

## The Crystal Structure of $\text{K}_4\text{Re}_2\text{OCl}_{10} \cdot \text{H}_2\text{O}$

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Single crystals of  $\text{K}_4\text{Re}_2\text{OCl}_{10} \cdot \text{H}_2\text{O}$  have been examined by means of X-ray diffraction. The unit cell has dimensions:

$$a = 7.070 \pm 0.004, \quad c = 17.719 \pm 0.005 \text{ \AA}.$$

The space group is  $I4/mmm$ ;  $Z$  is 2. The structure was determined from Patterson and electron density projections on (010). The complex anion  $\text{Re}_2\text{OCl}_{10}^{-4}$  consists of two octahedra with a common corner (oxygen atom). The double bond character of the Re–O bond is considered in light of molecular orbital treatment of the ruthenium analog by Dunitz & Orgel.

### Introduction

In the course of investigating reduction products of  $\text{KReO}_4$ , Jezowska-Trzebiatowska & Wajda (1954) measured the magnetic susceptibility of two of these, designated by them  $\text{K}_2\text{ReOHCl}_5$  and  $\text{K}_4\text{Re}_2\text{OCl}_{10}$ . The former was found to have the expected magnetic moment, corresponding to three unpaired electrons, whereas the latter was found to have weak temperature-independent paramagnetism. The value of structural information in explanation of this anomalous magnetism is clear from the studies (Mathieson, Mellor & Stephenson, 1952; Dunitz & Orgel, 1953) on the analogous diamagnetic ruthenium binuclear complex compound. For this reason, the structural investigation reported below was begun.

### Experimental procedure

Preparation of  $\text{K}_4\text{Re}_2\text{OCl}_{10} \cdot \text{H}_2\text{O}$  was effected by the reduction of pure  $\text{KReO}_4$ , obtained from the University of Tennessee Chemistry Department, with KI in the presence of HCl. Both the original procedure (Noddack & Noddack, 1933) and its recent modification (Jezowska-Trzebiatowska, 1953) produced a crude material which was refined by recrystallization from HCl solution. Transparent, red-brown rectangular parallelepipeds of suitable size were washed with 95% ethanol solution and, finally, with ethyl ether. Measurement of the density by sink-float method produced a value of  $3.3 \text{ g.cm.}^{-3}$ .

Repeated grinding of the crystals in an attempt to prepare 300 mesh powder was found to produce progressive alteration and complication of the Debye-Scherrer pattern. Although water of crystallization is not indicated in previously encountered formulas, its presence was suggested by the above results and by the known properties of the ruthenium analog. Dehydration was indeed observed to begin when the material was heated to  $125^\circ\text{C}$ ., the wt.% of water finally driven off with further temperature increase being 2.1, a figure close to the value 2.0 calculated for

$\text{K}_4\text{Re}_2\text{OCl}_{10} \cdot \text{H}_2\text{O}$ . After dehydration, the weight of the sample remained constant until the temperature reached  $260^\circ\text{C}$ . Slight weight loss observed on subsequent temperature increase appears to be due to loss of volatile rhenium compounds such as chloride or oxide formed by thermal decomposition.

Various single crystals were subjected to preliminary examination by the precession and Weissenberg methods using Cu  $K\alpha$  radiation and were found to be tetragonal. One crystal with the shape of a rectangular parallelepiped  $87 \times 66 \times 12$  cubic microns was mounted for  $b$ -axis rotation, that is, about a direction parallel to the 66 micron edges. For quantitative intensity purposes, equatorial Weissenberg photographs were recorded on Kodak Blue Brand film arranged six sheets in depth and interleaved with 1 mil. brass foil. Intensities were estimated visually by comparison with timed exposure scales produced by the diffracting crystal.

### Unit-cell parameters

Since water loss interfered with the production of samples suitable for high quality Debye-Scherrer photographs, unit-cell parameters were determined from  $b$ -axis equatorial Weissenberg photographs on the right and left margins of which were superimposed Debye-Scherrer patterns for aluminum metal. Values of the Bragg angle for single crystal spots were obtained by comparison with the aluminum pattern. Cu  $K\alpha$  (00 $l$ ) spectra with  $l=14, 18, 20$ , and 22 ( $\alpha_1$  and  $\alpha_2$  resolved for 22) and Cu  $K\beta$  spectra with  $l=14$  and 18 were used in a weighted least squares extrapolation of  $c$  against the square of  $\cos \theta$  to obtain the  $c$  parameter. Good ( $h00$ ) spectra in the high Bragg angle range were not available; hence the Cu  $K\alpha$  ( $h0l$ ) spectra, (806), (808), (8,0,10), (4,0,18), for which  $\alpha_1$  and  $\alpha_2$  were resolved, were used in conjunction with the known  $c$  parameter for a weighted least squares extrapolation of  $a$  against the square of  $\cos \theta$ . The results of the extrapolations are:

$$a = 7.070 \pm 0.004, \quad c = 17.719 \pm 0.005 \text{ \AA}.$$

The unit-cell size, with the experimental density described above, shows that the unit cell contains two  $K_4Re_2OCl_{10} \cdot H_2O$ .

### Space group and Patterson synthesis

Successful indexing of reflections on the basis of the above tetragonal unit cell showed the only systematic restriction on indices to be  $h+k+l=2n$ , so that the lattice is  $I$ . The  $n$ -level Weissenberg patterns showed symmetry  $C_{2l}$ , which fact indicated Laue symmetry  $D_{4h}$ . The existence of spectra such as (002), (101), and (114) rules out all the space groups with lattice  $I$  in this Laue class except  $I4/mmm$ ,  $I\bar{4}2m$ ,  $I4m2$ ,  $I4mm$ , and  $I422$ .

Lorentz-polarization and absorption corrections were used to obtain from the observed intensities quantities proportional to the magnitude of  $F_o$ . The latter correction, made appreciable by both the shape of the crystal and the strong absorption of Re, was obtained by the method of Howells (1950). A zero moment test (Howells, Phillips, & Rogers, 1950) was made using ( $h0l$ ) reflections in an effort to detect centrosymmetry in the (010) projection. Perhaps because the atoms are not in general positions, the results were not as clear-cut as one might wish, but they suggest centrosymmetry for the projection. Thus  $I4mm$  and  $I4m2$  which have acentric (010) projections, seemed unlikely space group choices. More information on the selection was provided by the (010) Patterson projection; values of

$$P(u, w) = A^{-1} \sum_h \sum_l |F_{h0l}|^2 \cos 2\pi(hu + lw)$$

were calculated and represented in contour map form.

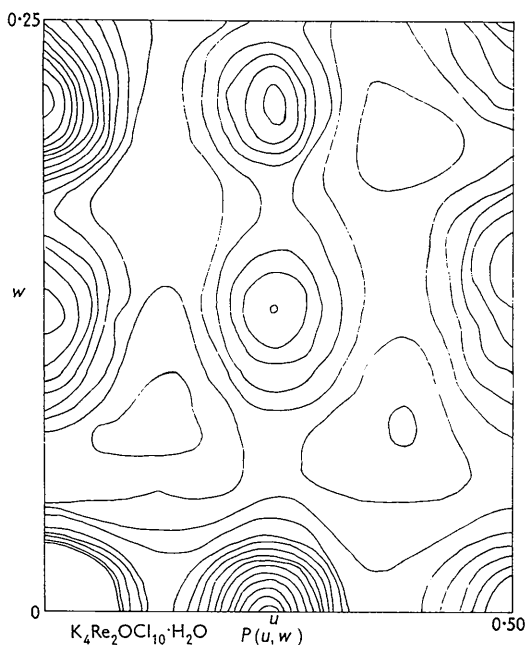


Fig. 1. Patterson projection on (010) obtained from observed intensities.

These calculations, like all other extensive ones described in this report, were made by the Univac 1105 system in the Research Computation Center of the University of North Carolina. For each possible accommodation of four rhenium atoms in each of the five possible space groups, Patterson peak locations and approximate heights were calculated. Comparison with Re-Re peak easily located on the map showed that the Re locations must be  $(0, z; 0, \bar{z}) + (\frac{1}{2}, \frac{1}{2})$ . This restriction rules out space group  $I4mm$ . Since the single Re-Re peak qualified as an appropriate image point, it was used to construct a map of the minimum function (Buerger, 1959),  $M_2(x, z)$ . The minimum function showed a number of features of the structure quite clearly. In particular, a strong peak corresponding to two superimposed chlorine atoms occupying positions  $(x, z; \bar{x}, z; \bar{x}, \bar{z}; x, \bar{z}) + (\frac{1}{2}, \frac{1}{2})$  is readily discernible. This feature enables one to select  $I4/mmm$  as the proper space group.

### Determination of the structure

The above description places rhenium in the  $4(e)$  space group positions and chlorine in  $16(m)$ . Oxygens associated with rhenium were located in the fixed positions  $2(a)$ , and the water molecules were placed in  $2(b)$ . The minimum function map was then assumed to be of sufficient clarity that only positions corresponding to peaks with reasonable heights could be possible locations for the remaining potassium and chlorine atoms. For the eight potassium ions, all eightfold positions can, on this basis, be ruled out and good agreement can be obtained by placing the potassium ions in  $4(c)$  and  $4(d)$ . The four remaining chlorines are in  $4(e)$ . Attempts to place the hydrogen atoms in equipoints of the space group resulted in hydrogen locations seemingly incompatible with chemical requirements for  $H_2O$ . Although it is possible that the true space group has symmetry lower than space group  $I4/mmm$  and can accommodate the hydrogen atoms in a fashion which is chemically satisfactory, it is also possible that the hydrogens are not ordered. Hydrogen scattering factors were not used in the computation of structure factors.

Trial values of rhenium  $4(e)$  parameter  $z_1$  and of chlorine  $16(m)$  parameters  $x$  and  $z_3$  were easily obtained from the minimum function map. Although it is apparent from the map that the chlorine  $4(e)$  parameter  $z_2$  is not too far from 0.25, overlap by the potassium ions makes this estimate of lower quality than the others. A better starting value was thought to be 0.24 calculated from the assumed location of rhenium and the Re-Cl separation found in  $K_2ReCl_6$  (Aminoff, 1936).

Refinement of the structural parameters was effected by successive  $F_o - F_c$  syntheses (Lipson & Cochran, 1953) projected on (010). The rhenium atom scattering factors required for structure factor calculations were Thomas-Fermi values (*Internationale*

*Tabellen zur Bestimmung von Kristallstrukturen*, 1935). Hartree-Fock values (Freeman, 1959) for potassium ion and for oxygen were employed. In an effort to make a slight improvement over the chlorine atom scattering factors of Viervoll & Øgrim (1949), the chloride ion values of Berghuis *et al.* (1955) were used for  $\lambda^{-1} \sin \theta \geq 0.5$ ; graphical interpolation was used to connect these smoothly with the atom values for smaller values of  $\lambda^{-1} \sin \theta$ . Anomalous scattering corrections were 0.27 for potassium ion, 0.23 for chlorine, and -1.15 for rhenium. The origin is taken at a symmetry center, and the temperature factor is  $\exp[-B(\sin^2 \theta)/\lambda^2]$ .

In the process of successive approximations for the refinement of parameters, estimation of corrections for  $z_1$ ,  $x$ ,  $z_3$ ,  $B(\text{Re})$ ,  $B(\text{Cl})$  was straightforward since rhenium and the 16(*m*) chlorine atoms are clearly resolved in the projection. Other parameter corrections required more detailed consideration. For chlorine in 4(*e*),  $B$  was assumed to be identical with that found for chlorine in 16(*m*). Removal of some difficulty arising from the overlap of 4(*d*) potassium and 4(*e*) chlorine was effected by examination of the difference between the electron density at (0,  $z$ ) and at ( $\frac{1}{2}$ ,  $z$ ). Potassium contributions cancel in this subtraction leaving the 4(*e*) chlorine position indicated. After this, adjustment of  $B(\text{K})$  in 4(*d*) could be considered. For potassium ions in 4(*c*),  $B$  was assumed to be identical with that found for the ions in 4(*d*). When the potassium ion thermal parameter had been determined, oxygen  $B$  values could be ascertained. The chemical differences between the 2(*a*) and 2(*b*) oxygens suggest that different temperature factors are required, but, for simplicity, the same  $B$  values were used for each oxygen atom in the initial estimate. Separate  $B$  values for the 2(*a*) and 2(*b*) oxygens were used as the refinement progressed. The overlap of potassium and oxygen and of chlorine and potassium does not permit very accurate estimates of  $B(\text{O})$  and  $B(\text{K})$ , in that they may be simultaneously varied quite a bit in opposite directions without appreciable change in calculated and observed structure factor agreement. Since initial examination showed  $B(\text{K})$  to be much larger than any other thermal parameter, it has arbitrarily been made as small as the uncertainty in its estimation will permit.

Early in the refinement sequence the difference synthesis near the location of Re exhibited features characteristic of use of an isotropic  $B$  in an anisotropic vibration situation. The method of representing an anisotropic atom of unit weight by means of isotropic atoms of fractional weights (Kartha & Ahmed, 1960) was employed for rhenium. The most important advantage offered by this application was that no change in the computer program for structure factors was needed to effect the change from isotropic to anisotropic representation. The properties of the vibration were such that satisfactory approximation was made using two rhenium half-atoms on the  $z$ -axis

placed symmetrically about the atom center, each distant 0.004 $c$  (i.e., 0.071 Å) from that center. Using the Kartha-Ahmed (1960) approximate relation (their equation (5)) between the half-atom separation and anisotropy in  $B$ , one estimates  $\Delta B$  to be about 0.43 Å<sup>2</sup>. In the calculation of structure factors used in the refinement procedure, four figures were used to represent parameters. For some of these the uncertainty makes rounding off to fewer figures a bit more appropriate in the final tabulation of results, as follows:

$z_1 = 0.1051$ (0.0002)	$B(\text{K}) = 5.0$
$z_2 = 0.239$ (0.002)	$B(\text{Cl}) = 3.2$
$z_3 = 0.112$ (0.001)	$B(\text{O}) = 2.8$
$x = 0.238$ (0.001)	$B(\text{H}_2\text{O}) = 3.5$
	$B(\text{Re}, x, y) = 2.25$
	$B(\text{Re}, z) = 2.68$

Numbers appearing in parentheses at the right of a result are estimates of standard deviation. For position parameters  $z_1$ ,  $z_3$ , and  $x$ , these were calculated by the method of Cruickshank (1949). This method cannot be applied to  $z_2$ , since the 4(*d*) potassiums partially overlap the 4(*e*) chlorines in projection.

Table 1 contains  $F_o$  and values of  $F_c$  calculated

Table 1. *Calculated and observed structure factors*

$h0l$	$F_c$	$F_o$	$h0l$	$F_c$	$F_o$
200	237	177	0,0,10	244	234
400	402	389	2,0,10	63	64
600	106	86	4,0,10	164	185
800	131	146	6,0,10	41	49
101	240	193	8,0,10	66	60
301	144	130	1,0,11	71	83
501	145	144	3,0,11	57	63
701	53	53	5,0,11	47	53
901	59	63	7,0,11	28	40
002	80	88	0,0,12	8	47
402	46	52	2,0,12	104	99
802	16	26	6,0,12	42	44
103	-125	-112	1,0,13	-77	-82
303	-72	-56	3,0,13	-44	-45
503	-79	-74	5,0,13	-64	-70
703	-24	-32	0,0,14	-198	-191
004	-238	-287	2,0,14	-48	-60
204	129	118	4,0,14	-142	-149
404	-154	-155	6,0,14	-36	-34
804	-67	-81	1,0,15	-112	-112
105	-234	-237	3,0,15	-89	-90
305	-149	-134	5,0,15	-79	-81
505	-155	-155	0,0,16	14	50
705	-56	-60	1,0,17	37	38
006	-267	-296	3,0,17	20	16
206	-87	-83	5,0,17	33	34
406	-166	-156	0,0,18	114	113
606	-53	-43	2,0,18	10	24
806	-64	-69	4,0,18	83	78
008	362	335	1,0,19	63	61
208	108	128	3,0,19	47	52
408	215	206	0,0,20	72	67
608	48	52	2,0,20	62	58
808	73	61	4,0,20	54	45
109	203	217	1,0,21	22	33
309	136	157	3,0,21	25	20
509	141	157	0,0,22	-48	-42
709	54	50			

from these parameters. For only three unobserved reflections, (307), (7,0,13), and (6,0,16), is  $F_c$  greater than the corresponding  $F$  calculated from the minimum detectable intensity. The ratio

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

is 10.4, only observed reflections being included in the summations.

### Discussion of the structure

From the above results comes indication that  $K_4Re_2OCl_{10} \cdot H_2O$  consists of potassium ions,  $Re_2OCl_{10}^{4-}$  ions, and water molecules. The complex anion consists of two octahedra with a common corner; at the common corner is oxygen, whereas chlorines are at all other corners. The atoms Cl-Re-O-Re-Cl are situated on the fourfold axis of the anion. Inside each octahedron is a rhenium atom located not in the chlorine plane perpendicular to the fourfold axis of the anion but on the axis 0.12 Å distant from the chlorine plane on the side toward the oxygen atom. Thus the Cl-Re-O bond angle is 94°. The standard deviation of this bond angle (*International Tables for X-ray Crystallography*, 1959) is 0.4° so that the 4° difference from a right angle seems significant. For all Re-Cl bonds in the anion the interatomic distances are 2.38 Å (standard deviation 0.02 Å). The Re-O separation is 1.86 Å (standard deviation 0.005 Å). The separation of chlorine atoms in the plane perpendicular to the direction of the Re-O bond and bonded to the same Re atom is 3.37 Å, a value which,

as is frequently the case, is close to but smaller than twice the van der Waals radius of chlorine (1.80 Å). The Cl-Cl internuclear distance for one in 4(e) and one in 16(m), both being bonded to the same Re atom, is 3.28 Å. The shortest Cl-Cl distance for Cl atoms in the anion but bonded to different rhenium atoms is 3.97 Å.

Each potassium ion in 4(c) is surrounded by eight chlorine atoms, two oxygen atoms, and two water molecules. The chlorine atoms form a rectangular parallelepiped  $3.37 \times 3.70 \times 3.97$  Å<sup>3</sup> about  $K^+$ , and the K-Cl separation is 3.19 Å. The  $K^+$  ion is at the center of a square at the corners of which are the oxygens of two anions and two water molecules. The K-O separation is  $a/2$  or 3.54 Å. Each potassium ion in 4(d) is surrounded by twelve chlorine atoms, eight 3.50 Å away and four distant 3.54 Å; all the K-Cl separations are thus seen to be essentially the same. The coordination polyhedron formed by these twelve chlorine atoms is a distortion of that formed about the 4(c) potassiums by chlorine and oxygen. The four chlorines at 3.54 Å are not actually coplanar as are their oxygen counterparts in the previous case, but they are quite close to the plane  $z = \frac{1}{4}$ . Furthermore, the eight chlorines at 3.50 Å form not a rectangular parallelepiped but a figure with four trapezoidal and two rectangular faces.

Each water molecule is at the center of a tetragonal prism with chlorine atoms at the corners, 3.29 Å distant from the center. The 4(c) potassium ions form a square about the water molecule. Similar coordination exists for oxygen in the complex anion except that the chlorine prism is formed by atoms all from a single anion with O-Cl distance 3.10 Å and that two rhenium atoms are within the prism.

The packing of ions in the crystal appears to be determined by contact of chlorine atoms with other chlorines and with potassium ions. Contact is suggested by the K-Cl separation of 3.19 Å, which is very close to the radius sum (3.13 Å) and by the interanion Cl-Cl separations 3.70 Å (16(m) type with 16(m) type) and 3.72 Å (16(m) type with 4(e) type), which values are not far from the radius sum (3.62 Å).

The Re-Cl separation observed in the complex anion is almost identical with the value 2.37 Å found in  $K_2ReCl_6$  (Aminoff, 1936). The observed Re-O separation in the complex anion is 1.86 Å. Comparison of the tabulated value of 0.52 Å for the  $Re^{+6}$  ionic radius with tabulated Mn ion radii (Wyckoff, 1948) leads to an estimate of 0.55 Å for  $Re^{+4}$ . The corresponding ionic Re-O radius sum is 1.95 Å, a value greater than the observed separation. This observed value, 1.86 Å, is about 5% larger than the Re-O separation of 1.77 Å in  $KReO_4$  (Morrow, 1960), but a change of just about that much is expected in the shift from octahedral to tetrahedral coordination about rhenium. These comparisons suggest that the Re-O bond in the complex anion has considerable double bond character.

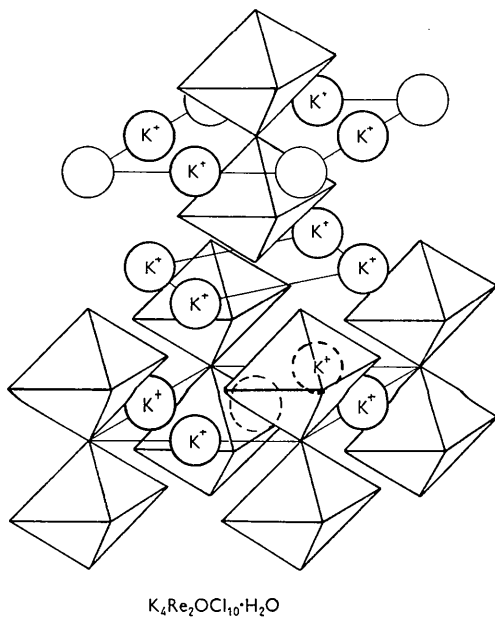


Fig. 2. Schematic diagram of the structure. Joined octahedra represent complex anions. Labelled spheres are  $K^+$  ions. Unlabelled spheres are oxygen atoms of  $H_2O$ .

The molecular orbital treatment given by Dunitz & Orgel (1953) for the complex anion  $\text{Ru}_2\text{OCl}_{10}^{4-}$  would seem directly applicable to the  $\text{Re}_2\text{OCl}_{10}^{4-}$  ion since the two have the same molecular geometry. The result of this group-theoretical treatment for  $\text{Re}_2\text{OCl}_{10}^{4-}$  would be a sigma representation involving five chlorine and one oxygen bonds to metal and a representation providing  $E_u$  (bonding and antibonding),  $B_{2g}$ ,  $B_{2u}$ , and  $E_g$  orbitals, these latter three types being approximately degenerate. Ten electrons, three from each rhenium and the four  $p(x, y)$  from oxygen, can be placed in these orbitals, but the relatively high energy antibonding  $E_u$  orbital is not needed. The bonding  $E_u$  orbital is described by Dunitz & Orgel (1953) as a degenerate bonding  $\pi$  orbital. With four electrons in the  $E_u$  bonding orbital, six remain to be placed in the approximately degenerate group mentioned above. If Hund's Rule is followed, one expects to find two of these six electrons unpaired and to find a paramagnetism of one unpaired electron per rhenium. The experimental magnetic susceptibility (Jezowska-Trzebiatowska & Wajda, 1954) is extremely small and temperature independent and may, according to Jezowska-Trzebiatowska & Wajda, even be due to contamination with related paramagnetic rhenium oxychloro complex compounds. This fact suggests that Hund's Rule is violated and that all the electrons are paired.

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## Effect of Errors of Atomic Co-ordinates on Structure Amplitude and Bijvoet Inequality

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The effect of errors of atomic parameters on the calculated values of the structure amplitude and the Bijvoet inequality is considered. Expressions for the standard deviations of the structure amplitude, Bijvoet inequality and the phase angle are derived and discussed. It is also shown that the fractional error in the structure amplitude can have as large a value as 50% or more for weak reflections at high values of  $\sin \theta$  even for a reasonably accurate structure.

### 1. Introduction

While the problem of finding out how the errors in intensity  $|F|^2$  or structure amplitude  $|F|$  affect the atomic positions has been discussed by a number of authors (see for instance Lipson & Cochran, 1957), not much attention seems to have been paid to the

converse problem namely how any errors in the atomic co-ordinates affect the calculated values of  $|F|$ . This problem was met with in connection with the author's work on the evaluation of the anomalous dispersion factor  $\Delta f''$  from experimental measurements of the Bijvoet inequality ( $\Delta I/I$ ) for various reflections  $hkl$  (Parthasarathy, 1961). Consequently this general