and calculated structure factors is given in Table IV.

If the structure is indeed centrosymmetric, the odd hydrogen atom would have to lie on a special position, as mentioned above. Since the rhenium atom has been chosen at the centre of symmetry at the origin, the odd hydrogen would lie on one of the seven remaining centres of symmetry in the unit cell. If the distances between two atoms

Table III

Table of Atomic Coordinates and Temperature Factors

Species	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.0000	0.0000	0.0000	0.0296 (10)	0.0086 (2)	0.0060 (3)	0.0012 (3)	0.0060 (7)	0.0026 (2)
Cl	0.1650 (22)	0.0336 (9)	0.7220 (13)	0.0511 (45)	0.0116 (9)	0.0128 (13)	0.0018 (19)	0.0156 (40)	0.0044 (10)
O(1)	0.776 (5)	0.136 (3)	0.084 (4)	0.034 (10)	0.022 (4)	0.015 (5)	0.005 (6)	0.015 (10)	0.003 (4)
N(1)	0.238 (7)	0.242 (3)	0.111 (4)	0.045 (13)	0.013 (4)	0.012 (5)	0.604 (7)	0.604 (12)	0.003 (4)
N(2)	0.207 (9)	0.005 (5)	0.029 (3)	0.084 (25)	0.041 (8)	0.007 (4)	-0.021 (13)	0.021 (19)	0.016 (5)
C(1)	0.349 (8)	0.303 (4)	0.305 (5)	0.051 (16)	0.012 (4)	0.011 (5)	-0.001 (8)	0.007 (15)	0.004 (4)
C(2)	0.450 (7)	0.139 (4)	0.350 (4)	0.037 (15)	0.018 (5)	0.006 (5)	-0.004 (8)	0.019 (13)	0.004 (4)
O(2)	0.011 (9)	0.209 (6)	0.540 (6)	0.079 (23)	0.070 (12)	0.022 (9)	0.007 (14)	0.039 (17)	-0.012 (9)
O(3)	0.243 (9)	0.501 (5)	0.743 (8)	0.104 (3)	0.043 (9)	0.095 (21)	0.007 (12)	0.091 (21)	0.032 (11)
O(4)	-0.038 (8)	0.374 (4)	0.818 (5)	0.107 (23)	0.024 (6)	0.030 (9)	0.020 (10)	0.044 (18)	0.016 (6)
O(5)	0.340 (11)	0.242 (6)	0.802 (7)	0.134 (3)	0.059 (11)	0.057 (15)	0.041 (18)	0.045 (25)	0.042 (12)

The quantities in brackets indicate the errors in the last figure.

TABLE IV   43

Observed and Calculated Structure Factors

H	K	L	F(OBS)	F(CALC)	SIGMA	H	K	L	F(OBS)	F(CALC)	SIGMA
0	8	0	16.92	23.76	2.14	4	2	0	22.64	26.93	2.26
0	7	0	20.85	27.28	2.62	4	3	0	17.28	18.85	1.79
0	6	0	48.26	48.01	4.77	4	4	0	25.74	26.89	2.62
0	5	0	33.01	34.66	3.22	5	-3	0	18.47	18.12	2.50
0	4	0	48.14	45.08	3.69	5	-2	0	18.47	23.73	2.50
0	3	0	87.34	70.65	6.55	5	0	0	24.19	24.66	3.22
0	2	0	36.11	32.04	2.74	5	1	0	23.36	24.93	2.86
1	-7	0	26.81	28.55	2.86	0	-10	0	11.16	13.57	1.03
1	-6	0	41.23	40.80	3.22	0	-9	0	19.61	25.61	2.00
1	-5	0	40.40	44.66	5.12	0	-8	0	25.29	23.76	3.20
1	-4	0	60.65	54.86	4.53	0	-7	0	24.32	27.28	1.52
1	-3	0	55.65	50.02	4.17	0	-6	0	44.69	48.01	2.82
1	-2	0	30.03	33.10	2.98	0	-5	0	29.95	34.66	1.52
1	-1	0	118.92	93.05	8.94	0	-4	0	36.94	45.08	1.84
1	0	0	99.26	96.24	7.39	0	-3	-0	59.26	70.65	2.98
1	1	0	14.54	13.30	1.55	0	-2	0	25.57	32.04	1.25
1	2	0	100.57	81.38	7.39	0	-9	1	21.61	20.43	2.17
1	3	0	91.28	85.37	6.79	0	-8	1	38.29	36.06	2.82
1	4	0	31.46	27.92	2.38	0	-7	1	23.89	24.56	1.73
1	5	0	44.09	43.45	3.34	0	-6	1	28.49	24.73	2.11
1	6	0	35.27	36.86	2.74	0	-5	1	61.26	58.66	3.90
2	-7	0	28.84	31.83	2.74	0	-4	1	45.82	39.53	2.27
2	-6	0	25.38	30.73	2.38	0	-3	1	54.00	55.15	4.06
2	-5	0	32.89	36.80	3.22	0	-2	1	93.32	109.84	8.18
2	-4	0	47.66	42.51	3.57	0	-1	1	54.00	49.50	4.06
2	-3	0	51.24	50.05	3.93	0	1	1	83.85	90.90	7.31
2	-2	0	40.40	38.95	4.05	0	2	1	26.87	26.71	1.68
2	-1	0	62.80	55.05	4.77	0	3	1	54.06	52.80	2.71
2	0	0	31.94	32.68	3.22	0	4	1	56.06	55.95	2.82
2	1	0	44.80	52.23	4.41	0	5	1	30.98	31.18	1.90
2	2	0	65.06	60.37	6.55	0	6	1	36.67	34.93	2.49
2	3	0	39.80	41.97	2.98	0	7	1	37.32	33.24	2.33
2	4	0	25.74	26.05	2.50	0	8	1	20.53	18.51	1.95
2	5	0	37.54	42.45	3.69	0	9	1	18.85	18.01	1.90
3	-5	0	30.15	28.42	2.98	0	-10	2	19.66	21.32	2.00
3	-4	0	43.26	41.35	3.22	0	-9	2	18.09	18.04	1.84
3	-3	0	35.39	36.24	2.62	0	-7	2	41.38	38.16	2.60
3	-2	0	51.36	45.43	3.81	0	-8	2	23.99	25.96	1.46
3	-1	0	54.46	47.75	5.48	0	-6	2	21.61	23.07	1.41
3	0	0	30.98	35.21	3.10	0	-5	2	52.38	53.15	2.60
3	1	0	34.91	36.10	3.46	0	-4	2	49.07	50.45	2.44
3	2	0	33.72	31.50	3.46	0	-3	2	17.71	18.18	0.92
3	3	0	22.40	24.17	2.38	0	-2	2	70.85	71.44	5.20
3	4	0	32.89	34.90	3.22	0	-1	2	93.11	99.16	8.12
3	5	0	31.10	34.94	3.10	0	0	2	15.76	12.41	1.03
4	-5	0	30.62	29.38	2.14	0	1	2	67.65	73.81	5.09
4	-4	0	20.14	23.78	1.55	0	2	2	45.34	47.53	2.27
4	-3	0	24.07	16.85	2.62	0	3	2	30.60	29.19	1.57
4	-2	0	44.45	36.01	4.53	0	4	2	46.26	46.26	2.87
4	-1	0	30.27	31.96	2.98	0	5	2	42.57	41.33	2.65
4	0	0	35.39	34.47	3.69	0	6	2	19.28	19.57	1.57
4	1	0	43.02	39.50	4.17	0	7	2	28.06	26.91	1.79

TABLE IV (Continued)

H	K	L	F(OBS)	F(CALC)	SIGMA	H	K	L	F(OBS)	F(CALC)	SIGMA
0	8	2	25.51	26.67	1.95	0	-1	5	34.83	35.82	2.17
0	9	2	10.35	12.22	0.97	0	0	5	30.33	26.96	1.90
0	-11	3	9.59	9.69	0.97	0	1	5	54.65	55.24	3.41
0	-10	3	23.34	22.68	1.79	0	2	5	45.55	45.64	2.82
0	-9	3	30.87	28.05	1.95	0	3	5	26.27	26.03	1.68
0	-8	3	17.28	15.94	1.35	0	4	5	34.12	33.12	2.55
0	-7	3	38.73	37.56	2.38	0	5	5	28.92	25.13	2.11
0	-6	3	51.67	49.54	3.25	0	6	5	18.90	18.00	1.90
0	-5	3	24.37	19.69	3.03	0	7	5	17.93	20.10	1.35
0	-4	3	51.46	49.43	2.55	0	-11	6	11.16	13.17	1.08
0	-3	3	63.97	61.63	4.01	0	-10	6	23.29	23.29	1.73
0	-2	3	59.20	57.72	3.68	0	-9	6	17.39	17.59	1.79
0	-1	3	92.29	93.60	6.93	0	-8	6	23.13	21.42	2.76
0	0	3	67.11	58.06	5.04	0	-7	6	40.46	37.28	3.03
0	1	3	31.63	30.65	1.57	0	-6	6	28.54	25.58	2.17
0	2	3	61.53	57.17	3.68	0	-5	6	27.24	25.44	2.06
0	3	3	47.83	48.21	2.98	0	-4	6	46.53	40.99	3.47
0	4	3	28.17	26.78	1.79	0	-3	6	43.17	40.99	3.25
0	5	3	35.75	33.19	2.22	0	-2	6	38.24	36.46	2.87
0	6	3	35.15	33.30	2.22	0	-1	6	40.84	41.32	3.09
0	7	3	22.97	21.51	1.73	0	0	6	31.69	31.21	2.38
0	8	3	20.85	20.09	1.57	0	1	6	30.93	28.61	2.33
0	-11	4	21.34	17.33	1.62	0	2	6	37.81	35.24	2.82
0	-10	4	19.39	16.69	2.00	0	3	6	25.67	24.16	1.95
0	-9	4	37.59	27.37	2.33	0	4	6	22.32	22.67	1.62
0	-8	4	32.39	27.66	2.00	0	5	6	25.89	27.82	1.90
0	-7	4	20.91	19.95	1.35	0	6	6	14.73	17.00	1.41
0	-6	4	52.86	49.18	2.65	0	-11	7	11.70	13.19	1.14
0	-5	4	45.12	43.80	2.22	0	-10	7	17.71	18.60	2.11
0	-4	4	49.34	44.87	2.49	0	-9	7	23.94	22.67	1.84
0	-3	4	74.91	71.89	3.95	0	-8	7	20.04	17.33	2.00
0	-2	4	73.77	73.27	5.52	0	-7	7	30.44	28.20	2.33
0	-1	4	72.69	67.23	5.36	0	-6	7	37.64	33.11	2.82
0	0	4	65.92	64.86	4.12	0	-5	7	20.69	24.62	2.06
0	1	4	31.47	29.53	3.95	0	-4	7	41.49	40.05	3.09
0	2	4	37.75	34.84	2.38	0	-3	7	53.08	50.85	4.01
0	3	4	54.38	52.74	3.41	0	-2	7	31.63	28.54	2.38
0	4	4	39.00	38.33	2.44	0	-1	7	28.54	26.07	2.17
0	5	4	26.22	24.61	1.62	0	0	7	40.30	38.25	3.03
0	6	4	34.50	31.17	2.17	0	1	7	26.81	26.27	1.95
0	7	4	21.50	20.89	2.06	0	2	7	26.32	27.44	2.00
0	8	4	9.15	10.93	0.92	0	3	7	30.82	31.65	2.33
0	-11	5	18.69	20.18	1.41	0	4	7	19.50	19.90	2.00
0	-10	5	20.15	17.45	2.00	0	5	7	21.99	19.47	1.62
0	-9	5	17.12	16.44	1.68	0	-10	8	11.70	12.46	1.14
0	-8	5	38.78	34.00	4.82	0	-9	8	21.23	20.07	1.90
0	-7	5	29.14	25.84	1.84	0	-8	8	28.71	27.27	2.17
0	-6	5	29.25	29.50	1.84	0	-7	8	22.10	22.31	1.62
0	-5	5	59.53	56.86	3.68	0	-6	8	31.63	31.13	2.38
0	-4	5	43.71	42.18	3.25	0	-5	8	43.66	41.23	3.30
0	-3	5	48.15	45.16	3.03	0	-4	8	32.17	31.61	2.38
0	-2	5	64.24	62.01	4.82	0	-3	8	31.69	32.55	2.38

TABLE IV (Continued)

H	K	L	F(OBS)	F(CALC)	SIGMA	H	K	L	F(OBS)	F(CALC)	SIGMA
-1	5	-1	50.25	56.13	7.24	0	-2	8	36.34	37.32	2.76
-1	6	-1	45.24	48.55	5.66	0	-1	8	23.07	25.44	1.73
-1	7	-1	19.74	20.17	2.53	0	0	8	30.87	30.59	2.27
-1	8	-1	24.34	25.34	3.11	0	1	8	33.91	34.72	2.55
-1	10	-1	16.37	12.81	2.17	0	2	8	23.62	24.00	1.79
2	0	-1	18.64	17.31	2.35	0	3	8	23.51	23.72	1.73
2	1	-1	63.94	54.04	6.46	0	4	8	19.55	21.84	1.46
2	2	-1	82.27	72.76	8.16	0	-10	9	17.01	16.20	1.30
2	3	-1	55.34	50.67	5.59	0	-9	9	16.74	17.31	1.62
2	4	-1	55.41	56.55	5.48	0	-8	9	22.86	23.90	1.68
2	5	-1	47.73	41.48	4.96	0	-7	9	25.35	24.94	1.90
2	6	-1	23.74	23.05	3.02	0	-6	9	20.64	20.48	2.06
2	7	-1	32.06	29.69	4.06	0	-5	9	28.87	27.94	2.11
2	8	-1	16.83	19.99	2.10	0	-4	9	29.90	29.39	2.22
2	9	-1	15.71	14.21	2.63	0	-3	9	20.91	21.26	2.06
2	10	-1	19.45	17.51	2.44	0	-2	9	26.65	28.20	2.06
-2	1	-1	26.08	25.65	2.70	0	-1	9	27.57	28.72	2.06
-2	2	-1	59.59	54.52	5.95	0	0	9	23.24	22.96	1.79
-2	3	-1	65.99	68.09	6.64	0	1	9	26.70	27.60	2.00
-2	4	-1	34.84	34.54	3.48	0	2	9	18.63	20.59	1.84
-2	5	-1	25.52	26.88	3.23	0	3	9	10.94	13.16	1.08
-2	6	-1	42.92	40.69	4.29	0	-9	10	16.74	16.29	1.25
-2	7	-1	25.68	27.26	3.27	0	-8	10	13.43	13.43	1.35
-2	8	-1	18.69	15.26	2.42	0	-7	10	19.44	20.20	1.84
-2	9	-1	23.79	21.78	3.05	0	-6	10	20.20	20.43	2.00
-2	0	-1	55.60	48.75	5.47	0	-5	10	17.49	17.18	1.79
3	0	-1	48.24	48.52	4.82	0	-4	10	26.32	26.82	1.95
3	1	-1	51.30	45.21	5.25	0	-3	10	22.15	23.09	1.73
3	2	-1	37.03	31.71	3.70	0	-2	10	13.54	14.67	1.30
3	3	-1	24.02	25.69	3.04	0	-1	10	23.18	22.96	1.73
3	4	-1	38.11	38.39	3.81	0	0	10	20.74	20.42	1.52
3	5	-1	22.54	22.19	2.26	0	1	10	11.54	13.55	1.19
3	6	-1	27.64	26.96	2.77	0	-8	11	16.79	16.50	1.19
3	7	-1	30.82	26.98	3.09	0	-7	11	16.25	15.46	0.81
3	8	-1	17.66	14.90	2.21	0	-6	11	22.97	22.12	1.68
-3	0	-1	41.36	36.47	3.74	0	-5	11	20.69	21.12	1.52
-3	1	-1	38.49	40.88	3.85	0	-4	11	16.36	16.91	1.62
-3	2	-1	25.30	29.97	2.53	0	-3	11	18.79	19.45	1.35
-3	3	-1	43.80	47.79	4.38	0	-2	11	15.76	17.21	1.52
-3	4	-1	44.22	45.67	4.42	1	2	-1	96.45	100.67	9.68
-3	5	-1	17.56	22.28	2.20	1	3	-1	70.17	67.71	7.08
-3	6	-1	15.33	22.09	1.90	1	4	-1	48.87	45.53	4.88
-3	7	-1	21.66	26.61	2.78	1	5	-1	55.49	54.59	5.55
-3	8	-1	15.16	15.67	2.53	1	6	-1	42.60	23.08	4.25
4	0	-1	48.04	41.55	4.90	1	7	-1	31.73	34.82	3.08
4	1	-1	34.25	31.29	3.42	1	8	-1	30.47	30.29	3.04
4	2	-1	19.13	22.27	2.39	1	9	-1	17.65	15.27	2.21
4	3	-1	31.47	32.55	3.93	1	10	-1	19.00	16.92	2.36
4	4	-1	24.53	24.00	3.13	-1	1	-1	10.31	10.46	1.32
4	5	-1	17.49	17.01	2.27	-1	2	-1	66.70	74.78	6.62
4	6	-1	21.95	22.53	2.83	-1	3	-1	30.37	33.16	3.03
4	7	-1	15.29	15.94	2.54	-1	4	-1	26.05	24.66	3.26

TABLE IV (Continued)

H	K	L	F(OBS)	F(CALC)	SIGMA	H	K	L	F(OBS)	F(CALC)	SIGMA
-4	0	-1	32.01	29.05	4.04	-2	-7	-1	17.87	17.35	2.33
-4	1	-1	45.11	39.84	4.46	3	-1	-1	29.98	29.27	2.99
-4	2	-1	33.05	29.22	4.12	3	-2	-1	63.41	67.39	6.35
-4	3	-1	23.99	21.91	3.05	3	-3	-1	37.38	40.20	3.73
-4	4	-1	31.88	28.47	3.99	3	-4	-1	19.77	16.18	2.47
-4	5	-1	20.82	19.74	2.69	3	-5	-1	31.15	31.83	3.93
-4	6	-1	16.59	15.10	2.07	3	-6	-1	23.31	27.68	2.33
-4	7	-1	23.20	20.32	2.98	3	-7	-1	25.25	16.24	2.52
-4	8	-1	13.13	15.16	3.27	3	-8	-1	12.19	23.68	3.03
-4	9	-1	13.89	12.88	3.47	3	-9	-1	20.72	15.21	2.70
5	0	-1	33.47	28.01	4.18	-3	0	-1	36.55	36.47	3.66
5	1	-1	23.83	22.31	2.97	-3	-1	-1	31.34	33.18	3.13
5	2	-1	23.04	23.16	2.95	-3	-2	-1	38.92	43.47	3.89
5	3	-1	27.40	24.85	3.42	-3	-3	-1	34.72	37.22	3.47
5	4	-1	14.25	13.18	2.38	-3	-4	-1	16.68	22.66	2.09
5	5	-1	17.18	14.39	2.15	-3	-5	-1	29.36	30.98	2.94
5	6	-1	12.76	15.58	3.21	-3	-6	-1	20.91	22.19	2.69
5	7	-1	13.43	10.63	3.35	-3	-7	-1	12.01	12.03	3.01
1	-2	-1	51.67	50.51	5.13	4	-1	-1	36.42	21.02	3.65
1	-3	-1	55.42	53.33	5.54	4	-2	-1	33.18	31.00	3.32
1	-4	-1	55.40	53.96	5.38	4	-3	-1	38.35	38.15	3.84
1	-5	-1	46.81	42.98	4.68	4	-4	-1	17.08	18.45	2.14
1	-6	-1	26.96	26.94	3.37	4	-5	-1	16.60	20.85	2.15
1	-7	-1	34.89	33.29	4.36	4	-6	-1	26.32	23.10	3.35
1	-8	-1	21.53	22.73	2.77	4	-7	-1	11.99	15.59	2.99
1	-9	-1	12.51	15.07	1.57	4	-8	-1	15.70	16.64	2.63
1	-10	-1	19.11	17.56	2.39	-4	0	-1	28.95	29.05	3.61
-1	-1	-1	73.07	68.59	7.27	-4	-1	-1	29.58	26.11	3.70
-1	-2	-1	53.06	47.18	5.30	-4	-2	-1	27.44	26.19	3.42
-1	-3	-1	57.10	61.95	8.40	-4	-3	-1	16.08	17.80	2.09
-1	-4	-1	34.44	38.58	3.53	-4	-4	-1	20.09	20.38	2.59
-1	-5	-1	16.59	14.54	2.14	-4	-5	-1	22.80	22.64	2.86
-1	-6	-1	29.48	33.59	2.95	-4	-6	-1	12.14	14.82	3.02
-1	-7	-1	22.90	27.88	2.94	5	-2	-1	21.62	14.04	2.76
-1	-8	-1	18.62	18.23	2.42	5	-3	-1	16.65	22.48	2.16
-1	-9	-1	22.10	19.46	3.32	5	-4	-1	15.54	18.13	1.94
-1	0	-1	75.85	80.13	7.58	5	-5	-1	16.32	17.34	2.04
2	-1	-1	53.18	53.32	5.29	1	3	-2	45.86	37.99	4.37
2	-2	-1	78.84	76.45	7.91	1	4	-2	98.41	82.72	9.40
2	-3	-1	49.62	49.46	4.91	1	5	-2	38.62	34.07	3.86
2	-4	-1	47.86	43.94	4.72	1	6	-2	22.87	22.39	3.43
2	-5	-1	48.51	49.00	4.53	1	7	-2	41.17	39.69	3.81
2	-6	-1	22.02	22.43	2.74	1	8	-2	21.11	22.44	3.52
2	-7	-1	18.67	20.30	2.33	1	9	-2	24.67	19.88	3.52
2	-8	-1	24.89	25.15	3.18	1	10	-2	26.57	22.30	3.80
2	-9	-1	15.55	13.76	2.60	-1	1	-2	79.07	68.36	8.24
-2	-1	-1	38.79	37.58	3.83	-1	2	-2	85.91	71.26	8.48
-2	-2	-1	37.65	44.85	3.70	-1	3	-2	37.00	23.89	3.22
-2	-3	-1	52.68	58.03	5.26	-1	4	-2	43.77	41.84	4.21
-2	-4	-1	23.72	27.64	3.01	-1	5	-2	43.45	47.29	4.14
-2	-5	-1	27.73	26.28	3.51	-1	6	-2	28.47	29.22	2.84
-2	-6	-1	31.19	35.11	3.90	-1	7	-2	39.23	35.37	3.27

TABLE IV (Continued)

H	K	L	F(OBS)	F(CALC)	SIGMA	H	K	L	F(OBS)	F(CALC)	SIGMA
-1	8	-2	22.96	28.85	3.27	4	8	-2	17.07	17.64	2.85
-1	9	-2	18.73	16.88	2.34	-4	0	-2	30.88	30.91	3.08
-1	10	-2	22.50	18.78	4.51	-4	1	-2	28.50	28.65	3.29
2	0	-2	117.54	105.05	11.73	-4	2	-2	21.02	21.11	3.00
2	1	-2	34.58	30.72	3.40	-4	3	-2	32.38	29.62	5.06
2	2	-2	35.77	35.76	3.73	-4	4	-2	27.66	24.57	2.51
2	3	-2	68.28	59.93	6.88	-4	5	-2	17.35	16.86	2.18
2	4	-2	69.47	67.72	6.83	-4	6	-2	24.01	20.17	3.42
2	5	-2	32.43	29.49	3.69	-4	7	-2	16.52	15.60	2.76
2	6	-2	44.05	46.52	5.18	5	0	-2	22.71	21.23	2.84
2	7	-2	36.71	33.51	4.59	5	1	-2	19.69	19.36	3.28
2	8	-2	15.38	15.35	2.56	5	2	-2	28.26	28.35	3.54
2	9	-2	21.38	20.96	4.27	5	3	-2	22.16	21.92	3.17
2	10	-2	14.52	17.03	3.61	5	4	-2	21.25	18.30	3.54
-2	0	-2	42.61	44.15	4.18	5	5	-2	23.96	19.56	3.43
-2	1	-2	69.91	33.80	6.89	-5	0	-2	20.06	18.01	4.02
-2	2	-2	38.78	58.57	3.69	-5	1	-2	23.56	22.16	3.36
-2	3	-2	41.69	36.63	4.27	-5	2	-2	12.62	14.81	3.16
-2	4	-2	46.01	42.09	4.41	-5	3	-2	15.66	13.86	2.62
-2	5	-2	33.85	47.81	3.08	-5	4	-2	18.49	15.55	2.31
-2	6	-2	24.58	32.57	2.46	6	1	-2	22.15	15.12	3.70
-2	7	-2	28.98	23.19	3.62	6	2	-2	20.45	16.63	4.09
-2	8	-2	17.98	25.21	2.24	1	-1	-2	15.59	17.84	1.44
-2	9	-2	13.62	16.76	3.42	1	-2	-2	49.79	43.74	6.30
3	0	-2	61.45	61.06	6.21	1	-3	-2	45.17	48.51	4.41
3	1	-2	37.56	37.31	3.85	1	-4	-2	36.27	43.92	3.54
3	2	-2	55.12	51.99	5.58	1	-5	-2	46.95	50.42	4.88
3	3	-2	50.27	49.90	6.39	1	-6	-2	30.63	30.56	3.41
3	4	-2	28.83	26.85	3.40	1	-7	-2	19.57	16.90	3.26
3	5	-2	34.42	32.27	3.28	1	-8	-2	26.27	25.54	2.91
3	6	-2	34.25	36.17	3.80	-1	0	-2	57.59	56.56	5.68
3	7	-2	22.95	19.20	3.27	-1	-1	-2	76.04	81.01	7.64
3	8	-2	16.12	17.85	2.67	-1	-2	-2	34.78	35.92	3.36
3	9	-2	19.91	20.79	2.48	-1	-3	-2	30.67	29.72	3.26
-3	0	-2	44.73	44.01	4.36	-1	-4	-2	38.88	45.47	3.79
-3	1	-2	30.11	28.53	3.17	-1	-5	-2	23.57	26.78	1.96
-3	2	-2	42.98	39.13	4.52	-1	-6	-2	21.33	24.94	2.67
-3	3	-2	44.81	43.67	4.60	-1	-7	-2	34.15	31.02	4.02
-3	4	-2	31.77	28.33	3.52	-1	-8	-2	27.09	17.50	3.02
-3	5	-2	27.35	27.61	3.42	-1	-9	-2	16.94	11.71	2.83
-3	6	-2	36.46	28.45	3.84	2	-1	-2	68.28	57.08	6.74
-3	7	-2	17.78	17.02	2.22	2	-2	-2	60.22	54.19	5.96
-3	8	-2	18.92	19.38	2.37	2	-3	-2	56.33	55.51	5.59
-3	9	-2	20.11	19.61	2.52	2	-4	-2	37.62	36.89	3.76
4	0	-2	49.79	44.00	4.98	2	-5	-2	36.53	33.04	3.65
4	1	-2	37.28	37.40	3.99	2	-6	-2	32.25	33.28	3.40
4	2	-2	39.35	31.39	3.93	2	-7	-2	14.09	14.58	2.34
4	3	-2	25.79	26.93	3.22	2	-8	-2	21.76	21.45	3.62
4	4	-2	15.60	14.34	1.95	2	-9	-2	25.48	20.42	3.65
4	5	-2	29.70	28.58	3.43	-2	0	-2	40.40	44.15	4.04
4	6	-2	27.62	21.96	2.76	-2	-1	-2	56.78	61.51	5.73
4	7	-2	22.73	15.40	3.79	-2	-2	-2	39.14	42.97	3.84

H	K	L	F(OBS)	F(CALC)	SIGMA	H	K	L	F(OBS)	F(CALC)	SIGMA
-2	-3	-2	37.77	41.09	3.88	-1	2	-3	59.86	46.85	5.84
-2	-4	-2	37.72	40.12	3.54	-1	3	-3	62.49	56.43	6.25
-2	-5	-2	23.15	22.53	2.32	-1	4	-3	62.05	63.96	6.33
-2	-6	-2	27.71	23.09	3.47	1	3	-3	63.78	56.47	7.97
-2	-7	-2	35.87	20.61	3.17	1	4	-3	67.52	65.91	6.75
-2	-8	-2	23.06	12.63	3.84	1	5	-3	36.25	36.36	3.63
-2	-9	-2	17.56	14.81	2.94	0	6	-3	47.46	49.54	4.74
3	0	-2	60.79	61.06	6.08	1	6	-3	45.27	45.57	4.52
3	-1	-2	58.82	51.37	5.88	1	7	-3	17.79	18.78	2.32
3	-2	-2	43.40	35.84	4.35	1	8	-3	21.21	20.81	2.65
3	-3	-2	48.68	47.08	5.02	1	9	-3	32.45	28.54	4.06
3	-4	-2	23.40	27.00	2.70	-1	5	-3	30.78	26.03	3.84
3	-5	-2	24.67	23.69	3.08	-1	6	-3	36.82	32.05	4.60
3	-6	-2	34.80	33.52	3.48	-1	7	-3	44.69	44.45	4.47
3	-7	-2	14.67	17.97	2.45	-1	8	-3	24.94	20.22	3.11
-3	0	-2	37.81	44.01	4.05	-1	9	-3	25.12	17.82	3.23
-3	-1	-2	37.44	37.57	3.94	-1	10	-3	22.75	22.40	2.96
-3	-2	-2	22.30	21.45	2.79	2	1	-3	29.74	21.32	2.97
-3	-3	-2	30.03	31.08	3.16	2	2	-3	51.94	49.64	5.20
-3	-4	-2	28.73	29.30	2.88	2	3	-3	61.41	60.11	6.24
-3	-5	-2	21.16	19.58	3.03	2	5	-3	48.13	37.14	4.82
-3	-6	-2	19.26	20.70	3.84	2	6	-3	36.94	36.08	4.62
-3	-7	-2	16.06	15.82	2.66	2	7	-3	24.63	25.51	5.88
4	-1	-2	39.19	39.59	4.19	2	8	-3	28.11	27.83	3.51
4	-2	-2	10.97	14.32	1.82	2	9	-3	23.46	22.24	2.92
4	-3	-2	34.30	34.61	3.95	-2	1	-3	51.75	46.58	5.18
4	-4	-2	27.92	25.06	2.79	-2	2	-3	39.22	39.12	3.92
4	-5	-2	10.96	14.95	2.72	-2	3	-3	29.07	28.30	3.68
4	-6	-2	23.57	24.09	4.42	-2	4	-3	46.64	47.87	4.66
4	-7	-2	20.03	21.37	4.02	-2	5	-3	41.03	38.72	4.11
-4	0	-2	26.88	30.91	2.69	-2	6	-3	28.90	25.20	3.66
-4	-1	-2	14.27	15.76	1.79	-2	7	-3	34.32	31.31	4.29
-4	-2	-2	14.85	17.69	1.86	-2	8	-3	25.98	24.76	3.24
-4	-3	-2	25.91	25.46	2.36	-2	9	-3	17.00	15.25	2.83
-4	-4	-2	14.33	17.13	2.39	3	1	-3	46.78	39.50	4.68
-4	-5	-2	15.23	15.46	2.55	3	2	-3	62.92	55.74	6.35
-4	-6	-2	13.22	15.77	3.28	3	3	-3	48.20	46.42	4.82
5	-3	-2	18.72	19.74	3.12	3	4	-3	28.67	25.30	2.87
5	-4	-2	32.14	27.64	3.02	3	5	-3	45.50	48.28	4.55
5	-5	-2	17.01	17.15	2.13	3	6	-3	31.19	31.01	3.95
-5	0	-2	21.25	18.01	3.04	3	7	-3	22.90	25.67	2.95
-5	-1	-2	11.61	13.82	2.89	3	8	-3	22.75	22.97	2.84
-5	-2	-2	14.65	18.03	2.45	-3	1	-3	30.80	26.45	3.89
-5	-3	-2	12.43	13.93	3.13	-3	2	-3	38.85	35.81	4.89
0	3	-3	66.87	61.63	8.44	-3	3	-3	28.52	30.22	3.56
0	4	-3	50.65	49.43	4.87	-3	4	-3	33.43	32.28	4.18
0	5	-3	22.57	19.69	2.82	-3	5	-3	34.95	31.77	4.37
0	7	-3	38.89	37.56	4.87	-3	6	-3	19.39	20.35	2.52
0	8	-3	14.96	15.94	2.49	-3	7	-3	20.48	17.24	2.66
0	9	-3	24.71	28.05	3.18	-3	8	-3	23.76	20.45	2.97
0	10	-3	26.58	22.68	3.41	4	1	-3	52.35	47.59	5.33
-1	1	-3	97.32	79.94	12.23	4	2	-3	54.98	55.66	5.69

TABLE IV (Continued)

H	K	L	F(OBS)	F(CALC)	SIGMA	H	K	L	F(OBS)	F(CALC)	SIGMA
4	3	-3	25.81	25.18	3.23	2	-7	-3	24.86	23.14	3.18
4	4	-3	33.08	29.52	4.14	-2	0	-3	37.55	33.72	3.75
4	5	-3	32.90	29.98	4.11	-2	-1	-3	42.43	58.27	4.18
4	6	-3	19.50	15.53	2.52	-2	-2	-3	46.14	48.18	4.61
4	7	-3	18.52	19.93	2.32	-2	-3	-3	45.90	19.31	4.77
-4	1	-3	22.42	21.57	2.88	-2	-4	-3	26.86	29.13	3.39
-4	2	-3	30.55	26.31	4.11	-2	-5	-3	32.26	27.69	4.04
-4	3	-3	21.01	21.84	2.63	-2	-7	-3	22.08	18.52	2.77
-4	4	-3	17.56	17.85	2.20	3	0	-3	31.67	27.24	3.29
-4	5	-3	25.65	22.10	3.20	3	-1	-3	70.54	81.42	8.77
-4	6	-3	18.87	17.70	2.34	3	-2	-3	36.47	39.47	3.65
5	1	-3	11.52	25.82	2.87	3	-3	-3	32.35	34.76	3.23
5	2	-3	24.65	24.24	3.15	3	-4	-3	37.66	35.62	3.77
5	3	-3	11.87	15.13	2.97	3	-5	-3	17.50	17.01	2.18
5	4	-3	32.51	29.81	4.06	3	-6	-3	15.71	21.84	1.96
5	5	-3	18.11	17.36	2.27	3	-7	-3	24.25	27.08	3.04
-5	1	-3	16.42	14.50	2.73	-3	0	-3	24.74	24.72	3.13
-5	2	-3	23.21	17.58	2.90	-3	-1	-3	34.41	31.88	3.45
-5	3	-3	23.39	17.65	2.93	-3	-2	-3	21.11	22.83	2.64
-5	6	-3	20.53	15.08	2.56	-3	-3	-3	18.95	23.56	2.43
6	3	-3	16.24	16.94	2.72	-3	-4	-3	29.83	28.94	3.78
6	4	-3	19.24	17.41	2.41	-3	-5	-3	14.39	17.32	2.40
0	-1	-3	30.04	30.65	3.00	-3	-6	-3	12.66	13.26	3.16
0	-2	-3	52.83	57.17	5.28	4	0	-3	15.63	20.69	1.96
0	-3	-3	44.10	48.21	4.41	4	-1	-3	37.73	39.70	3.77
0	-4	-3	25.07	26.78	3.14	4	-2	-3	33.51	30.89	3.34
0	-5	-3	33.52	33.19	3.36	4	-3	-3	18.63	18.83	2.33
0	-6	-3	32.67	33.30	4.12	4	-4	-3	32.65	30.38	4.11
0	-7	-3	21.91	21.51	2.82	4	-5	-3	24.40	23.99	3.05
0	-8	-3	18.16	20.09	2.27	4	-6	-3	16.70	18.08	2.09
1	-1	-3	39.49	33.46	5.00	4	-7	-3	20.19	21.19	2.63
1	-2	-3	40.58	48.56	4.10	-4	0	-3	22.51	21.70	2.82
1	-3	-3	53.62	58.75	5.26	-4	-1	-3	22.06	21.04	2.82
1	-4	-3	37.97	42.59	3.80	-4	-2	-3	15.37	16.75	1.91
1	-5	-3	23.79	27.42	3.01	-4	-3	-3	18.10	18.77	2.36
1	-6	-3	30.47	30.37	3.86	-4	-4	-3	14.86	16.91	2.47
1	-7	-3	18.32	17.84	2.37	5	-1	-3	16.69	19.89	2.10
-1	0	-3	32.97	36.16	3.22	5	-2	-3	29.26	30.64	3.70
-1	-1	-3	50.18	52.17	5.09	5	-3	-3	14.94	19.44	1.87
-1	-2	-3	57.18	70.99	5.80	5	-4	-3	17.72	19.94	2.29
-1	-3	-3	32.06	34.09	3.20	5	-5	-3	14.63	19.07	2.45
-1	-4	-3	26.03	24.15	3.29	-5	-0	-3	16.47	16.57	2.06
-1	-5	-3	32.32	37.48	4.09						
-1	-6	-3	24.68	24.55	3.09						
-1	-7	-3	17.14	17.83	2.14						
2	0	-3	51.98	52.59	6.52						
2	-1	-3	57.86	75.04	7.24						
2	-2	-3	36.00	39.20	3.60						
2	-3	-3	38.05	44.67	3.95						
2	-4	-3	38.81	38.69	3.97						
2	-5	-3	23.39	20.58	2.92						
2	-6	-3	28.12	31.72	3.51						

lying across a centre of symmetry are such that a hydrogen bond could exist, it is possible that the hydrogen atom is at this special position. However, at this stage in the refinement there were no pair of oxygen atoms found to be closer than 3.2 $\overset{o}{A}$ and no pair of nitrogen atoms closer than 3.8 $\overset{o}{A}$ across a centre of symmetry. These distances are too large to represent a hydrogen bond and it must be concluded that the hydrogen atom does not lie on a special position and that the space group is P 1.

A further indication that the structure is non-centrosymmetric is found in the anisotropic temperature factors of the perchlorate ion, (Table III). The large anisotropy in the motion can be interpreted in more than one way. One is that the anion is librating, another is that we are observing the centrosymmetric average of two crystallographically unrelated $(ClO_4)^-$ groups . It will now be shown that both these physical situations will give rise to almost identical x-ray diffraction patterns.

In general for an atom at a position $\underline{r}$ with a temperature factor given by θ, the trigonometric part of the structure factor will be given by

$$F_1 = \exp(2\pi i \underline{s} \cdot \underline{r}) \exp \theta$$

Let us assume that we have an atom at $\underline{x}$ centrosymmetrically related to another at $-\underline{x}$. The temperature factor will be the same for both. Writing

$$\eta = 2\pi \underline{s} \cdot \underline{x}$$

$$F_1 = \exp(\theta)\{\exp(i\eta) + \exp(-i\eta)\}$$

$$= 2 \exp(\theta) \cos(\eta)$$

If, on the other hand, there are two atoms at $\underline{x} + \underline{\delta}$ and $-\underline{x} + \underline{\delta}$, where $\delta \ll 1$, each with a temperature factor $\exp(\theta')$ then

$$F_2 = \{\exp[2\pi i \underline{s} \cdot (\underline{x} + \underline{\delta})] + \exp[2\pi i \underline{s} \cdot (-\underline{x} + \underline{\delta})]\}\exp(\theta')$$

setting $\eta = 2\pi i \underline{s} \cdot \underline{x}$ as before

and $\qquad \Delta = 2\pi i \underline{s} \cdot \underline{\delta}$

then $\qquad F_2 = 2\exp(\theta')\{\cos(\eta)\}\{\cos\Delta + i\sin\Delta\}$

$\qquad \delta \ll 1$, Δ is small and $\cos\Delta > \sin\Delta$.

Thus, in summing over all the atoms in the unit cell, the real part of the structure factor will be much larger than the imaginary part, and the modulus of F_2 will be almost equal to the real part, that is,

$$|F_2| = 2 \exp(\theta') \cos\Delta \cos\eta$$

thus

$$|F_1| = |F_2| \quad \text{if} \quad \exp(\theta) = \exp(\theta') \cos\Delta$$

Both these functions can be expanded in power series of s^2. Over the limited range of s accessible to measurement and recalling that Δ is small, it is possible to set these two functions equal within the accuracy of the available measurements of F. Thus it is not possible to distinguish between the two situations.

A possible set of atomic positions for the oxygen atoms of the anion were calculated for a noncentrosymmetric

structure. It was assumed that the Cl atoms were not displaced from the values given in Table III and that the $(ClO_4)^-$ ions were tetrahedral but both rotated in the same sense about a direction almost parallel to [110] so as to destroy the centre of symmetry. The extent of the rotation was determined by displacing the oxygen atoms from the values in Table III by the amount of the RMS displacement indicated by the anisotropic temperature factors. These positions and anisotropic temperature factors for all the atoms, except the oxygen atoms of the perchlorate ions, were refined by least squares in the space group P 1. The R-factor dropped from 0.13 to 0.12, but this was not felt to be significant, considering the large number of additional variables which had been introduced in going from space group P $\bar{1}$ to P1.

Because of the small contribution of the imaginary part of the structure factor, in all cases $|F_{P1}| - |F_{P\bar{1}}|$ was much less than the standard deviation in the intensity measurements. The refinement could not be, therefore, carried further. The structure appears to be pseudo-centrosymmetric.

CHAPTER IV

DISCUSSION

Environment of the Rhenium

When refined in the space group P $\bar{1}$, the rhenium atom is surrounded by a distorted octahedral arrangement of ligand atoms, Figure VII. The interatomic distances and angles are given in Table V. The oxygen atoms, related through the centre of symmetry at the rhenium, have a bond length of 1.84 $\overset{o}{A}$. This is somewhat long for a double bond such as is found in the compound ReO_3Cl, where the Re-O bond length is found to be 1.76 $\overset{o}{A}$.[19] The nitrogen atoms of the ethylenediamine ring lie almost in a plane perpendicular to the Re-O direction, as can be seen from the angles in Table V. The distances of the nitrogen atoms are for Re-N(1) and Re-N(2) 2.16 and 2.11 $\overset{o}{A}$ respectively. These lengths can be compared with the Co-N lengths of 1.98 and 2.00 $\overset{o}{A}$ found by Nakajara, Saito and Kuroya[20], in $[Co(en)_2Cl_2]^+$. The radius of cobalt is expected to be smaller than that of rhenium and, this is reflected in the differences in the bond lengths.

The Re-N-C angles were found to be 109 and 113° for N(1) and N(2) respectively. This can be compared to the equivalent angles of 108 and 110° in $[Co(en)_2Cl_2]^+$. In the rhenium complex the angles are significantly larger and

Figure VII
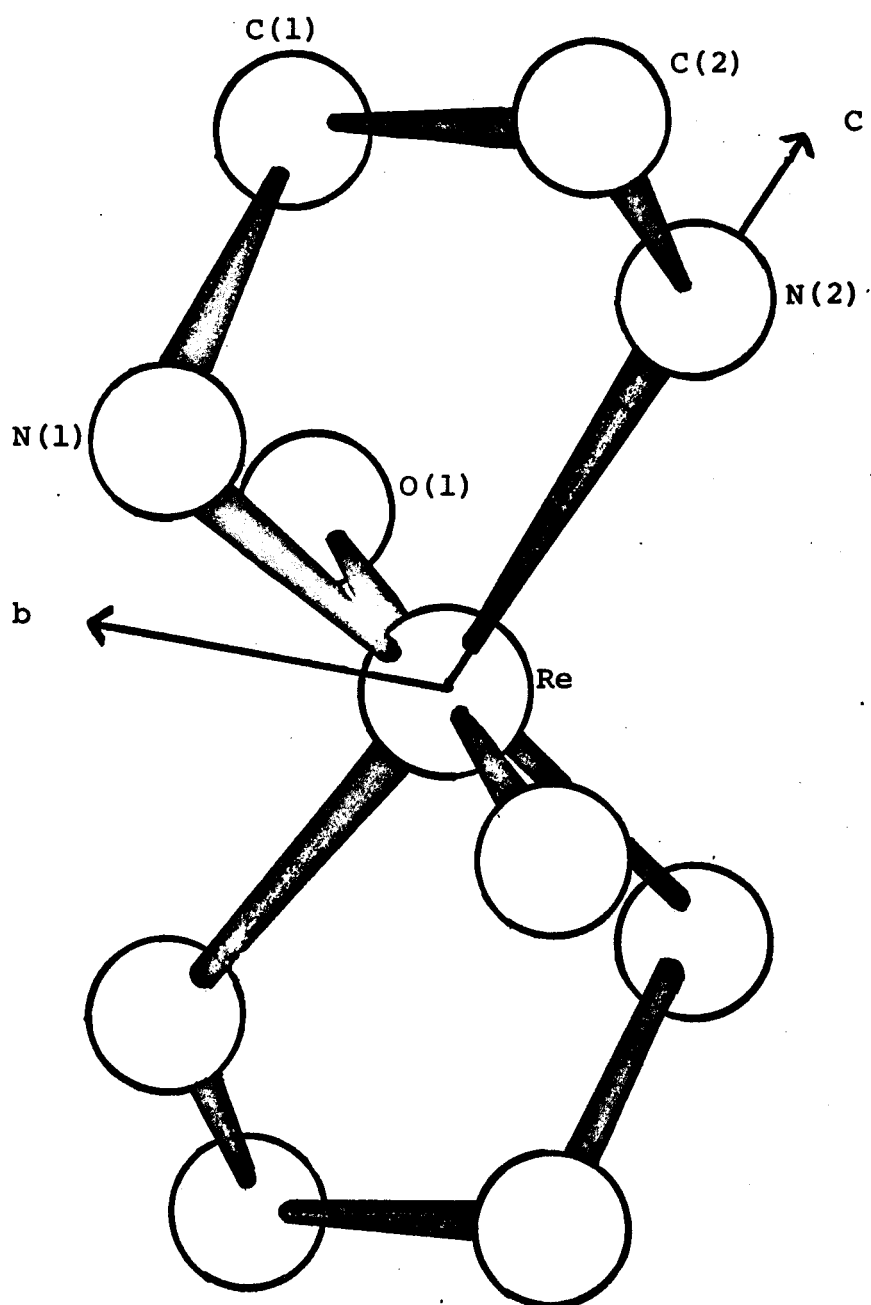
The Cation

Table V

Bond Lengths and Angles

Cation

Bond	Distance (Å)		Atoms Forming Angle	Angle (degrees)	
Re-O(1)	1.835	(29)	O(1)-Re-N(1)	88.4	(1.2)
Re-N(1)	2.163	(33)	O(1)-Re-N(2)	89.8	(1.7)
Re-N(2)	2.112	(20)	Re-N(1)-C(1)	109.1	(2.2)
N(1)-C(I)	1.504	(33)	Re-N(2)-C(2)	113.1	(2.5)
N(2)-C(2)	1.58	(6)	N(1)-C(1)-C(2)	109.2	(2.3)
C(1)-C(2)	1.570	(47)	N(2)-C(2)-C(1)	101.6	(2.7)
			N(1)-Re-N(2)	80.3	(1.5)

Anion

Bond	Distance (Å)		Atoms Forming Angle	Angle (degrees)	
Cl-O(2)	1.49	(4)	O(2)-Cl-O(3)	116	(4)
CI-O(3)	1.43	(6)	O(2)-Cl-O(4)	105	(3)
Cl-O(4)	1.57	(4)	O(2)-Cl-O(5)	109	(3)
Cl-O(5)	1.40	(5)	O(3)-Cl-O(4)	107	(3)
			O(3)-Cl-O(5)	115	(3)
			O(4)-Cl-O(5)	105	(3)

Bracketed quantities indicate the error in the last figure quoted

can be explained on the basis of the size of the metal

atom. If the radius of the rhenium atom is larger than

that of the cobalt atom, the Re-N bond lengths would be

longer than the Co-N bond lengths. Also, since the

ethylenediamine ring must remain approximately the same

in both complexes, the larger radius of the rhenium would

make the Re-N-C angles larger than the Co-N-C angles and

the N-Re-N angle smaller than the N-Co-N. The angle

subtended at the cobalt atom in the complex $[Co(en)_2Cl_2]^+$

was 89°. The same angle in the rhemium complex is 80°.

The carbon atoms are in a puckered arrangement

around the ring with the N-C-C angles of 109° and 101°.

The latter appears to be significantly different from the

expected tetrahedral angle. The N-C distances found were

1.58 and 1.50 $\overset{o}{A}$. The former distance is considerably

larger than the N-C distance of the cobalt complex of

1.48 $\overset{o}{A}$. Unfortunately, the standard deviation is very large

and thus, the distances could be considered to be in

agreement.

The C-C bond distance in the rhenium structure of

1.57 $\overset{o}{A}$ agrees within experimental error with the C-C bond

distance in the cobalt compound of 1.55 $\overset{o}{A}$. The cation

structure can, thus, be considered to be composed of a

pair of puckered rhenium ethylenediamine rings,with the

rhenium and the nitrogen atoms lying in the plane perpendicular

to the Re-O direction. The first neighbour atoms form a

distorted octahedron at distances of 1.84, 2.16 and 2.11 $\overset{o}{A}$,
centrosymmetrically related through the rhenium to the other
members of the cation.

Structure of the Anion

The structure of the anion cannot be considered as
accurately determined because of the large anisotropic thermal
vibrations found during the refinement. This, as stated
earlier, can be attributed to either a libration of the ion
or to the averaging of two crystallographically unrelated
$(ClO_4)^-$ groups. It is interesting to compare the average
bond length and angles found in the centrosymmetric structure
with the equivalent distances and angles in hydronium per-
chlorate[21]. In the present structure the average bond distance
is 1.47 $\overset{o}{A}$ with a standard deviation of 0.05 $\overset{o}{A}$, and the average
angle is 109° with a standard deviation of 3°. In the
hydronium perchlorate the average distance is 1.46 $\overset{o}{A}$ with
a standard deviation of 0.01 $\overset{o}{A}$ and an average angle of 109.6°,
with a standard deviation of 0.3°.

Although the structure is not completely determined,
it is possible to speculate on which of the two structures
proposed in Chapter I is correct. Both Re-O distances are
here the same, but this is because the refinement was
carried out in a centrosymmetric space group and does not
reflect the true structure of the complex. If the model D
(see Figure I) were correct, we would expect bond lengths
of about 1.8 $\overset{o}{A}$, with a large anisotropy in the temperature

factors of the cation oxygen atom, along the Re-O bond direction. Although the length of this bond is 1.84 $\overset{\text{o}}{\text{A}}$, the temperature factors are not very anisotropic and what anisotropy there is, appears as an elongation in a direction perpendicular to the bond.

If the structure, H, were correct, no anisotropy would be expected but the bond should be 2.0 $\overset{\text{o}}{\text{A}}$, much larger than observed.

Another possible structure which could exist is one in which the odd hydrogen atom has migrated to the cation and the compound could be formulated as $[ReO_2(en)_2]^+(ClO_4)^-$ $(HClO_4)$. This, however, is unlikely since this arrangement would require that perchloric acid should crystallize out of solution in an unionized form.

There is also the possibility that perhaps the odd hydrogen atom is not present at all but, as discussed in Chapter I, this seems equally unlikely.

Thus, the dispute has not been resolved and nothing definite can be said about the bonding in this complex.

The inaccuracy in the intensity measurements is one of the major factors in the difficulty of refining the structure further. The error in the intensities would have to be of the order of 1 to 2% for the imaginary part of the structure factor to be detectable. At present, the best accuracy which can be attained is of the order of 5 to 7%, which is not sufficient to remove the ambiguity.

Anomolous dispersion in the rhenium atom could provide a way out of the difficulty. In anomolous dispersion the scattering factor for an atom has an imaginary component.

The structure factor for a particular value of $\underline{s}$ is given earlier as

$$F(\underline{s}) = \sum_j f_j \exp(2\pi i \underline{s} \cdot \underline{R}_j) \qquad (20)$$

If the scattering factors of the atoms are complex the structure factor takes the form

$$F(\underline{s}) = \sum_j (f_j^R + if_j^I)\exp(2\pi i \underline{s} \cdot \underline{R}_j) \qquad (21)$$

where f_j^R is the real part and f_j^I is the imaginary part of the scattering factor. If one atom, in this case, the rhenium atom, is at the origin and is the only atom for which the condition $f_j^R \gg f_j^I$ is not true, then (21) becomes

$$F(\underline{s}) = f_{Re}^R + if_{Re}^I + \sum_\ell f_\ell \exp\left\{2\pi i(\underline{s} \cdot \underline{R}_\ell)\right\} \qquad (22)$$

where ℓ runs over all atoms of the unit cell except the rhenium atom. The intensity is written as I, which is proportional to FF^* and

$$FF^* = [f_{Re}^R + if_{Re}^I + \sum_\ell f_\ell \exp(2\pi i\underline{s} \cdot R_\ell)][f_{Re}^R - if_{Re}^I + \sum_m \exp 2\pi i\underline{s} \cdot R_m] \qquad (23)$$

rewriting (23) in the form

$$F(\underline{s}) = f_{Re}^R + \sum_\ell \cos 2\pi \underline{s} \cdot \underline{R}_\ell + i[f_{Re}^I + \sum_\ell \sin 2\pi \underline{s} \cdot \underline{R}_\ell]. \qquad (24)$$

and setting in (24)

$$f^R_{Re} + \Sigma\ f_\ell\ \cos 2\pi \underline{s} \cdot \underline{R} = A.$$

$$f^I_{Re} = B$$

$$\Sigma_\ell\ f_\ell\ \sin 2\pi \underline{s} \cdot \underline{R}_\ell = C$$

(23 becomes)

$$I(\underline{s}) = F(\underline{s})\ F^*(\underline{s}) = (A + iB + iC)(A + iB - iC) = A^2 + (B + C)^2.$$

For the reflection corresponding to the reciprocal lattice

point $-\underline{s}$

$$I(-\underline{s}) = (A + iB - iC)(A - iB + iC) = A^2 + (B - C)^2\ .$$

In this case Friedel's law breaks down, that is to say,

$I(\underline{s})$ is not equal to $I(-\underline{s})$. Further $I(\underline{s}) - I(-\underline{s}) = $

$4BC = 4f^I_{Re} + \Sigma f_\ell\ \sin 2\pi \underline{s} \cdot \underline{R}_\ell$. It is possible that this might

be observable. For a typical reflection ($0\bar{5}5$), A = 54.5,

B = 7.9 and C = 8.2 for MoKα radiation so that

$$I(\underline{s}) = (54.5)^2 + (16.1)^2 = 3259$$
$$I(-\underline{s}) = (54.5)^2 + (0.3)^2 = 3004$$

Thus, the difference in intensity which is of the order of 9%

should be observable.

Since the x-ray interaction with the odd hydrogen is

small compared to the remaining atoms, a large error in

intensity measurements masks the contribution of this atom.

As a result its position cannot be precisely determined by

x-rays. However, hydrogen is an appreciable scatterer of

neutrons, and since the other atoms scatter in proportion

to $Z^{1/3}$ for neutrons, as compared to Z for x-rays, it is

quite possible that neutron diffraction techniques could locate the hydrogen atom positions. The result of this experiment would be that the hydrogens of the ethylenediamine rings, as well as the odd hydrogen, could be accurately located and the dispute as to the correct structure of the cation would be resolved beyond doubt.

Bibliography

1.   R. K. Murman, J. Inorg. Nucl. Chem., 18, (1961),226.

2.   N. P. Johnson, C. J. L. Lock and G. Wilkinson:

     J. Chem. Soc., 204, (1964), 1054.

3.   Ibid.

4.   Baldwin, J. Chem. Soc., (1960) 4369.

5.   R. K. Murmann and Forrester, J. Phys. Chem., 67 (1963), 1383.

6.   L. I. Evteev, Zhur. Neorg. Khim. 10 (1965), 1000.

7.   A. K. Murmann, J. Inorg. Nucl. Chem., 18, (1961), 226.

8.   C. Kittel, Introduction to Solid State Physics,

     John Wiley and Sons, Publishing Co., Second Edition,

     47,(1963).

9.   H. Lipson and W. Cochran, The Crystallinstate State, Vol. 3,

     G. Bell and Son Publishing Co., 275 (1966).

10. M. J. Buerger, Crystal-Structure Analysis, John Wiley

     and Sons, Inc. Publishing Co. 84 (1963).

11. D. C. Phillips, Acta Cryst, 7,(1954), 746.

12. D. C. Phillips, Acta Cryst, 9, (1956), 819.

13. A. K. Singh, Acta Cryst., 21 (1966) 447.

14. M. J. Buerger ,Crystal-Structure Analysis, John Wiley

     and Sons Inc.,Publishing Co., 156, (1963).

15. M. J. Buerger, Crystal-structure Analysis, John Wiley

     and Sons, Inc. Publishers, 27 (1963).

16. R. K. Murmann, J. Inorg. Nucl. Chem. 18, (1961) 226.

17. International Tables for X-ray Crystallography, Volume
    III Kynoch Press, Birmingham, England, 157 (1952).

18. M. E. Straumanis, T. Ejima and W. J. James, Acta Cryst,
    14 (1961) 493.

19. R. Javan and A. Engelbrecht, Physical Review 96 (1954)
    649.

20. A. Nakahara, Y. Saito and H. Kuroya, Bull. Chem. Soc.
    Japan, 25 (1952) 331.

21. C. E. Nordman, Acta Cryst , 15 (1962) 18.