

CRYSTAL STRUCTURE OF $[\text{Re}(\text{C}_5\text{H}_5\text{N})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$

X-RAY CRYSTAL STRUCTURE

INVESTIGATION OF

$[\text{Re}(\text{C}_5\text{H}_5\text{N})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$

By

NARASIMHAN KRISHNAMACHARI, B. Sc.

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 $[\text{Re}(\text{C}_5\text{H}_5\text{N})_4\text{O}_2]\text{Cl}\cdot 1.2\text{H}_2\text{O}$

AUTHOR: Narasimhan Krishnamachari, B.Sc. (Madras University)

SUPERVISOR: Professor C. J. L. Lock

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SCOPE AND CONTENTS: The crystal structure of dioxotetrapyridinerhenium(V) chloride dihydrate has been determined by single crystal x-ray diffraction methods. The structure has been found to belong to the trans-dioxo- group of compounds. The Re=O bond in the structure has been shown to have a bond-order of about 2, with the average Re=O bond length of 1.76(3) Å. The probable structures of the monohydrate and anhydrous dioxotetrapyridinerhenium(V) chloride have been discussed on the basis of the observed pseudo-symmetric structure for the dihydrate with a non-centrosymmetric space group. The nature and strength of the hydrogen bonds in the structure have also been discussed.

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To

Those who made it possible for me
to have the benefit of education
at the Graduate level
upto this point
and beyond.

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CHAPTER I

I N T R O D U C T I O N

Many compounds belonging to the class called "dioxo-complexes" (i.e. those having two oxygen atoms linked only to the central metal atom) are known. It has been observed in all of these compounds studied that there is no band in their infra-red spectra in the region 850 cm^{-1} to 1050 cm^{-1} . This region is generally accepted as the diagnostic region for the M=O stretch (1, 2). However, a band was observed in all these cases at about 820 cm^{-1} (Table I-1) which could not be assigned to any other infra-red active mode (3). In an attempt to explain the absence of a band in the region 850 cm^{-1} to 1050 cm^{-1} and the presence of the unaccounted band around 820 cm^{-1} , Johnson, Lock and Wilkinson (3) postulated that the latter band was caused by the M=O stretch and that the unusually low stretching frequency of the M=O bond was a consequence of the linear trans-dioxo-system. The main aim of the present work is to investigate the correctness of the postulated linear trans-dioxo-system in the case of dioxotetrapyridinerhenium(V) chloride by establishing its crystal structure.

TABLE I-1

INFRA-RED STRETCHING FREQUENCIES IN COMPLEXES OF THE

TYPE $[\text{MO}_2\text{L}_4]^{n+}$

Compound	$\nu_{\text{M=O}}$ (cm^{-1})	Reference
$[\text{Re}(\text{py})_4\text{O}_2] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$	814 vs	11
$[\text{Re}(\text{py})_4\text{O}_2] \cdot \text{Cl} \cdot \text{H}_2\text{O}$	820 s	10
$[\text{Re}(\text{py})_4\text{O}_2] \cdot \text{I} \cdot \text{H}_2\text{O}$	824 vs	11
$[\text{Re}(\text{py})_4\text{O}_2] \cdot \text{I}$	823 s	11
$[\text{Re}(\text{py})_4\text{O}_2] \cdot \text{Br} \cdot 2\text{H}_2\text{O}$	819 vs	11
$[\text{Re}(\text{en})_2\text{O}_2] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$	814 vs	11
$[\text{Re}(\text{en})_2\text{O}_2] \cdot \text{Cl}$	830 s	10
$[\text{Re}(\text{en})_2\text{O}_2] \cdot \text{I}$	819 vs	11
$\text{MoO}_2(\text{acac})_2$	906 vs	11
$\text{K}_3[\text{ReO}_2(\text{CN})_4]$	780 vs	11
$\text{Cs}_2[\text{RuO}_2\text{Cl}_4]$	814, 824	13
$\text{K}_2[\text{OsO}_2(\text{OH})_4]$	790 vs	14
$\text{K}_2[\text{OsO}_2\text{Cl}_4]$	837	15
$\text{Cs}_2[(\text{OsO}_2(\text{CN})_4)]$	830 vs	14
$[\text{OsO}_2(\text{NH}_3)_4] \cdot \text{Cl}_2$	808	15
$[\text{Re}(\text{py})_4\text{O}_2] \cdot \text{BPh}_4$	812 vs	11
$[\text{Re}(\text{py})_4\text{O}_2]_2 \cdot \text{PtCl}_6 \cdot 4\text{H}_2\text{O}$	816 vs	11
$\text{K}_2[\text{OsO}_2(\text{OCH}_3)_4]$	820	15
$[\text{Re}(\text{NH}_3)_4\text{O}_2] \cdot \text{Cl}$	835	18

py = pyridine $\text{C}_5\text{H}_5\text{N}$; en = ethylenediamine $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$
 Ph = phenyl $(\text{C}_6\text{H}_5)^-$; (acac) = acetylacetonate $(\text{CH}_3\text{COCHCOCH}_3)^-$
 vs = very strong; s = strong.

The nature of the rhenium-oxygen bond in $[\text{Re}(\text{py}^*)_4\text{O}_2]\text{Cl}$ has been discussed in terms of a simple molecular orbital approach (17). Of the five d orbitals, two ($d_{x^2-y^2}$ and d_{z^2}) are involved in σ -bonding. As a consequence of the tetragonal distortion from the octahedral field resulting from the non-equivalence of the axial and equatorial ligands, each set of t_{2g} orbitals is split into a degenerate pair having e_g symmetry and a singlet with b_{2g} symmetry. The b_{2g} (d_{xy}) orbitals are occupied by the two d electrons of $\text{Re}(\text{V})$ ion, as is indicated by the observed diamagnetism of $\text{Re}(\text{V})$ complexes (11). The d_{xz} and d_{yz} orbitals of rhenium atom, and the p_x and p_y orbitals of both the oxygen atoms, are available for forming π -bonds. These six orbitals together form two bonding, two non-bonding and two anti-bonding orbitals, as is indicated in Fig.I-1. There are eight electrons from the two oxygen atoms to be accommodated in these six orbitals. Four electrons occupy the two bonding orbitals and the remaining four occupy the two non-bonding orbitals. Thus a total of two π -bonds are formed between the rhenium atom and the two oxygen atoms, or, on the average one π -bond is formed between each oxygen atom and the rhenium atom. Each rhenium-oxygen bond is expected to be a double bond consisting of one σ -bond and one π -bond, with each oxygen atom contributing two out of the four π -electrons for π -bonding. Each oxygen atom will be left

*(py) represents the pyridine group ($\text{C}_5\text{H}_5\text{N}$).

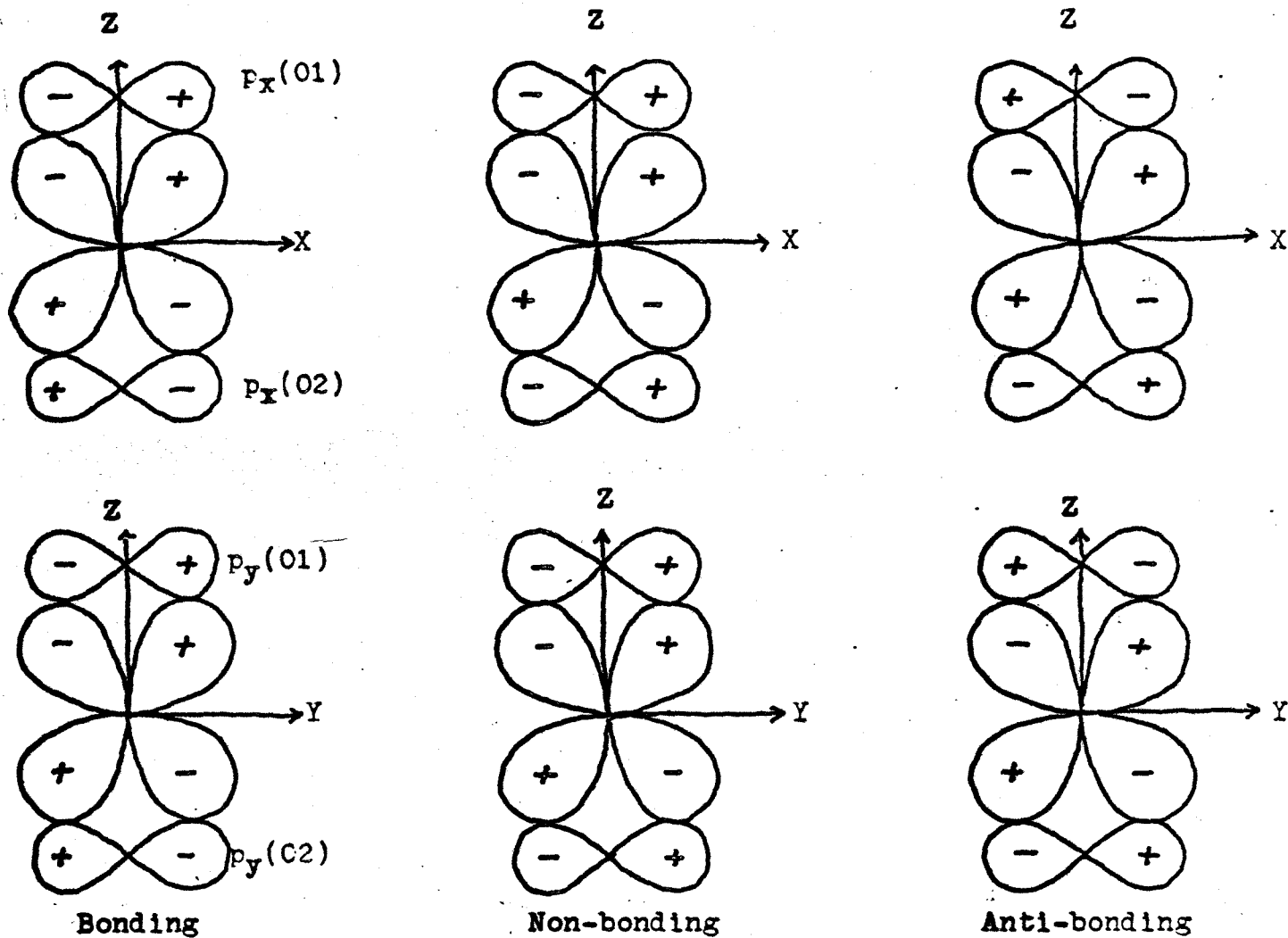
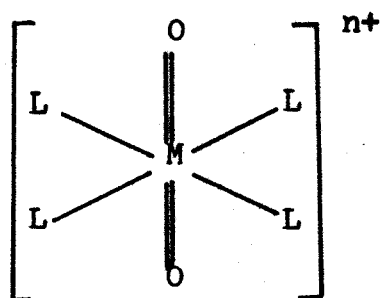


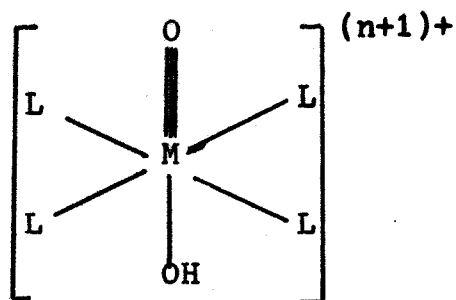
Fig.I-1. The d_{xz} and d_{yz} orbitals of the rhenium atom and the four p orbitals from the two oxygen atoms together give rise to two bonding, two non-bonding and two anti-bonding molecular orbitals.

with four non-bonded electrons. Thus, based on a trans-dioxo-structure one expects a bond-order of 2 between the rhenium atom and each oxygen atom, and also four non-bonded electrons with each oxygen atom.

The Re-O bonds in dioxo-compounds of the type $[MO_2L_4]^{n+}$ and the oxohydroxo-compounds of the type $[MO(OH)L_4]^{(n+)+}$ have been compared using the bonding scheme described above (11).



I. Dioxo-compound



II. Oxohydroxo-compound

To a first approximation, the bonding in the oxohydroxo-compound II is same as that in the dioxo-compound I, except that all the four π -electrons for the two π -bonds between the rhenium atom and the oxo-oxygen atom are now contributed by the same oxygen atom. There is thus a triple bond between the rhenium atom and the oxo-oxygen atom of compound II, consisting of one σ -bond and two π -bonds. Also, because all four $p\pi$ -electrons of this oxygen atom are now involved in π -bonding, there are only two non-bonded electrons with this oxygen atom. In the dioxo-compound I there should be a double bond between the rhenium atom and each oxygen atom with each oxygen atom having four non-bonded electrons,

while in the oxohydroxo-compound II there should be a triple bond between the rhenium atom and the oxo-oxygen atom, with the oxygen atom having only two non-bonded electrons.

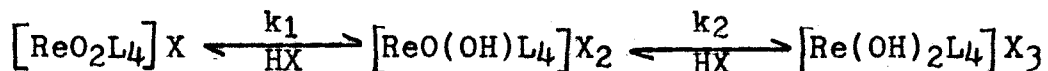
The reduction of the rhenium-oxygen bond order from 3 in the oxohydroxo-compound to 2 in the dioxo-compound, and the greater availability of non-bonded electrons in the dioxo-compound as compared to the oxo-compound, have been qualitatively found to be correct by indirect experimental evidence.

A comparison of the metal-oxygen bond-length between dioxo-compounds and oxo-compounds suggests that the bond in dioxo-compounds is longer. Thus, the M-O bond* is 1.75(2) Å in $K_2[OsO_2Cl_4]$ (4), 1.77 Å in $K_2[OsO_2(OH)_4]$ (5), and 1.87 Å in $K_3[ReO_2(CN)_4]$ (6), but is only 1.6 Å in the oxo-compound trans-oxotrichlorobis(diethylphenylphosphine)rhenium(V) (7). The longer bond-length in the dioxo-compound is indicative of the decrease in the Re-O bond order. Also, the Re-O stretch occurs at about 967 cm^{-1} in the case of the oxo-compound, which is the suggested region for an $Re\equiv O$ bond (11), compared with about 820 cm^{-1} in the case of the dioxo-compounds, indicating a bond order considerably lower than 3.

Protonation studies have indicated the relative availability of non-bonded electrons in the dioxo-compounds. The equilibrium constants k_1 and k_2 for the protonation of the dioxo-

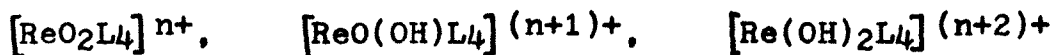
*The error in the bond distances is not included in cases where the original reference does not indicate the error.

compounds have been determined for X = Cl, L = ethylenediamine, 1,2-propylenediamine and 1,3-propylenediamine (8).

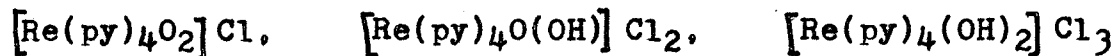


It is found in all these cases that the protonation of the dioxo-compound to the oxohydroxo-compound is substantially more rapid than the subsequent protonation of the oxohydroxo-compound to the dihydroxo-compound. The greater availability of non-bonded electrons in the dioxo-compounds as compared with oxohydroxo-compounds supports the bonding scheme discussed earlier. Thus, while in the dioxo-compounds each oxygen atom has four non-bonded electrons, in the oxohydroxo-compound there are only two non-bonded electrons with the oxo-oxygen atom, since now all four p π electrons of this oxygen atom are involved in π -bonding with the rhenium atom. The same has been observed in the case of $[\text{Re}(\text{en})_2\text{O}_2]\text{Cl}$, the monoprotection occurring relatively rapidly leading to the oxohydroxo-species $[\text{Re}(\text{en})_2\text{O}(\text{OH})]\text{Cl}_2$, while the subsequent protonation of the oxohydroxo-species to the dihydroxo-species $[\text{Re}(\text{en})_2(\text{OH})_2]\text{Cl}_3$ is so slow that the equilibrium constant could only be estimated (8). $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}$ is converted to $[\text{Re}(\text{py})_4\text{O}(\text{OH})]\text{Cl}_2$ with such ease that even passing hydrogen chloride gas over $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}$ at 20° C leads to mono-protonation (9), while protonation of the resulting oxohydroxo-species could only be achieved in presence of 36 M sulphuric acid (10).

In their comparison of Re-O bond lengths between dioxo- and oxohydroxo-compounds, Johnson, Lock and Wilkinson (11) have neglected the influence of the equatorial ligands on the axial ligands. While the oxo-compound under discussion had two chlorine atoms and two diethylphenylphosphine groups as the axial ligands, the dioxo-compounds had pyridine, ethylenediamine, cyanide, chloride or hydroxogroups as the axial ligands. A rigorous comparison between the Re-O bond lengths in the dioxo- and oxohydroxo-compounds can be made only if the equatorial ligands are the same in the compounds compared. Thus it will be of interest to compare the Re-O bond lengths in the series



where L is the same in all the three cases. The structure investigation of the pyridine compound $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}$ was undertaken as part of the series



When the structures of $[\text{Re}(\text{py})_4\text{O}(\text{OH})]\text{Cl}_2$ and $[\text{Re}(\text{py})_4(\text{OH})_2]\text{Cl}_3$ are known, a more detailed comparison of the theoretically predicted differences in properties of the dioxo- and oxohydroxo-compounds may be undertaken.

CHAPTER II

EXPERIMENTS

The compound dioxotetra(pyridine)rhenium(V) chloride dihydrate was prepared in the following manner: Rhenium metal (3 g) was dissolved in excess H₂O₂ (30%), and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in 18 N hydrochloric acid (7 ml), and the solution added to a stirred suspension of triphenylphosphine (25 g) in glacial acetic acid (250 ml). After being stirred for about half an hour, the product was filtered and washed with glacial acetic acid and diethyl ether. The resulting trans-oxotrichlorobis-(triphenylphosphine)rhenium(V) (1 g) was dissolved in excess hot pyridine and the solution allowed to stand overnight⁺. As the pyridine evaporated, needle-shaped orange crystals of [Re(py)₄O₂]Cl_{1.2}H₂O were obtained. (Found: C, 40.3; H, 4.3; N, 9.5; Cl, 6.0; O, 11.0%. Calculated for C₂₀H₂₄Cl₁N₄O₄Re: C, 39.6; H, 4.0; N, 9.2; Cl, 5.9; O, 10.6%)^{**}.

+ No special precautions were taken to dry the pyridine.

** Microanalyses were performed by M/s. Galbraith Laboratories, Knoxville, Tennessee, except for the oxygen analysis which was performed by the Microchemical Laboratories, Imperial College, London, by courtesy of Prof. G. Wilkinson.

A single crystal (~ 0.015 cm thick and 0.04 cm long) was mounted on a glass fibre with its long axis parallel to the fibre. The Weissenberg camera and Cu $K\alpha$ radiation were used to obtain the zeroth, first and second layer photographs. An examination of these photographs indicated that the crystal was monoclinic with a C-centered space group if the axis of rotation were chosen to be the \underline{c} axis. The oscillation photograph showed that the odd layers were substantially weaker than the even ones, indicating the existence of pseudo-symmetry.

The goniometer head was transferred to the precession camera and the crystal aligned so that the \underline{c}^* axis was parallel to the goniometer axis. Precession photographs of the $[010]$ and $[100]$ zones were obtained with Mo $K\alpha$ radiation.

From the Weissenberg photographs indexed as hkn ($n=0,1,2$) and the precession photographs of the $[010]$ and $[100]$ zones, a search was made for any further symmetry elements indicated by systematic absences. The ℓ odd reflections were missing in the $[010]$ zone photograph indicating the presence of a c-glide plane. Further, all $hk\ell$ reflections with $h+k$ odd were absent, confirming that the lattice was C-centered. Since no other systematic absences were noted, the space group possibilities are Cc or C2/c.

The accurate unit cell parameters of the crystal were obtained by calibration with tetragonal TiO_2 crystal as standard, the lattice parameters for the latter being taken as $a=4.5929(5)$ A and $c=2.9591(3)$ A (19). The $hk0$ reflections

from the rhenium compound and the $hk0$ reflections from the TiO_2 crystal were recorded on the same film using Weissenberg camera and $Cu K\alpha$ radiation. The distance x_{hk0} for a few high angle reflections were measured, where x_{hk0} is the perpendicular distance in millimeters from the spot indexed as $(hk0)$ to the zero-beam track on the Weissenberg film. Only those reflections were measured for which the α_1 and α_2 components were completely resolved. The values for the wavelengths of the $Cu K\alpha$ doublet were taken as $\lambda_{\alpha_1} = 1.54081 \text{ \AA}$ and $\lambda_{\alpha_2} = 1.54433 \text{ \AA}$ (20). The relation

$$\theta_{hk0} = \frac{57.3 x_{hk0}}{2 R} \quad (1)$$

was used to calculate the effective camera radius R , where θ_{hk0} for the TiO_2 reflection indexed as $(hk0)$ is obtained from the relation

$$\begin{aligned} \lambda_{hk0} &= 2 d_{hk0} \sin \theta_{hk0} \\ &= 2 \frac{(h^2 + k^2)}{a^2} \sin \theta_{hk0} \end{aligned}$$

The x_{hk0} values for a few high angle reflections of the rhenium compound were then measured, and the θ_{hk0} values for these reflections obtained from relation (1), using the value of R obtained above. The values for \underline{a}^* and \underline{b}^* were obtained by means of a least squares fit to these calculated values of θ . 20 independent values of θ were used in the refinement. The final values for the parameters are $\underline{a}^* = 0.08203(2) \text{ \AA}^{-1}$ and $\underline{b}^* = 0.08352(2) \text{ \AA}^{-1}$. The value for \underline{b}^* thus obtained was used to get the value of \underline{c}^* from the $[100]$ zone precession

photograph assuming isotropic film shrinkage. The value for β^* was obtained from the $[010]$ zone precession photograph. The final values for the parameters are $a=13.592(2)\text{\AA}$, $b=11.973(2)\text{\AA}$, $c=15.55(1)\text{\AA}$, $\beta=116.2(1)^\circ$.

The density of the salt was measured by the flotation method using a mixture of bromoform and carbon tetrachloride as the flotation medium. The composition of the mixture was varied till the density of the mixed solvent was the same as that of the crystals as determined by the fact that the crystals remained suspended in the medium. The solvent mixture was then transferred to a calibrated 25 ml specific gravity bottle and weighed. The density was found to be 1.77 g per ml⁺. The calculated density based on four molecules of $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ per unit cell was 1.78 g per ml.

Intensity photographs containing the $(h0l)$, $(0kl)$ and $(hk2\bar{h})$ type reflections were recorded using precession technique and Mo $K\alpha$ radiation. Three exposures of each level were taken to cover the full range of intensities. Accurately known exposure times of x hrs, $3x$ hrs, and $9x$ hrs with $x=1$ hr 40 mins. were used. Precautions were taken to see that the three films were developed under nearly identical conditions of developing time, temperature and concentration of the developing chemicals. The intensities of the reflections were measured by visual comparison using a logarithmic scale. If the intensity of a given reflection is assigned

⁺The measurements were made at room temperature ($\sim 20^\circ\text{C}$).

a value I_1 on the film exposed for x hrs, the intensity of the same reflection on the film exposed for $3x$ hrs should be $I_2 = 3 I_1$ and that on the film exposed for $9x$ hrs for the same reflection should be $I_3 = 9 I_1$. The logarithms to the base 3 of the intensities of the reflection under consideration on the three films are then simply related to each other. Thus, if $\log_3 I_1 = y$, then $\log_3 I_2 = 1+y$, and $\log_3 I_3 = 2+y$. For measurement of intensities, a reflection of very low intensity was chosen on the film exposed for x hrs, and arbitrarily assigned a value of $y=1$. The intensities of this reflection on the logarithmic scale are then 2 and 3 on the films exposed for $3x$ hrs and $9x$ hrs respectively. These three spots were used as standards, and the intensities of other reflections were estimated by visual comparison of the darkening of the spots relative to these standards.

Intensity photographs of hkn reflections ($n=0$ to 5) were taken on the Weissenberg camera using Cu $K\alpha$ radiation. The multiple film technique (21) was used for recording the intensities. Three films were inserted in the camera and exposed simultaneously. Each film of the pack acts as a uniform absorber and reduces the x-ray intensities which arrive at the film underneath it by a constant factor called the 'Film factor'. This factor was taken as 2.75 for Cu $K\alpha$ radiation and the Ilford film used for photographing (22). It was noticed that the odd layer line photographs (hkn with

n=1,3,5) contained many reflections which were in general much weaker than the even layer line reflections. Consequently, the time for which the odd layer line photographs were taken was increased to twice that allowed for even layer photographs. The intensities of the reflections were measured by the same method as that used for the precession films, except that the factor by which the intensities of the three films differ is now 2.75, as compared to a factor of 3 in the precession case.

The intensities were corrected for Lorentz-polarisation effects. Corrections for absorption (23) were applied assuming cylindrical geometry for the crystal (radius approximately 0.007 cm). The corrected intensities were used to prepare the Patterson synthesis. The Patterson function is defined as

$$P(u,v,w) = V \iiint P(x,y,z) P(x+u,y+v,z+w) dx dy dz$$

where $P(x,y,z)$ is the electron density at (x,y,z) . When the expression

$$P(x,y,z) = \frac{1}{V} \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} F_{hkl} \exp -2\pi i(hx+ky+lz)$$

is substituted in the above equation, it reduces to

$$P(u,v,w) = \frac{1}{V} \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} |F_{hkl}|^2 \exp 2\pi i(hu+kv+lw)$$

This function can be calculated using the measured intensities, since the Fourier coefficients $|F_{hkl}|^2$ are directly proportional to the measured intensities. The Patterson

function can be visualised as the product of electron densities at the two points (x,y,z) and $(x+u,y+v,z+w)$. We expect peaks in the Patterson function if there are atoms simultaneously at (x,y,z) and $(x+u,y+v,z+w)$. The height of the peak is proportional to the product of the electron densities at the two points. The Patterson function will thus give information on the interatomic vectors between atoms. If the atoms at (x,y,z) and $(x+u,y+v,z+w)$ are electronically rich or prominent x-ray scatterers, the peak at (u,v,w) will be large. In the present case with 4 rhenium atoms per unit cell having space group Cc, we expect 4^2 Re-Re peaks in the Patterson, 4 of which will be coincident with the origin (corresponding to the self-vector between each rhenium atom). The remaining 12 peaks will be made of 6 independent peaks, and 6 peaks centrosymmetrically related to these peaks. The height of a Re-Re double peak should correspond to 40% of the height of the origin peak. Since rhenium in a general position (x,y,z) has a symmetry-related rhenium at $(x,\bar{y},\frac{1}{2}+z)$ in addition to those generated by the C-centering operation, one would expect rhenium-rhenium interaction peaks at $(0,2y,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2})$. The Patterson syntheses using the intensity data of the $[010]$, $[001]$, and $[100]$ zones showed no peaks of this height except at the origin and the symmetry-related positions $(0,0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. This can be interpreted by assigning the rhenium atom to the $y=0$ plane. The values $x=0$ and $z=0$ were chosen for convenience and the rhenium atom was assigned the co-ordinates $(0,0,0)$.

The ambiguity in the choice of the space group as one of Cc or C2/c was solved using information from the Patterson syntheses. The general position in space-group Cc is four-fold while in space-group C2/c it is eight-fold. Since the unit-cell of $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ has four molecules based on density determination, the four rhenium atoms and the four chlorine atoms in one unit cell would lie in special positions if the space-group were to be C2/c. The rhenium atom has been assigned to the special position (0,0,0) based on information from the Patterson maps. Thus, the chlorine atom should occupy one of the remaining four-fold special positions $(0, y, \frac{1}{4})$, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$, $(\frac{1}{4}, \frac{1}{4}, 0)$ or $(0, \frac{1}{2}, 0)$, if the space group were C2/c (24). With the rhenium atom at the origin, this should lead to a Re-Cl peak at $(u=0, w=\frac{1}{4})$ in the Patterson in the first case, at $(u=\frac{1}{4}, w=\frac{1}{4})$ in the second case, at $(u=\frac{1}{4}, w=0)$ in the third case, and at $(u=0, v=\frac{1}{2})$ in the last case. None of these peaks were observed (Fig.II-1 and Fig.II-2), indicating that the chlorine atom does not occupy any of these special positions. Thus, it has to occupy a four-fold general position, and this suggested that the space-group should be Cc.

The largest non-origin peak found in the Patterson was at (-0.07, 0.37, 0.12). This peak was assigned to an Re-Cl vector, and the chlorine atom was accordingly assigned the co-ordinates (-0.07, 0.37, 0.12). With the chlorine atom at this position and with the rhenium atom at the origin, structure factors, $F_c(hkl)$, were calculated for the 92 reflections of the [100] zone, 131 reflections of the [010] zone,

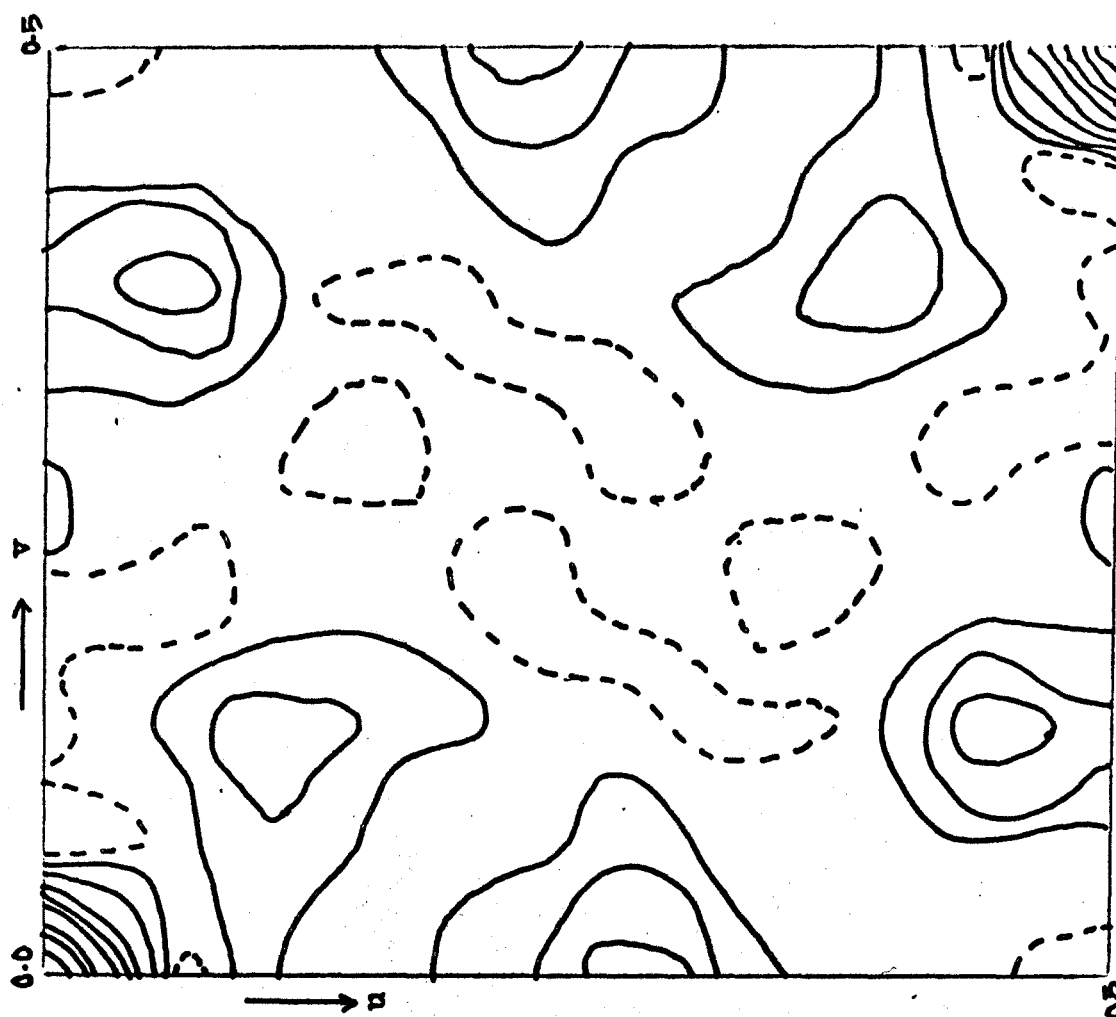


FIG. II-1-1. Patterson function of $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$
 $(hk0)$ projection

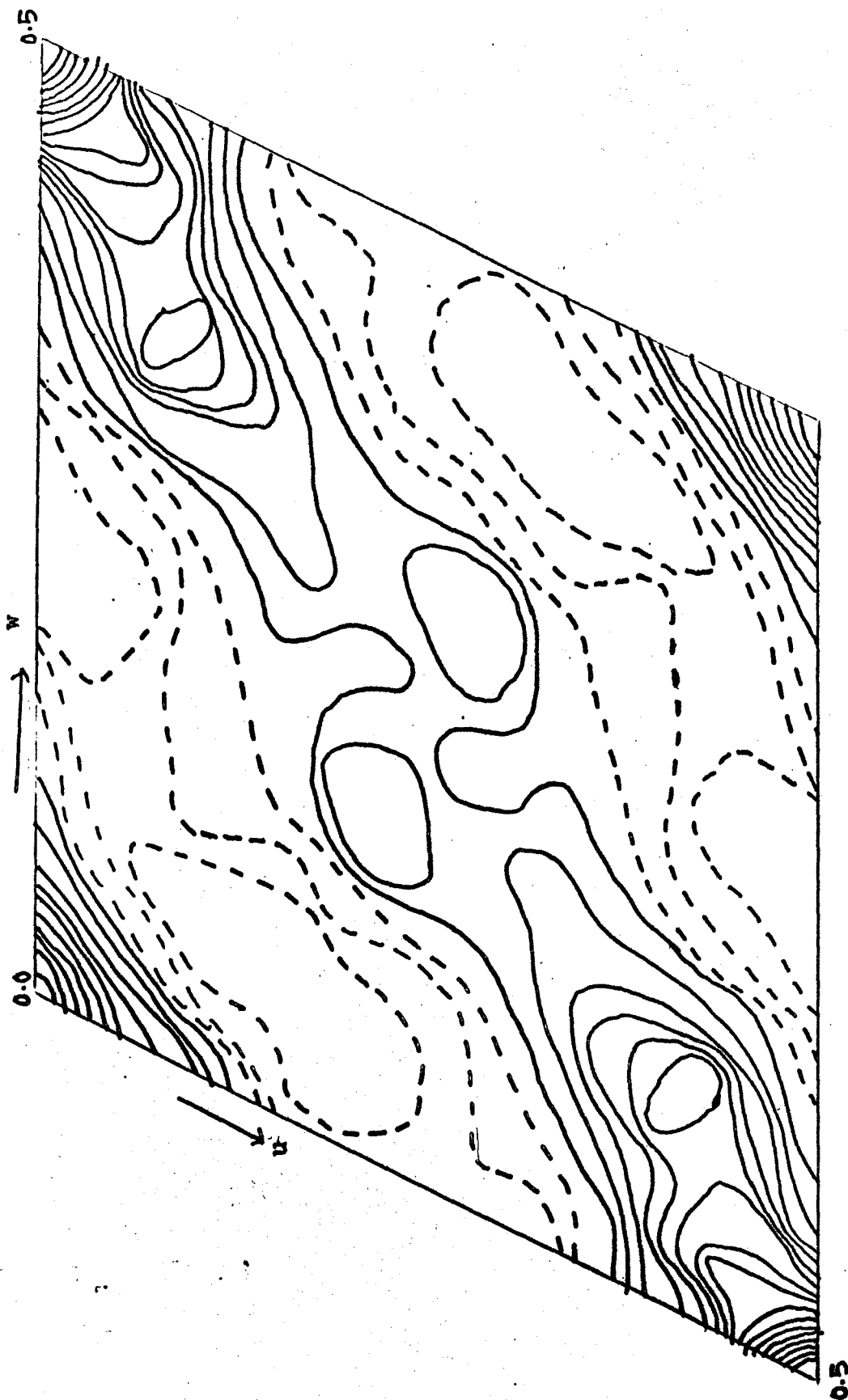


Fig. II-2. Patterson function of $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$
[h0l] projection.

0.5

and 121 reflections of the [001] zone, using the expression

$$F_c(hk\ell) = \sum_i f_i(hk\ell) \exp 2\pi i(hx_1 + ky_1 + \ell z_1) \exp \left\{ -B_1 \left(\frac{\sin \theta}{\lambda} \right)^2 \right\}$$

where $f_i(hk\ell)$ is the scattering factor of the i th species for the angle of scattering determined by $(hk\ell)$. (x_1, y_1, z_1) are the coordinates of the i th species, and B_1 are constants called 'temperature factors' and related to the mean square amplitude of vibration of the i th species, the sum being taken over all the species in the unit cell. The structure factor $F_c(hk\ell)$ thus calculated is related to the observed structure factor $F_o(hk\ell)$ by a constant of proportionality, K , called the scale constant, where

$$K F_o(hk\ell) = F_c(hk\ell)$$

The scattering factors used in the calculation were obtained from the International Tables (20) for carbon, nitrogen, oxygen and chlorine, and from the tabulation of Thomas and Umeda (26) for rhenium. The scattering curves of O^- , Cl^- , and $Re(IV)$ species were used in the cases of oxygen, chlorine and rhenium respectively, and the scattering curves of the neutral species were in the case of carbon and nitrogen. The scattering factors for rhenium and chlorine were corrected for dispersion effects using the relation

$$f = f_o + f' + if''$$

where f' and f'' are the real and imaginary dispersion corrections (20).

The trial structure with the positions of rhenium and

chlorine atoms had an overall reliability factor, R , of 0.17 on refinement of the positional parameters, individual isotropic temperature factors and scale constants, where

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

with the summation over all the measured reflections.

At this point, 1093 reflections had been measured. The data were scaled to F_c and used to compute the three-dimensional Patterson function sections along the z direction at intervals of $z=1/60$, upto $z=10/60$. Since the structure was expected to have the rhenium atom bonded to two oxygen atoms and four nitrogen atoms with bond-lengths of the order of 2 Å, a search was made to find peaks within about 2.5 Å around the rhenium atom. Since there are two non-translati-
onally equivalent rhenium atoms per unit cell, each with six atoms bonded to it, twelve interactions are expected in the Patterson, together with their centrosymmetric counterparts. Six of these interactions were chosen approximately octahed-
rally arranged around the rhenium atom, as the probable rhenium-ligand positions. Four of these positions were at about 2.1 Å from the rhenium atom and the remaining two at about 1.8 Å. Since it is difficult to distinguish the nitro-
gen atom with 7 electrons from the oxygen ion with 10 elec-
trons in the presence of Re(V) ion with 70 electrons, use was made of the known metal-oxygen bond distances in other dioxo-
compounds, and the two positions at about 1.8 Å were assigned

to the two oxo-oxygen atoms and the four positions at about 2.1 Å to the nitrogen atoms of the four pyridine groups. The two trial oxygen atoms were approximately centrosymmetrically related to each other, and therefore indicated that the compound has a trans-dioxo-structure.

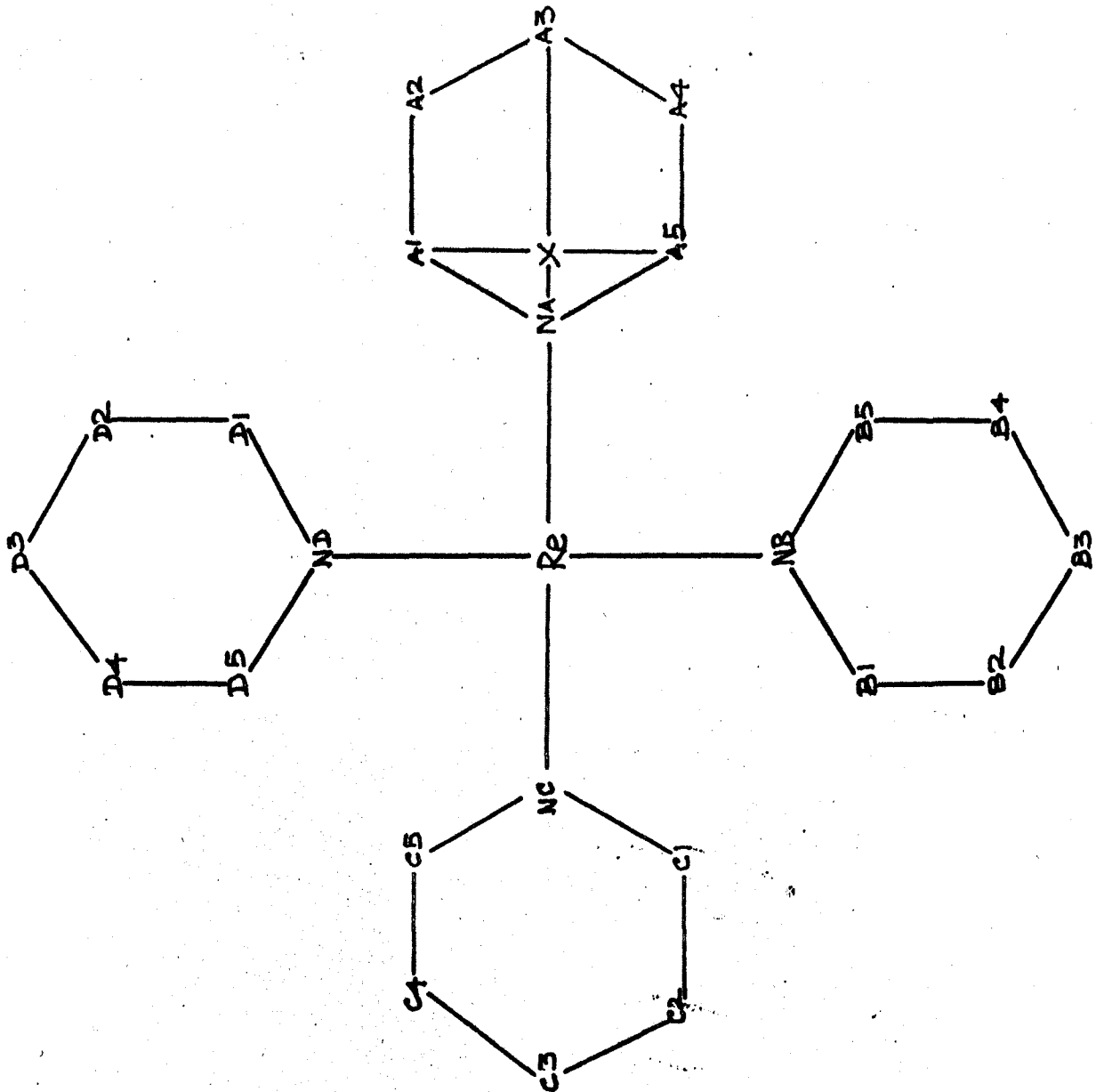
These six positions were included in the trial structure, and their positional parameters refined by least squares method using a program written by J.S. Stephens for the IBM 7040. The overall unweighted R-value for the 1093 reflections was 0.16. The R-values for the layers containing only even l reflections were much lower than those containing only odd l reflections. Thus the R-values for the $(hk0)$, $(h0l)$, $(hk\bar{2}h)$, $(hk2)$ and $(hk4)$ type reflections were 0.16, 0.23, 0.17, 0.14 and 0.15 respectively, while for the $(hk1)$, $(hk3)$ and $(hk5)$ type reflections the R-values were 0.43, 0.50 and 0.47 respectively. The poor agreement between observed and calculated structure factors of odd l reflections implies that the remaining atoms make a significant contribution to the structure factors of odd l reflections. However, their contribution to the even l reflections will be relatively small, since the rhenium atom dominates the contribution to their structure factors. The greater sensitivity of the structure factors of the odd l reflections to the remaining atom positions indicated that it is useful to employ only the odd l reflections for the initial determination of the remaining light atom positions.

The refined positional coordinates of nitrogen atom

NA (Fig.II-3) were used to choose position A3 of the para-carbon atom of the pyridine group (NA...A5) assuming benzene-like arrangement of atoms in the pyridine ring, with distance of 1.4 Å between adjacent atoms in the ring. Position A1 of the carbon atom adjacent to NA was chosen arbitrarily except that the vectors Re-X and X-A1 were perpendicular to each other (Fig.II-3). Based on these coordinates of atom A1, the coordinates of positions A2, A4 and A5 were calculated, assuming the ring to be planar. This gives one possible orientation for the pyridine ring, in which the position of atom NA is known correctly, the position A3 of the para-carbon atom is approximately known, but the other positions have been chosen arbitrarily. The straight line Re-NA-A3 (Fig.II-3) was then kept fixed as the rotation axis and the pyridine ring was rotated at 30° intervals starting from this position. The R-value for the 426 reflections with odd l values was computed at each of these orientations. The orientation at which the R-value was lowest was then chosen and the coordinates of atoms corresponding to this particular orientation of the pyridine group were used in further refinement. This procedure was repeated for the remaining pyridine groups as well. The coordinates of these positions were included with those of the rhenium and chlorine atoms in the trial structure. Refinement of the positional coordinates of these atoms and the scale constants using all the measured reflections gave an overall R-value of 0.15.

At this stage, Cruickshank weighting scheme was used

Figure II-3



and each reflection assigned a weight w in the refinement where w was taken as proportional to $(a + bF_o + cF_o^2)$ with $a = 3.0$, $b = 0.015$, $c = 0.001$. (25). The overall weighted R-value, R_w , defined as

$$R_w = \left\{ \frac{\sum w^2 ||F_o| - |F_c||^2}{\sum w^2 |F_o|^2} \right\}^{1/2}$$

with the summation over all reflections, was 0.13.

The trial structure at this stage included all the atoms (except the hydrogen atoms) of the unit $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}$. Electron density difference maps were prepared using the $[100]$, $[010]$ and $[001]$ zone reflections. Two peaks of relatively large height were found in these maps which had not been accounted for. These two peaks were assigned to the oxygen atoms of two water molecules. This assignment was based on oxygen analysis (Chapter II) and is supported by better agreement between the measured and calculated densities if the salt is taken to be the dihydrate rather than the monohydrate or the anhydrous salt.

On including these two atom positions to the trial structure and refining the positional parameters and scale constants, the overall unweighted R-value, R , was 0.10 and the overall weighted R_w -value was 0.12. The temperature factors of the rhenium and chlorine atoms were then converted to anisotropic temperature factors using the relation

$$B \sin^2 \theta = (\beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + \beta_{12} hk + \beta_{23} kl + \beta_{13} hl)$$

with β_{12} and β_{23} being taken as zero for the rhenium atom because of the restriction of the rhenium atom to the glide plane at $y=0$. The temperature factors of the other atoms were varied isotropically. The overall unweighted R-value was 0.099 and the overall weighted R_w -value was 0.117. The final values of the positional parameters of the atoms (except hydrogen atoms), together with their esd's, are listed in Table II-1. The agreement between the observed and calculated structure factors is shown in Table II-2. In this table, the unobserved reflections are marked with an asterisk (*), and the unreliable reflections with the symbol \emptyset . The value of $|F_o|$ quoted for the unobserved reflections is $|F_{min}|$.

The crystal structure of the compound is discussed in detail in the next chapter.

TABLE II-1

Positional and thermal parameters for atoms in
 $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$

Atom	$x=X/a$	$y=Y/b$	$z=Z/c$	B(T)
NA	-0.049(4)	-0.141(4)	0.061(6)	3.3
A1	-0.106(4)	-0.133(4)	0.107(5)	2.8
A2	-0.137(4)	-0.216(4)	0.143(5)	3.0
A3	-0.107(5)	-0.322(4)	0.130(6)	3.4
A4	-0.053(4)	-0.342(4)	0.086(5)	3.0
A5	-0.017(4)	-0.255(4)	0.028(7)	3.0
NB	-0.123(4)	-0.035(5)	-0.151(5)	2.8
B1	-0.104(4)	-0.118(5)	-0.186(5)	2.5
B2	-0.177(5)	-0.139(5)	-0.284(6)	3.3
B3	-0.264(4)	-0.062(4)	-0.328(6)	3.0
B4	-0.287(5)	0.026(5)	-0.279(6)	2.9
B5	-0.209(5)	0.026(5)	-0.184(7)	2.9
NC	0.055(4)	0.151(4)	-0.049(6)	3.2
C1	0.120(5)	0.140(5)	-0.086(6)	3.8
C2	0.162(4)	0.231(4)	-0.119(5)	3.3
C3	0.122(4)	0.334(4)	-0.108(5)	3.0
C4	0.067(4)	0.348(4)	-0.036(5)	3.5
C5	0.021(5)	0.247(4)	-0.035(6)	3.0
ND	0.115(4)	0.035(5)	0.143(5)	2.9
D1	0.105(5)	0.119(6)	0.204(6)	3.6
D2	0.168(5)	0.142(5)	0.291(6)	3.1
D3	0.270(4)	0.094(4)	0.336(6)	3.4
D4	0.285(5)	0.009(4)	0.284(6)	3.0
D5	0.217(5)	-0.029(6)	0.184(7)	3.1
O1	0.105(2)	-0.080(2)	-0.013(3)	2.9
O2	-0.089(2)	0.084(2)	0.021(2)	1.3
O3 ^{1/2}	0.226(2)	0.278(2)	0.481(3)	3.0
O4	0.020(2)	0.385(3)	0.349(3)	3.0
Cl	-0.066(1)	0.374(1)	0.130(1)	**
Re	0.000	0.000	0.000	**

** Anisotropic temperature factors for the rhenium atom and chlorine atom:

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
Re	0.003	0.002	0.003	0.000	0.001	0.000
Cl	0.008	0.004	0.002	0.002	0.002	0.005

TABLE II-2. OBSERVED AND CALCULATED STRUCTURE FACTORS (x5)

UNOBSERVED REFLECTIONS ARE MARKED WITH AN ASTERISK (*), AND UNRELIABLE REFLECT(QNS WITH THE SYMBOL (B)).

F _{obs} / F _{calc}			F _{obs} / F _{calc}			F _{obs} / F _{calc}			F _{obs} / F _{calc}			F _{obs} / F _{calc}		
H	K	L = 0	H	K	L = 2	H	K	L = 2	H	K	L = 3	H	K	L = 4
000	000	0	000	000	0	000	000	0	000	000	0	000	000	0
001	001	660	001	001	29	001	001	20	001	001	285	001	001	37
002	002	660	002	002	46	002	002	16	002	002	167	002	002	30
003	003	660	003	003	33	003	003	27	003	003	155	003	003	49
004	004	660	004	004	34	004	004	27	004	004	155	004	004	29
005	005	660	005	005	56	005	005	65	005	005	14	005	005	48
006	006	660	006	006	110	006	006	29	006	006	102	006	006	74
007	007	660	007	007	110	007	007	29	007	007	102	007	007	19
008	008	660	008	008	110	008	008	29	008	008	102	008	008	29
009	009	660	009	009	110	009	009	29	009	009	102	009	009	29
010	010	660	010	010	110	010	010	29	010	010	102	010	010	29
011	011	660	011	011	110	011	011	29	011	011	102	011	011	29
012	012	660	012	012	110	012	012	29	012	012	102	012	012	29
013	013	660	013	013	110	013	013	29	013	013	102	013	013	29
014	014	660	014	014	110	014	014	29	014	014	102	014	014	29
015	015	660	015	015	110	015	015	29	015	015	102	015	015	29
016	016	660	016	016	110	016	016	29	016	016	102	016	016	29
017	017	660	017	017	110	017	017	29	017	017	102	017	017	29
018	018	660	018	018	110	018	018	29	018	018	102	018	018	29
019	019	660	019	019	110	019	019	29	019	019	102	019	019	29
020	020	660	020	020	110	020	020	29	020	020	102	020	020	29
021	021	660	021	021	110	021	021	29	021	021	102	021	021	29
022	022	660	022	022	110	022	022	29	022	022	102	022	022	29
023	023	660	023	023	110	023	023	29	023	023	102	023	023	29
024	024	660	024	024	110	024	024	29	024	024	102	024	024	29
025	025	660	025	025	110	025	025	29	025	025	102	025	025	29
026	026	660	026	026	110	026	026	29	026	026	102	026	026	29
027	027	660	027	027	110	027	027	29	027	027	102	027	027	29
028	028	660	028	028	110	028	028	29	028	028	102	028	028	29
029	029	660	029	029	110	029	029	29	029	029	102	029	029	29
030	030	660	030	030	110	030	030	29	030	030	102	030	030	29
031	031	660	031	031	110	031	031	29	031	031	102	031	031	29
032	032	660	032	032	110	032	032	29	032	032	102	032	032	29
033	033	660	033	033	110	033	033	29	033	033	102	033	033	29
034	034	660	034	034	110	034	034	29	034	034	102	034	034	29
035	035	660	035	035	110	035	035	29	035	035	102	035	035	29
036	036	660	036	036	110	036	036	29	036	036	102	036	036	29
037	037	660	037	037	110	037	037	29	037	037	102	037	037	29
038	038	660	038	038	110	038	038	29	038	038	102	038	038	29
039	039	660	039	039	110	039	039	29	039	039	102	039	039	29
040	040	660	040	040	110	040	040	29	040	040	102	040	040	29
041	041	660	041	041	110	041	041	29	041	041	102	041	041	29
042	042	660	042	042	110	042	042	29	042	042	102	042	042	29
043	043	660	043	043	110	043	043	29	043	043	102	043	043	29
044	044	660	044	044	110	044	044	29	044	044	102	044	044	29
045	045	660	045	045	110	045	045	29	045	045	102	045	045	29
046	046	660	046	046	110	046	046	29	046	046	102	046	046	29
047	047	660	047	047	110	047	047	29	047	047	102	047	047	29
048	048	660	048	048	110	048	048	29	048	048	102	048	048	29
049	049	660	049	049	110	049	049	29	049	049	102	049	049	29
050	050	660	050	050	110	050	050	29	050	050	102	050	050	29
051	051	660	051	051	110	051	051	29	051	051	102	051	051	29
052	052	660	052	052	110	052	052	29	052	052	102	052	052	29
053	053	660	053	053	110	053	053	29	053	053	102	053	053	29
054	054	660	054	054	110	054	054	29	054	054	102	054	054	29
055	055	660	055	055	110	055	055	29	055	055	102	055	055	29
056	056	660	056	056	110	056	056	29	056	056	102	056	056	29
057	057	660	057	057	110	057	057	29	057	057	102	057	057	29
058	058	660	058	058	110	058	058	29	058	058	102	058	058	29
059	059	660	059	059	110	059	059	29	059	059	102	059	059	29
060	060	660	060	060	110	060	060	29	060	060	102	060	060	29
061	061	660	061	061	110	061	061	29	061	061	102	061	061	29
062	062	660	062	062	110	062	062	29	062	062	102	062	062	29
063	063	660	063	063	110	063	063	29	063	063	102	063	063	29
064	064	660	064	064	110	064	064	29	064	064	102	064	064	29
065	065	660	065	065	110	065	065	29	065	065	102	065	065	29
066	066	660	066	066	110	066	066	29	066	066	102	066	066	29
067	067	660	067	067	110	067	067	29	067	067	102	067	067	29
068	068	660	068	068	110	068	068	29	068	068	102	068	068	29
069	069	660	069	069	110	069	069	29	069	069	102	069	069	29
070	070	660	070	070	110	070	070	29	070	070	102	070	070	29
071	071	660	071	071	110	071	071	29	071	071	102	071	071	29
072	072	660	072	072	110	072	072	29	072	072	102	072	072	29
073	073	660	073	073	110	073	073	29	073	073	102	073	073	29
074	074	660	074	074	110	074	074	29	074	074	102	074	074	29
075	075	660	075	075	110	075	075	29	075	075	102	075	075	29
076	076	660	076	076	110	076	076	29	076	076	102	076	076	29
077	077	660	077	077	110	077	077	29	077	077	102	077	077	29
078	078	660	078	078	110	078	078	29	078	078	102	078	078	29
079	079	660	079	079	110	079	079	29	079	079	102	079	079	29
080	080	660	080	080	110	080	080	29	080	080	102	080	080	29
081	081	660	081	081	110	081	081	29	081	081	102	081	081	29
082	082	660	082	082	110	082	082	29	082	082	102	082	082	29
083	083	660	083	083	110	083	083	29	083	083	102	083	083	29
084	084	660	084	084	110	084	084	29	084	084	102	084	084	29
085	085	660	085	085	110	085	08							

TABLE II-2 (CONCLUDED)

F(0BS) F(CALC)		F(0BS) F(CALC)		F(0BS) F(CALC)		F(0BS) F(CALC)		F(0BS) F(CALC)	
11	237	10	268	10	32	10	399	12	70
11	162	10	247	10	35	10	316	12	83
11	328	10	257	10	31	10	190	12	88
11	442	10	158	10	90	10	144	12	406
11	450	10	290	10	68	10	130	12	417
11	439	10	310	10	87	10	362	12	314
11	387	10	311	10	59	10	242	12	285
11	201	10	356	10	99	10	279	12	204
11	392	10	201	10	21	10	202	12	279
11	390	10	172	10	82	10	105	12	77
11	403	10	265	10	75	10	169	12	79
11	405	10	290	10	67	10	155	12	81
11	437	10	235	10	55	10	143	12	88
11	278	10	270	10	34	10	277	12	81
11	188	10	187	10	46	10	400	12	87
11	377	10	160	10	28	10	449	12	86
11	355	10	273	10	53	10	436	12	86
11	437	10	264	10	53	10	274	12	86
11	360	10	207	10	28	10	129	12	86
11	176	10	225	10	26	10	108	12	86
11	192	10	158	10	49	10	107	12	86
11	290	10	231	10	26	10	127	12	86
11	383	10	130	10	69	10	131	12	86
11	440	10	250	10	38	10	110	12	86
11	249	10	191	10	57	10	108	12	86
11	241	10	181	10	82	10	105	12	86
11	185	10	145	10	33	10	245	12	86
11	312	10	179	10	45	10	191	12	86
11	329	10	181	10	33	10	368	12	86
11	222	10	129	10	54	10	179	12	86
11	194	10	163	10	16	10	152	12	86
11	230	10	154	10	7	10	140	12	86
11	310	10	40	10	83	10	211	12	86
11	265	10	315	10	56	10	153	12	86
11	210	10	120	10	77	10	102	12	86
11	222	10	117	10	20	10	199	12	86
11	172	10	117	10	28	10	146	12	86
11	297	10	33	10	66	10	327	12	86
11	194	10	26	10	26	10	264	12	86
11	183	10	86	10	39	10	161	12	86
11	299	10	45	10	29	10	153	12	86
11	223	10	45	10	33	10	120	12	86
11	201	10	51	10	31	10	135	12	86
11	181	10	51	10	39	10	141	12	86
11	200	10	29	10	34	10	145	12	86
11	187	10	29	10	32	10	179	12	86
11	163	10	132	10	34	10	189	12	86
11	202	10	48	10	37	10	174	12	86
11	180	10	77	10	32	10	180	12	86
11	170	10	36	10	47	10	127	12	86
11	358	10	98	10	30	10	175	12	86
11	358	10	66	10	15	10	104	12	86
11	422	10	10	10	36	10	105	12	86
11	357	10	48	10	23	10	107	12	86
11	321	10	30	10	12	10	131	12	86
11	444	10	42	10	22	10	102	12	86
11	444	10	33	10	67	10	139	12	86
11	444	10	110	10	46	10	167	12	86
11	686	10	62	10	39	10	133	12	86
11	372	10	56	10	275	10	107	12	86
11	326	10	33	10	431	10	121	12	86
11	317	10	32	10	380	10	136	12	86
11	300	10	80	10	227	10	113	12	86
11	207	10	49	10	222	10	140	12	86
11	160	10	80	10	199	10	113	12	86
11	439	10	54	10	149	10	81	12	86
11	437	10	54	10	705	10	28	12	86
11	468	10	33	10	1194	10	73	12	86
11	419	10	55	10	921	10	29	12	86
11	358	10	34	10	438	10	30	12	86
11	259	10	34	10	422	10	45	12	86
11	204	10	90	10	222	10	29	12	86
11	206	10	33	10	466	10	30	12	86
11	437	10	44	10	244	10	29	12	86
11	589	10	29	10	368	10	29	12	86
11	489	10	45	10	307	10	29	12	86
11	480	10	48	10	392	10	29	12	86
11	373	10	25	10	470	10	29	12	86
11	321	10	33	10	65	10	29	12	86
11	213	10	29	10	76	10	29	12	86
11	156	10	32	10	484	10	29	12	86
11	475	10	32	10	211	10	29	12	86
11	604	10	20	10	337	10	29	12	86
11	470	10	48	10	179	10	29	12	86
11	379	10	26	10	30	10	29	12	86
11	300	10	37	10	75	10	29	12	86
11	241	10	30	10	42	10	29	12	86
11	188	10	23	10	51	10	29	12	86
11	493	10	23	10	315	10	29	12	86
11	296	10	29	10	345	10	29	12	86
11	415	10	36	10	345	10	29	12	86
11	381	10	68	10	721	10	29	12	86
11	265	10	126	10	797	10	29	12	86
11	167	10	70	10	58	10	29	12	86
11	493	10	107	10	338	10	29	12	86
11	333	10	33	10	22	10	29	12	86
11	418	10	11	10	338	10	29	12	86
11	402	10	274	10	205	10	29	12	86
11	312	10	145	10	592	10	29	12	86
11	270	10	71	10	579	10	29	12	86
11	57	10	59	10	523	10	29	12	86
11	192	10	34	10	523	10	29	12	86
11	479	10	34	10	523	10	29	12	86
11	282	10	34	10	44	10	29	12	86
11	385	10	22	10	213	10	29	12	86
11	287	10	290	10	213	10	29	12	86
11	174	10	44	10	270	10	29	12	86
11	339	10	72	10	164	10	29	12	86
11	387	10	87	10	497	10	29	12	86
11	313	10	22	10	333	10	29	12	86
11	199	10	42	10	333	10	29	12	86
11	335	10	42	10	509	10	29	12	86
11	289	10	87	10	742	10	29	12	86
11	289	10	87	10	436	10	29	12	86

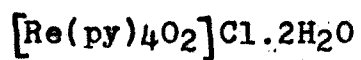
CHAPTER III

CRYSTAL STRUCTURE OF $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$

The unit cell parameters and space-group for the crystal are listed in Table III-1. The rhenium atom in each molecule of the complex is bonded to two oxygen atoms and four nitrogen atoms. The Re-N and Re-O bond distances, and the angles subtended by these atoms at the rhenium atom are tabulated in Table III-2. The rhenium-oxygen bond distances of 1.81(3) Å and 1.71(3) Å are not significantly different from each other. The rhenium-nitrogen bond distances of 2.18(5) Å, 2.24(4) Å, 2.21(5) Å and 2.12(4) Å also do not differ significantly. The average Re-N bond distance is 2.19 Å and is of the same order as found in $[\text{ReO}(\text{OH})(\text{en})_2](\text{ClO}_4)_2$ where the average Re-N bond distance is 2.13(3) Å (27). The six atoms bonded to the rhenium atom are located at the corners of an irregular octahedron. The four nitrogen atoms are nearly coplanar and the two oxygen atoms are perpendicular to this plane. The angle subtended by the two oxygen atoms at the rhenium atom is 180° within the limits of error. Thus the molecule has the trans-dioxo- structure as had been predicted (11). The angle subtended by each pair of trans-nitrogen atoms at the central rhenium atom is also close to 180° . Thus as far as these near-neighbour atoms of rhenium are concerned,

TABLE III-1

Space group and unit cell parameters for



Space group: Cc

Monoclinic Symmetry

$$\underline{a} = 13.592(2) \text{ \AA}$$

$$\underline{b} = 11.973(2) \text{ \AA}$$

$$\underline{c} = 15.55(1) \text{ \AA}$$

$$\beta = 116.2(1)^\circ$$

$$D_m = 1.77 \text{ g/ml}$$

$$D_c = 1.78 \text{ g/ml}$$

$$Z = 4$$

TABLE III-2

Geometry of the irregular octahedral arrangement of the four nitrogen and two oxygen atoms around the rhenium atom.
(See Fig.III-3a)

Bonded atoms	Distance (A)	Bonded atoms	Angle (°)
Re-NA	2.18(5)	NA-Re-NB	95.
Re-NB	2.24(4)	NA-Re-ND	85.
Re-NC	2.21(5)	NA-Re-O1	93.
Re-ND	2.21(5)	NA-Re-O2	90.
Re-O1	1.81(3)	NB-Re-NC	90.
Re-O2	1.71(3)	NB-Re-O1	93.
		NB-Re-O2	92.
		NC-Re-ND	90.
		NC-Re-O1	89.
		NC-Re-O2	88.
		ND-Re-O1	88.
		ND-Re-O2	87.
		NA-Re-NC	175.
		NB-Re-ND	179.
		O1-Re-O2	174.

there appears to be a pseudo-centre of symmetry at the rhenium atom. The pyridine groups trans- to each other are also nearly centrosymmetrically related to each other. In fact when the structure-factors of the ℓ odd reflections were calculated for various orientations of the pyridine groups as described in Chapter II, it was found that the best agreement with the observed structure-factors was obtained when the planes of each pair of trans- pyridine groups deviated by only about 7 degrees. It thus seems that the complex is almost centric with the rhenium atom at the centre of symmetry, and that the pyridine groups are only very slightly but definitely displaced from the ideal centrosymmetric position. The geometry of the four pyridine groups is given in Table III-3. The nitrogen-carbon distances and carbon-carbon distances vary between 1.22 Å and 1.59 Å. The angle subtended at each atom by its two neighbouring atoms in each pyridine group ranges between 100° and 130° . The error in the bond-distances is of the order of 0.08 Å and the error in the bond-angles is about 8° .

The atoms in one unit cell are shown in projection on to the xz and yz planes respectively in Fig.III-1 and Fig.III-2. All the atoms of the pyridine groups (NA...A5) and (NC...C5) lie almost in the diagonal plane perpendicular to the xz plane. This is responsible for the large accumulation of peaks in the $(h0\ell)$ Patterson projection along the (101) direction. The similarity in the arrangement of molecules between the two halves of the unit cell in the

TABLE III-3

The geometry of the pyridine groups (See Fig.III-3)

Bonded atoms	Distance(A)	Bonded atoms	Angle (°)
NA-A1	1.28(7)	NA-A1-A2	125.
A1-A2	1.29(7)	A1-A2-A3	119.
A2-A3	1.37(8)	A2-A3-A4	122.
A3-A4	1.24(8)	A3-A4-A5	127.
A4-A5	1.59(7)	A4-A5-NA	100.
A5-NA	1.59(7)	A5-NA-A1	125.
NB-B1	1.22(8)	NB-B1-B2	116.
B1-B2	1.42(6)	B1-B2-B3	116.
B2-B3	1.42(8)	B2-B3-B4	124.
B3-B4	1.42(8)	B3-B4-B5	109.
B4-B5	1.38(7)	B4-B5-NB	125.
B5-NB	1.27(8)	B5-NB-B1	126.
NC-C1	1.26(8)	NC-C1-C2	124.
C1-C2	1.42(8)	C1-C2-C3	113.
C2-C3	1.40(7)	C2-C3-C4	121.
C3-C4	1.59(7)	C3-C4-C5	106.
C4-C5	1.37(8)	C4-C5-NC	125.
C5-NC	1.30(7)	C5-NC-C1	123.
ND-D1	1.43(8)	ND-D1-D2	130.
D1-D2	1.27(7)	D1-D2-D3	119.
D2-D3	1.36(8)	D2-D3-D4	115.
D3-D4	1.35(7)	D3-D4-D5	130.
D4-D5	1.48(7)	D4-D5-ND	109.
D5-ND	1.46(9)	D5-ND-D1	115.

Fig.III-1. The atoms in one unit cell shown in projection on the xz plane.

The origin is at the centre of the plane. The pyridine groups and the oxygen atoms associated with the rhenium atoms in the $y=0$ plane are drawn in continuous lines. The groups associated with the rhenium atoms in the $y=\frac{1}{2}$ plane are drawn in broken lines. Thick lines have been used to connect atoms above the plane and thin lines for atoms below the plane. The chlorine atoms are represented by large circles and the oxygen atoms of the water molecules are represented by smaller circles.

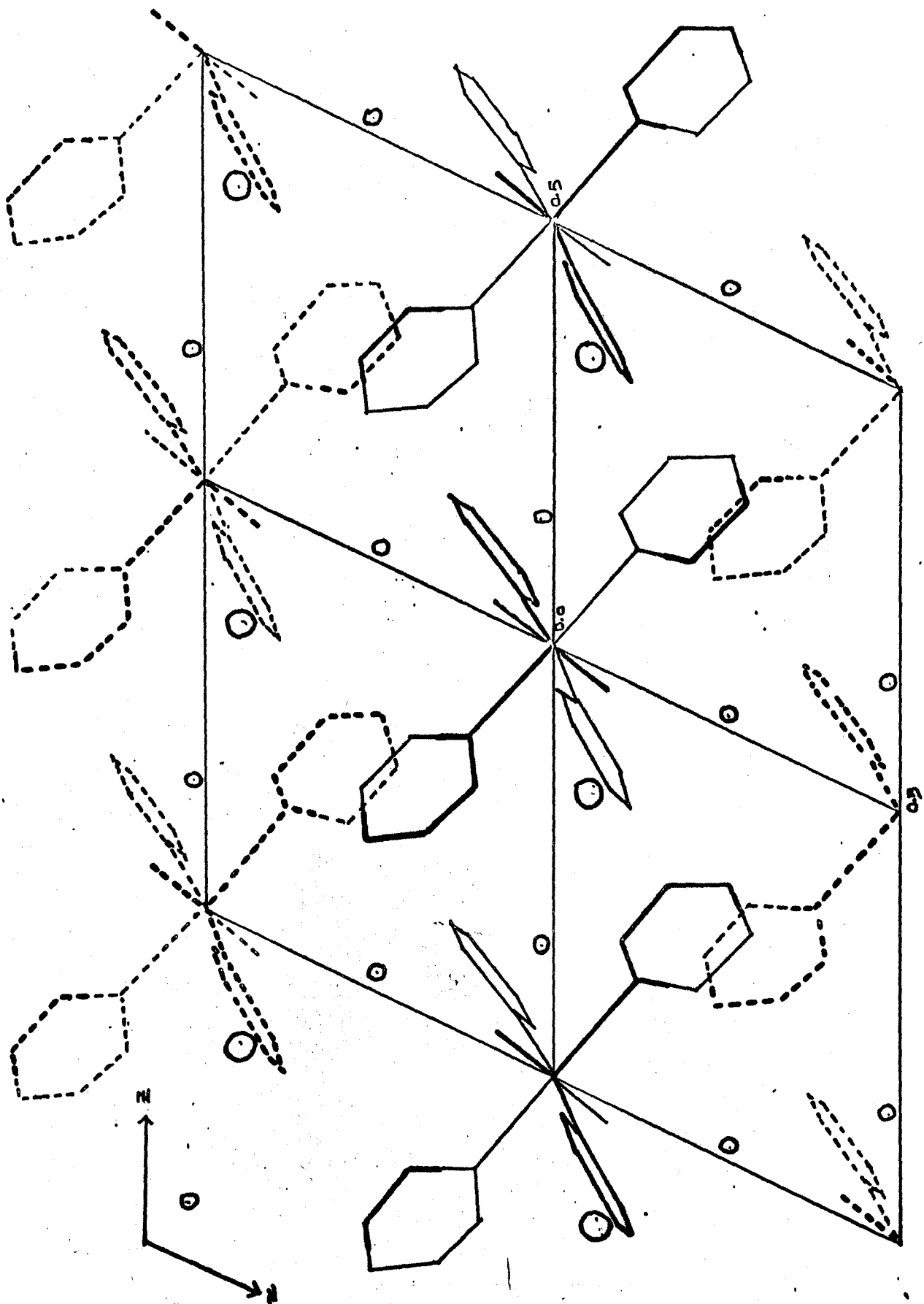


Fig. III-1. The atoms in one unit cell in projection
on the xz plane.

Fig.III-2. The atoms in one unit cell
shown in projection on the yz plane.

The origin is at the centre of the plane. The pyridine groups and the oxygen atoms associated with the rhenium atoms in the $x=0$ plane are drawn in continuous lines. The groups associated with the rhenium atoms in the $x=\frac{1}{2}$ plane are drawn in broken lines. Thick lines have been used to connect atoms above the plane and thin lines for atoms below the plane. Within each pyridine ring, the orientation in the x-direction is indicated by representing that edge of the pyridine ring which is pointing towards the positive direction of the x-axis by double lines. The chlorine atoms are represented by large circles and the oxygen atoms of the water molecules are represented by smaller circles.

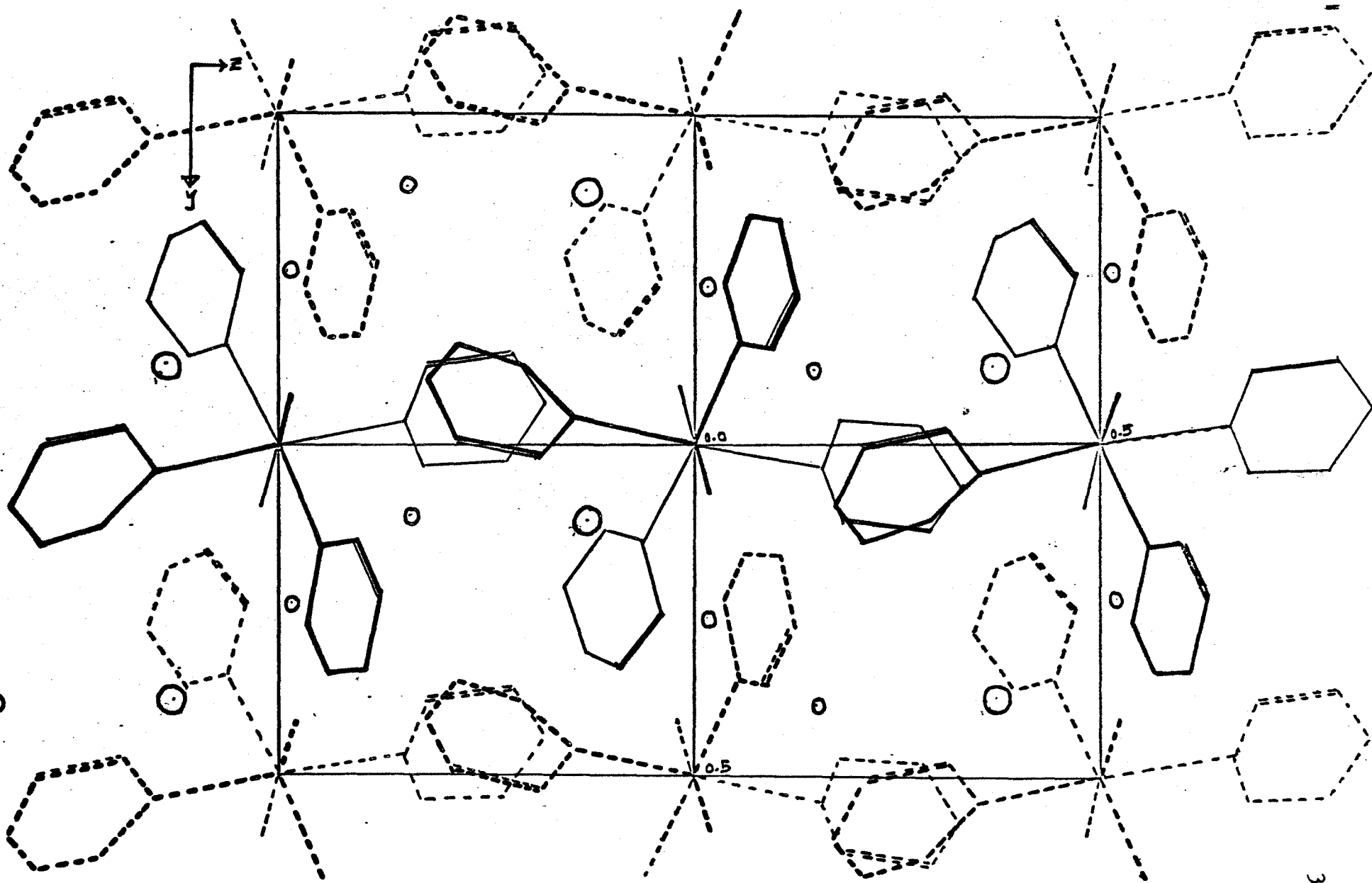


Fig.III-2. The atoms in one unit cell in projection
on the yz plane.

c direction which leads to the observed pseudo-symmetry in the structure is clearly recognisable.

Fig.III-3a and Fig.III-3b show one unit of the dihydrate of $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}$ in projection on the xy plane at $z = 0$ and $z = \frac{1}{2}$ respectively. The two units are similar to each other, with the difference that the signs of y -coordinates of all the atoms are reversed on translation from $z = 0$ to $z = \frac{1}{2}$. The similarity in orientation between the unit with rhenium atom at $(0,0,0)$ and the one with rhenium atom at $(0,0,\frac{1}{2})$ is responsible for the pseudo-symmetry. If these two units had been identical by translation of $c/2$ in the c direction then the unit cell would have been only half as long in the c direction as was actually observed.

The question arises why this packing does not occur and why only the pseudo-symmetric structure is observed. The explanation lies in packing considerations. Thus, let us assume that the atoms with coordinates (x,y,z) repeat themselves at $(x,y,\frac{1}{2}+z)$, resulting in a unit cell only half the observed length in the c-direction. We will have the arrangement shown in Fig.III-3a for the atoms of $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ with the rhenium atom at $(0,0,0)$. The atoms will repeat themselves on translation by $c/2$ in the c direction. With this arrangement, one notices that the atom C3 at $(0.12, 0.33, -0.11 + 0.5)$ will be just about 1.5 Å away from atom O4 at $(0.02, 0.39, 0.35)$. Also, the pyridine group (NC...C5) associated with the rhenium atom at $(0,0,\frac{1}{2})$ will be pointing below the $z=\frac{1}{2}$ plane, and the pyridine group (ND...D5) associated

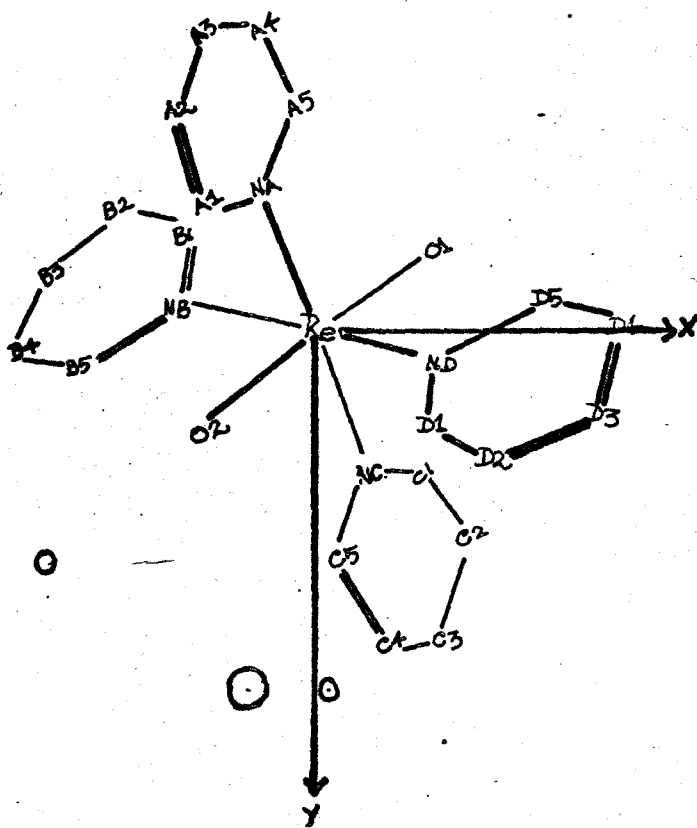


Fig.III-3a. One unit of $[\text{Re}(\text{py})_4\text{O}_2] \text{Cl} \cdot 2 \text{H}_2\text{O}$ projected on the xy plane. (Re at $(0,0,0)$).

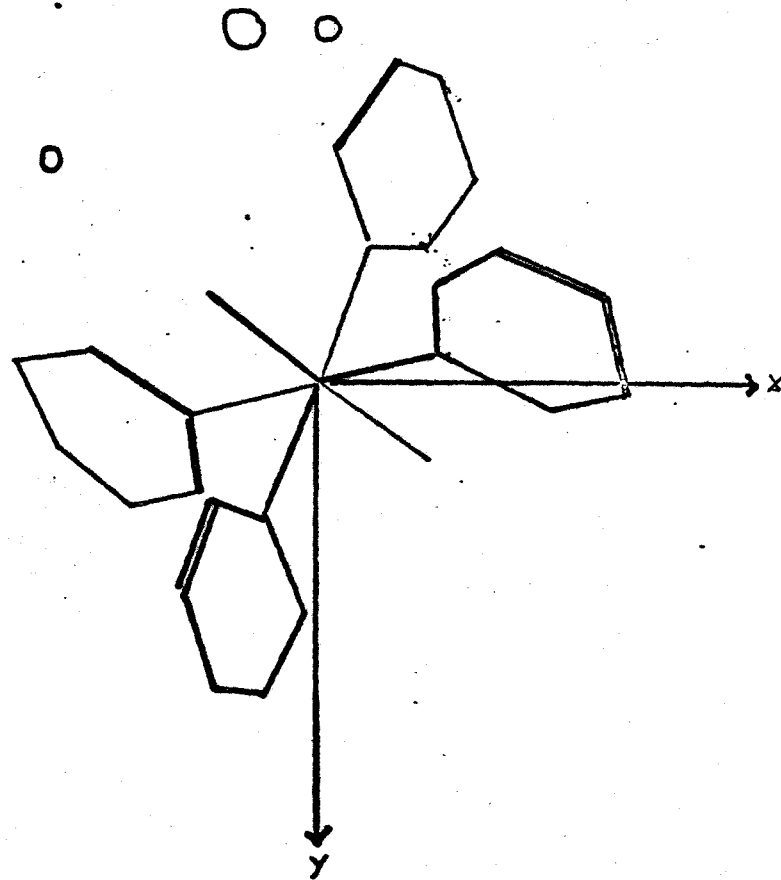


Fig.III-3b. One unit of $[\text{Re}(\text{py})_4\text{O}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$ with rhenium at $(0,0, \frac{1}{4})$ projected on the xy plane.

with the rhenium atom at (0,0,0) will be pointing above the $z=0$ plane, and the lower end of the first pyridine group will be too close to the upper end of the second pyridine group to allow packing of the atoms. The same will hold true between the pyridine groups (NB...B5) and (NA...A5). Thus, with the present arrangement of atoms, it does not appear feasible to achieve packing of atoms in such a way that the unit cell is only half as long in the c direction as is actually observed, without extensive changes in the unit cell geometry. However, one might speculate that if the atom O4 of the water molecule hydrogen-bonded to the chlorine atom were not present in the structure, then it might be possible to tilt the pyridine groups (NC...C5) and (ND...D5) relative to each other in such a way that they are sufficiently far from each other to allow packing of atoms without seriously altering the unit cell geometry. Thus it might be possible to achieve the packing of the atoms with the unit cell only half as long in the c direction as is actually observed, if the chlorine atom did not have one of the water molecules (the water molecule with the oxygen atom labelled O4) hydrogen-bonded to it. It is thus possible that the monohydrate of dioxo-tetrapyridine-rhenium(V) chloride might crystallise with this unit cell.

It was also indicated above that the four pyridine groups and the two oxo-oxygen atoms are pseudo-centric with the rhenium atom at the pseudo-centre of symmetry. The only atoms in the unit of $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ that are not related in this fashion are those of the two water molecules and the

chlorine atom. The centrosymmetric space-group with the extinctions observed in the present case is $C2/c$. A point to consider is why the compound does not crystallise with the centrosymmetric space-group $C2/c$, but rather in the non-centrosymmetric space-group Cc . The space-group $C2/c$ has an eight-fold general position. For the 4 molecules of dioxotetrapyridinerhenium(V) chloride $C_{20}H_{24}ClN_4O_4Re$ to be arranged in the unit cell with space-group $C2/c$, both the rhenium atom and the chlorine atom should lie at four-fold special positions. These are $(0,0,0)$, $(0,y,\frac{1}{2})$, $(\frac{1}{4},\frac{1}{4},\frac{1}{2})$, $(\frac{1}{4},\frac{1}{4},0)$ and $(0,\frac{1}{2},0)$ for this space-group. With the rhenium atom at $(0,0,0)$, this leaves the positions $(0,y,\frac{1}{2})$, $(\frac{1}{4},\frac{1}{4},\frac{1}{2})$, $(\frac{1}{4},\frac{1}{4},0)$ and $(0,\frac{1}{2},0)$ as the possible positions for the chlorine atom, in order for the crystal to belong to the centrosymmetric space-group $C2/c$. Calculation of interatomic distances with the chlorine atom at the position $(\frac{1}{4},\frac{1}{4},0)$ or $(0,\frac{1}{2},0)$ shows that the unit cell will have to be considerably distorted in order to accommodate the chlorine atom at either of these positions. However, it is possible to assign the special position $(\frac{1}{4},\frac{1}{4},\frac{1}{2})$ to the chlorine atom if atom O3 of the water molecule were not present in the structure. It is also possible to assign the 4-fold special position $(0,y,\frac{1}{2})$ with $y \approx 0.4$ to the chlorine atom if atom O4 of the second water molecule were not present. Thus it is possible to achieve packing of the atoms in the unit cell with space-group $C2/c$ if either one of the two water molecules were not present in the structure or if they occupied other positions. The

monohydrate of dioxotetrapyrridinerhenium(V) chloride could possibly crystallise with the centrosymmetric space group $C2/c$.

To pursue the matter of whether the dihydrate can still have the space-group $C2/c$ with the chlorine atom at one of the two four-fold special positions mentioned above, there are two possibilities: (1) To assign the special position $(0, y, \frac{1}{4})$ with $y \approx 0.4$ to the chlorine atom, and remove atom O4 from the trial structure. This leaves atom O3 very close to the special position $(\frac{1}{4}, \frac{1}{4}, 0)$ and hence assigned to this position in the space group $C2/c$. In this case the oxygen atom of the second water molecule should also lie in a 4-fold special position. This is not possible since all the available 4-fold special positions are already occupied. (2) To assign the position $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ to the chlorine atom and remove atom O3 from the trial structure. This leaves atom O4 of the second water molecule in an eight-fold general position of the $C2/c$ space group, which will generate the eight water molecules in the unit cell containing four formula-weights of the dihydrate. However, in this case the oxygen atom O1 at $(x, y, \frac{1}{2}+z)$ and the oxygen atom O2 at $(x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2})$ will be at about 2.8 Å from the chlorine atom. This is smaller than the sum of the ionic radii of Cl^- and O^{2-} (≈ 3.21 Å), and there will have to be considerable distortion of the rhenium atom environment in order to accommodate the chlorine atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$. It is also noticed that there is no favourable hydrogen-bond formation between the chloride

ion and the water molecules as they are greater than 3.4 Å apart.

This accounts for the observed non-centrosymmetric space-group Cc for the dihydrate, in which the water molecules are in favourable positions to form hydrogen-bonds with the chloride ion and with the oxo-oxygen atoms.

The atoms in the structure which can take part in hydrogen-bond formation and which lie within 3.5 Å from the oxygen atom O3 and O4 of the two water molecules are listed in Table III-4. The angles subtended by these atoms at the oxygen atoms of the water molecules are also listed. Oxygen atom O3 has 4 nearest neighbours. The distances suggest that all 4 atoms are favourably located to form hydrogen bonds with the water molecule containing the oxygen atom labelled O3. However, the angle of 112° subtended by atoms O4 and O2(1) at O3 would suggest that these are the two atoms linked through hydrogen bonds to the atom O3. Oxygen atom O4 of the second water molecule has two neighbours, O2 and O3, at 2.94(4) Å and 3.07(3) Å respectively. The angle of 122° subtended by these two atoms at atom O4 suggests that these two atoms are linked by hydrogen bonds to atom O4.

It is possible to draw some conclusions on the nature of the hydrogen bond strength in the structure. The fact that the water molecules enter the crystal lattice from the medium of crystallisation (aqueous pyridine) suggests that energetically it is favourable for the water molecules to be in the crystal lattice in preference to the pyridine

TABLE III-4

Bond distances and angles between atoms likely to be involved in hydrogen-bonding in the structure, with their positional parameters.

Atom	x=X/a	y=Y/b	z=Z/c
O3	0.226(2)	0.278(2)	0.481(3)
O4	0.020(2)	0.385(2)	0.349(3)
C6	-0.066(1)	0.374(1)	0.130(1)
C6(1)	0.434(1)	0.126(1)	0.630(1)
O2(1)	0.411(2)	0.416(2)	0.521(2)
O1(1)	0.105(2)	0.080(2)	0.487(3)

Bonded atoms	Distance(A)	Bonded atoms	Angle(°)
03-04	2.94(4)	04-03-C6(1)	171.
03-C6(1)	3.30(3)	04-03-O2(1)	112.
03-O2(1)	2.83(4)	04-03-O1(1)	90.
03-O1(1)	2.91(4)	O2(1)-03-C6(1)	77.
		O2(1)-03-O1(1)	158.
		C(1)-03-O1(1)	81.
04-03	2.94(4)	03-04-C6	122.
04-C6	3.07(3)		

medium. Thus it can be expected that the hydrogen-bonds in the crystal lattice should be relatively stronger than those in aqueous pyridine.

CHAPTER IV

DISCUSSION

Chemical analysis of the compound dioxotetrapyridinerhenium(V) chloride prepared by the method described in Ch.II indicates that the salt is a dihydrate. There is some discrepancy in the literature regarding the extent of hydration of the compound (10). Thus, while Johnson et al report this compound as a dihydrate (11), Beard et al report that their analysis indicates the salt to be a monohydrate. Burovaya (12) has reported the crystallographic constants of the salt $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}$. Beard's explanation that the difference in the extent of hydration is probably caused by a difference in drying time or temperature seems to be reasonable.

The postulated trans-dioxo-structure has been found to be correct for the dioxotetrapyridinerhenium(V) chloride. The trans-dioxo-structure was postulated for the dioxo-compounds on the basis of the band at around 820 cm^{-1} in their infra-red spectra. This has been found to be correct in the case of the structures of the dioxo-compounds whose crystal structures have been thus far established. Thus $\text{K}_2[\text{OsO}_2\text{Cl}_4]$, $\text{K}_2[\text{OsO}_2(\text{OH})_4]$, $\text{K}_3[\text{ReO}_2(\text{CN})_4]$, and $[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ have been shown to have the trans-dioxo-structures.

Evteev (28) is in disagreement with the formulation

of $[\text{Re}(\text{en})_2\text{O}_2]\text{Cl}$ as a dioxo-compound and has reformulated it as $[\text{Re}(\text{en}^-)_2(\text{OH})_2]\text{Cl}$. One of the reasons given in support of this reformulation is the presence of a broad band at 3470 cm^{-1} in the infra-red spectrum, which has been assigned by Evteev to the hydroxo-group. The paper does not indicate whether the peak at around 820 cm^{-1} was observed at all in the case of Evteev's compound. Johnson et al (11) and Beard et al (10) prepared the compound by different methods and observed a strong peak at about 820 cm^{-1} in the infra-red spectrum. Assuming that Evteev's compound is the same as that of Johnson and Beard, Evteev's reformulation of $[\text{Re}(\text{en})_2\text{O}_2]\text{Cl}$ as the dihydroxo-compound $[\text{Re}(\text{en}^-)_2(\text{OH})_2]\text{Cl}$ fails to account for this peak. Johnson reports that his compound was a dihydrate and that it was slowly hydrolysed by water. In view of the fact that Evteev's compound was prepared in aqueous medium, it is quite likely that his compound was in fact the hydrated dioxo-compound. This would account for the broad band at 3470 cm^{-1} . Neither hydrogen nor oxygen analyses are given for Evteev's compound. While only the crystal structure determination of the compound can establish whether the compound has the dioxo- or the dihydroxo-structure, on the basis of the known structures of this class of compounds it is felt that the dioxo-structure is the more probable one. In addition to explaining the peaks at 3470 cm^{-1} and at about 820 cm^{-1} the trans-dioxo-structure would also account for the observed shift in the $\text{Re}=\text{O}$ stretching frequency on protonation.

Betzner's crystal structure investigation (27) of the compound $[\text{Re}(\text{en})_2\text{O}(\text{OH})](\text{ClO}_4)_2$ indicates that Evteev's reformulation of this compound as $[\text{Re}(\text{en}^-)(\text{en})(\text{OH})_2](\text{ClO}_4)_2$ is probably not correct. The dihydroxo-structure proposed by Evteev should have two Re-O bonds with bond distance of about 2.1 Å (29), while the reported value (27) is 1.84(3) Å.

The observation that the odd layer photographs hkn ($n=1,3,5$) contained reflections which were in general much weaker than the even layer reflections, is explained by the fact that the rhenium atom is at the origin. The contribution to the structure factor by an atom in general position with space group C_0 is given (30) by $F = A + iB$ where

$$A = 4 \cos^2 2\pi \left(\frac{h+k}{4}\right) \cos 2\pi(hx+lz+l/4) \cos 2\pi(ky-l/4)$$

$$B = 4 \cos^2 2\pi \left(\frac{h+k}{4}\right) \sin 2\pi(hx+lz+l/4) \cos 2\pi(ky-l/4)$$

This simplifies to

$$\begin{array}{l} A = 4 \cos 2\pi(hx+lz) \cos 2\pi ky \\ B = 4 \sin 2\pi(hx+lz) \cos 2\pi ky \end{array} \quad \begin{array}{l} | \\ | \\ | \end{array} \quad \text{for } l=2n$$

and

$$\begin{array}{l} A = -4 \sin 2\pi(hx+lz) \sin 2\pi ky \\ B = 4 \cos 2\pi(hx+lz) \sin 2\pi ky \end{array} \quad \begin{array}{l} | \\ | \\ | \end{array} \quad \text{for } l=2n+1$$

With the rhenium atom at the origin, reflections with even l values have non-zero contribution to the structure factor, since $A \neq 0$ and $B = 0$. However, reflections with l odd have no contribution to the structure factor from the rhenium atom

since for an atom with $y = 0$, both A and B are zero when ℓ is odd. Thus, for odd ℓ reflections, the intensities which are proportional to the square of the structure factors are low, only the lighter atoms contributing to the intensities of these reflections.

It was also pointed out in Chapter II that the oscillation photograph with \underline{c} axis as the rotation axis had the odd layer lines very weak compared to the even layer lines. This indicates the existence of pseudo-symmetry in the structure. If the very weak odd layer lines had been completely missing, the unit cell would have been just half the true length in the \underline{c} direction. The very weak odd layer lines imply that the arrangement of atoms in the unit cell is similar to, but not identical with, the other half of the unit cell in the \underline{c} direction. This difference between the two halves gives rise to the weak odd ℓ reflections, which would have been completely absent if the two halves had been identical (16).

Thus, there are two factors which cause the intensities of odd ℓ reflections to be very weak. First, only light atoms (atoms other than rhenium) contribute to their intensities; second, there is pseudo-symmetry in the structure, with the two halves of the unit cell being similar to, but not identical with, each other in the \underline{c} direction. It follows that for good agreement between the observed and calculated structure factors for odd reflections, (a) the positions of the light atoms should be known quite accurately,

and (b) the difference in the two halves of the unit cell which are similar to each other should be sufficiently correctly brought out in the trial structure. Even slight inaccuracies in these can cause a poor agreement between the observed and calculated structure factors for odd reflections. This probably accounts for the relatively large R-values for odd l reflections (0.235, 0.153, and 0.233 for $hk1$, $hk3$, and $hk5$ type reflections respectively) as opposed to the lower R-values for even l reflections (0.134, 0.088, 0.098, 0.118, 0.103, and 0.099 for $(h0l)$, $(hk0)$, $(0kl, l=\text{even only})$, $(hk\bar{2}h)$, $(hk2)$ and $(hk4)$ type reflections respectively).

Burovaya (12) has investigated the optical properties of the compound $\text{ReO}_2\text{Cl}_{1.4}(\text{py})$ and has reported that the crystal belongs to monoclinic symmetry with $\underline{a}:\underline{b}:\underline{c} = 1.62:1:1.01$ and $\beta = 106^\circ$. From the formula the compound is the anhydrous dioxo-tetrapyridinerhenium(V) chloride. However, it is possible to choose a set of three axes from the lattice of trans-dioxotetrapyridinerhenium(V) chloride dihydrate which correspond to those reported by Burovaya. Thus, the translations $(2a_3 - a_1)/2$, a_2 , and $(2a_1 + a_3)/2$ have the interaxial ratios 1.63: 1: 1.03 with $\beta = 107^\circ 30'$. It is quite likely that Burovaya's compound is the dihydrate of the dioxotetrapyridinerhenium(V) chloride, the structure of which has been described in this thesis.

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