# Crystal Structure of Rhenium Oxide Tetrachloride

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Crystals of rhenium oxide tetrachloride are monoclinic, $Z = 8$, space-group $P2_1/c$, $a = 12{\cdot}61 \pm 0{\cdot}02$, $b = 5{\cdot}76 \pm 0{\cdot}01$, $c = 18{\cdot}51 \pm 0{\cdot}02$ Å, $\beta = 115{\cdot}5 \pm 0{\cdot}3°$. The structure was refined by three-dimensional least-squares methods to 0·069 for 954 reflections. The two crystallographically different $ReOCl_4$ units in the crystal have a square-pyramidal arrangement, with dimensions the same, within experimental error. The mean Re–O distances are 1·63, and mean Re–Cl 2·26 Å. The molecular units are weakly associated into dimer and endless chain arrangements through long Re · · · Cl interactions (3·55 and 3·65 Å) which are *trans* to the Re–O bonds.

OXIDE tetrachlorides have been reported [1] for molybdenum, tungsten, technetium, rhenium, and osmium, although only for the tungsten compound has the crystal structure been determined.[2] Crystals of the tungsten compound contain molecular units linked through asymmetric *trans*-oxygen bridges into endless chains. I.r. measurements of the solid rhenium analogue, $ReOCl_4$, have been interpreted [3] on the basis of unimolecular units; no evidence was obtained for any interaction of the type found in solid $WOCl_4$. The melting point [1] of $WOCl_4$ is 209°, whereas that of $ReOCl_4$ is 30°. The crystal structure of the rhenium compound has now been determined to investigate the importance of bridging interactions in the solid state.

## EXPERIMENTAL

Rhenium oxide tetrachloride was prepared by the action of sulphuryl chloride on rhenium metal in a Carius tube at 350°. Unlike the reported preparation,[4] the reaction was not complete after 3 days. The reaction products and excess sulphuryl chloride were removed and separated by vacuum distillation, and liquid rhenium oxide tetrachloride was distilled into thin-walled Pyrex capillaries.

Sections of capillary tube containing small amounts of the oxide tetrachloride were sealed under vacuum and single crystals grown by applying a temperature gradient along the tube.

*Crystal Data.*—$ReOCl_4$, $M = 344$, Monoclinic, $a = 12{\cdot}61 \pm 0{\cdot}02$, $b = 5{\cdot}76 \pm 0{\cdot}01$, $c = 18{\cdot}51 \pm 0{\cdot}02$ Å, $\beta = 115{\cdot}5 \pm 0{\cdot}3°$, $U = 1214$ Å$^3$, $Z = 8$, $D_c = 3{\cdot}76$, $F(000) = 1208$. Space-group $P2_1/c$ ($C^5_{2h}$, No. 14) from systematic absences: $h0l$ when $l \neq 2n$ and $0k0$ when $k \neq 2n$. Cu-$K_\alpha$ ($\lambda = 1{\cdot}5418$ Å) and Mo-$K_\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiations; $\mu$(Mo-$K_\alpha$) = 228 cm$^{-1}$. Single-crystal precession and Weissenberg photographs. (The non-space-group absence for $h0l$ when $(2h + l) \neq 4n$ was observed, caused by the pseudo-centring of the projection of the unit cell seen in Figure 1).

*Structure Determination.*—Integrated intensities were collected at $15 \pm 5°$ about the $b$ axis (layers $h0$—$4l$) by use of Mo-$K_\alpha$ radiation and a Nonius integrating camera. The relative intensities of 954 independent reflections were measured with a photometer of similar design to that described by Jeffery [5] and were corrected for Lorentz and polarisation factors. Unobserved reflections were excluded from all calculations.

Since the density of the crystals had not been measured, $Z = 8$ had been assumed from a comparison of the unit-cell volume with that of tungsten oxide tetrachloride.[2] A three-dimensional Patterson synthesis was interpreted to give the positions of two independent rhenium atoms in general positions corresponding to $Z = 8$. Structure factors were calculated using scattering factors for the neutral atom from ref. 6, and least-squares refinement gave $R$ 0·25. A three-dimensional electron-density map, phased on the rhenium atom positions, gave the positions of all the chlorine and oxygen atoms. Refinement of the positional and isotropic temperature factors, and layer scale-factors, was continued by full-matrix least-squares methods. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimised, first with unit weights and with $\sqrt{w} = |F_o|/67$ when $|F_o| \leqslant 67$, and $\sqrt{w} = 67/|F_o|$ when $|F_o| > 67$, during the final stages of refinement. Refinement was complete when $R$ was 0·126. Since the absorption coefficient was high, absorption corrections were calculated using a computer program, ABSCOR, for a crystal, elongated along $b$ with dimensions perpendicular to the needle axis of 0·1 and 0·2 mm. Application of these corrections and further cycles of refinement gave a final $R$ of 0·069. The final

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[1] J. H. Canterford and R. Colton, 'Halides of the Second- and Third-row Transition Metals,' Wiley–Interscience, New York, 1968.

[2] H. Hess and H. Hartung, *Z. anorg. Chem.*, 1966, **344**, 157.

[3] B. J. Brisdon and D. A. Edwards, *Inorg. Chem.*, 1968, **7**, 1898.

[4] D. A. Edwards and A. A. Woolf, *J. Chem. Soc.* (*A*), 1966, 91.

[5] J. W. Jeffery, *J. Sci. Instr.*, 1963, **40**, 494.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, p. 202.

parameter shifts were $<0{\cdot}1\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing $|F_o|$ was satisfactory. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20286 (11 pp., 1 microfiche).* Final positional parameters and isotropic temperature factors are listed in Table 1 and interatomic distances and angles in Table 2.

TABLE 1

Final atomic positional ($\times 10^4$) and thermal parameters ($\times 10^2$) with estimated standard deviations in parentheses

| Atom | $x/a$ | $y/b$ | $z/c$ | $B/\text{Å}^2$ |
|---|---|---|---|---|
| Re(1) | 0971(1) | 0084(4) | 1677(1) | 276(4) |
| Re(2) | 4037(2) | 3921(4) | 0808(1) | 276(5) |
| Cl(1) | 5836(11) | 2407(28) | 1441(7) | 394(26) |
| Cl(2) | 2813(12) | 6706(33) | 0015(8) | 443(28) |
| Cl(3) | 4610(13) | 6553(35) | 1779(9) | 483(29) |
| Cl(4) | 0334(13) | 2819(33) | 0716(9) | 469(29) |
| Cl(5) | 2214(11) | 2863(30) | 2460(8) | 409(26) |
| Cl(6) | 4045(11) | 2529(29) | −0335(8) | 396(26) |
| Cl(7) | −0883(11) | −1383(31) | 1075(8) | 422(26) |
| Cl(8) | 1047(10) | −1437(30) | 2833(7) | 372(24) |
| O(1) | 1810(32) | −1628(84) | 1440(22) | 451(75) |
| O(2) | 3207(40) | 2130(97) | 1010(28) | 617(103) |

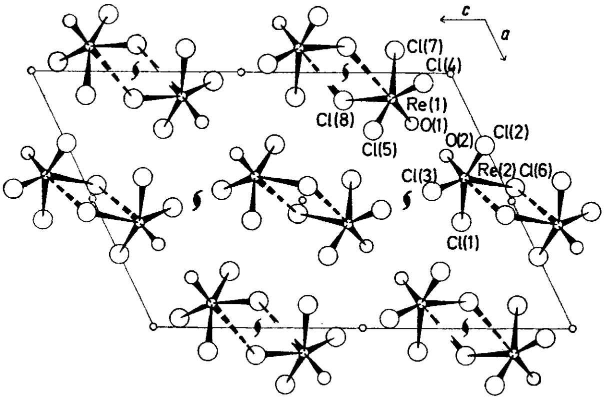

FIGURE 1 Projection of the structure down [010] showing the atom numbering

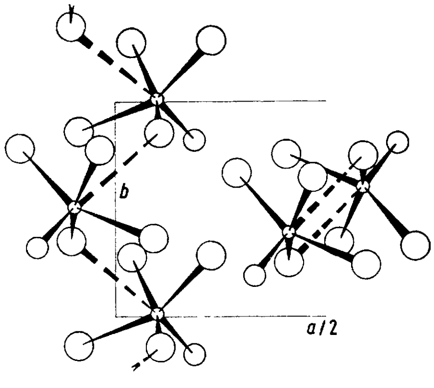

FIGURE 2 Projection of part of the structure down [001] showing the weak interactions between the monomer units

## DISCUSSION

The atomic arrangement is shown in Figures 1 and 2. The two crystallographically different rhenium atoms have almost identical nearest-neighbour arrangements, with a square-pyramidal co-ordination by four basal chlorine atoms and an apical oxygen atom. The mean Re–O distance is 1·63 and the mean Re–Cl distance 2·26 Å. These distances are very similar to those of 1·65 Å for Re–O in rhenium oxide tetrafluoride,[7] and the Re–Cl(terminal) distance of 2·24 Å in rhenium pentachloride [8] (although the oxidation state of rhenium in the latter compound is different and therefore the comparison is not strictly valid).

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

| | | | |
|---|---|---|---|
| Re(1)–Cl(4) | 2·25(2) | Re(2)–Cl(1) | 2·24(2) |
| Re(1)–Cl(5) | 2·27(2) | Re(2)–Cl(2) | 2·27(2) |
| Re(1)–Cl(7) | 2·28(2) | Re(2)–Cl(3) | 2·22(2) |
| Re(1)–Cl(8) | 2·28(2) | Re(2)–Cl(6) | 2·27(2) |
| Re(1)–O(1) | 1·64(4) | Re(2)–O(2) | 1·62(5) |
| Re(1) ··· Cl(8$^{\mathrm{I}}$) | 3·65(2) | Re(2) ··· Cl(6$^{\mathrm{II}}$) | 3·55(2) |
| Cl(4) ··· Cl(5) | 3·08(2) | Cl(1) ··· Cl(3) | 3·05(2) |
| Cl(4) ··· Cl(7) | 3·09(2) | Cl(2) ··· Cl(3) | 3·07(2) |
| Cl(5) ··· Cl(8) | 3·11(2) | Cl(1) ··· Cl(6) | 3·09(2) |
| Cl(7) ··· Cl(8) | 3·12(2) | Cl(2) ··· Cl(6) | 3·08(2) |
| O(1) ··· Cl(4) | 3·11(5) | O(2) ··· Cl(1) | 3·06(5) |
| O(1) ··· Cl(5) | 3·11(5) | O(2) ··· Cl(2) | 3·13(6) |
| O(1) ··· Cl(7) | 3·17(4) | O(2) ··· Cl(3) | 3·08(6) |
| O(1) ··· Cl(8) | 3·12(4) | O(2) ··· Cl(6) | 3·10(5) |
| Cl(4) ··· Cl(8$^{\mathrm{I}}$) | 3·80(2) | Cl(1) ··· Cl(6$^{\mathrm{II}}$) | 3·60(2) |
| Cl(5) ··· Cl(8$^{\mathrm{I}}$) | 3·93(2) | Cl(2) ··· Cl(6$^{\mathrm{II}}$) | 3·77(2) |
| Cl(7) ··· Cl(8$^{\mathrm{I}}$) | 3·55(2) | Cl(3) ··· Cl(6$^{\mathrm{II}}$) | 3·77(2) |
| Cl(8) ··· Cl(8$^{\mathrm{I}}$) | 3·74(2) | Cl(6) ··· Cl(6$^{\mathrm{II}}$) | 3·59(3) |

(*b*) Angles

| | | | |
|---|---|---|---|
| O(1)–Re(1)–Cl(4) | 105·2(1·5) | O(2)–Re(2)–Cl(1) | 103·9(1·8) |
| O(1)–Re(1)–Cl(5) | 104·3(1·4) | O(2)–Re(2)–Cl(2) | 105·7(1·8) |
| O(1)–Re(1)–Cl(7) | 106·9(1·5) | O(2)–Re(2)–Cl(3) | 105·4(1·8) |
| O(1)–Re(1)–Cl(8) | 104·4(1·5) | O(2)–Re(2)–Cl(6) | 104·6(1·8) |
| Cl(4)–Re(1)–Cl(5) | 85·7(6) | Cl(1)–Re(2)–Cl(3) | 86·4(6) |
| Cl(4)–Re(1)–Cl(7) | 86·0(6) | Cl(1)–Re(2)–Cl(6) | 86·6(5) |
| Cl(8)–Re(1)–Cl(5) | 86·1(5) | Cl(2)–Re(2)–Cl(3) | 86·3(7) |
| Cl(8)–Re(1)–Cl(7) | 86·4(5) | Cl(2)–Re(2)–Cl(6) | 85·5(5) |
| Cl(8$^{\mathrm{I}}$)–Re(1)–Cl(4) | 76·2(5) | Cl(6$^{\mathrm{II}}$)–Re(2)–Cl(1) | 73·0(4) |
| Cl(8$^{\mathrm{I}}$)–Re(1)–Cl(5) | 79·5(4) | Cl(6$^{\mathrm{II}}$)–Re(2)–Cl(2) | 77·3(5) |
| Cl(8$^{\mathrm{I}}$)–Re(1)–Cl(7) | 69·3(5) | Cl(6$^{\mathrm{II}}$)–Re(2)–Cl(3) | 77·7(5) |
| Cl(8$^{\mathrm{I}}$)–Re(1)–Cl(8) | 74·3(3) | Cl(6$^{\mathrm{II}}$)–Re(2)–Cl(6) | 72·4(5) |
| Re(1)–Cl(8$^{\mathrm{I}}$)–Re(1$^{\mathrm{I}}$) | 133·9(5) | Re(2)–Cl(6$^{\mathrm{II}}$)–Re(2$^{\mathrm{II}}$) | 107·6(5) |

(*c*) Contacts $<3{\cdot}7$ Å

| | | | |
|---|---|---|---|
| O(1) ··· O(2) | 3·10(6) | O(2) ··· Cl(4) | 3·45(5) |
| O(2) ··· Cl(5) | 3·44(5) | Cl(8) ··· Cl(7$^{\mathrm{I}}$) | 3·60(2) |
| Cl(2) ··· Cl(4$^{\mathrm{III}}$) | 3·61(2) | Cl(2) ··· Cl(7$^{\mathrm{III}}$) | 3·61(2) |
| Cl(4) ··· Cl(4$^{\mathrm{III}}$) | 3·48(3) | Cl(8) ··· Cl(2$^{\mathrm{IV}}$) | 3·68(2) |
| O(1) ··· Cl(2$^{\mathrm{V}}$) | 3·51(4) | O(1) ··· Cl(3$^{\mathrm{V}}$) | 3·47(4) |
| O(1) ··· Cl(4$^{\mathrm{V}}$) | 3·65(5) | O(1) ··· Cl(5$^{\mathrm{V}}$) | 3·62(5) |
| O(2) ··· Cl(2$^{\mathrm{V}}$) | 3·55(6) | O(2) ··· Cl(3$^{\mathrm{V}}$) | 3·65(6) |
| Cl(1) ··· Cl(6$^{\mathrm{VI}}$) | 3·54(3) | Cl(6) ··· Cl(6$^{\mathrm{VI}}$) | 3·64(3) |
| Cl(6) ··· Cl(7$^{\mathrm{VII}}$) | 3·68(2) | Cl(2) ··· Cl(8$^{\mathrm{VIII}}$) | 3·68(2) |
| Cl(1) ··· Cl(8$^{\mathrm{IX}}$) | 3·63(2) | Cl(3) ··· Cl(1$^{\mathrm{IV}}$) | 3·61(2) |
| Cl(5) ··· Cl(1$^{\mathrm{IX}}$) | 3·57(2) | | |

The Roman numerals as superscripts refer to atoms in the positions:

I $-x, \frac{1}{2}+y, \frac{1}{2}-z$
II $-x, -y, -z$
III $-1-x, \frac{1}{2}+y, \frac{1}{2}-z$
IV $x, \frac{1}{2}-y, \frac{1}{2}+z$
V $x, -1+y, z$
VI $-x, -1-y, -z$
VII $-1-x, -1-y, -z$
VIII $x, \frac{1}{2}-y, -\frac{1}{2}+z$
IX $1-x, \frac{1}{2}+y, \frac{1}{2}-z$

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[7] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1968, 2511.

[8] K. Mucker, G. S. Smith, and Q. Johnson, *Acta Cryst.*, 1968, **B24**, 874.

In both the crystallographically different $ReOCl_4$ units, the four basal chlorine atoms are co-planar, to within $\pm0{\cdot}02$ Å around Re(1), and to within $\pm0{\cdot}002$ Å around Re(2). The rhenium atoms are displaced from these planes by 0·60 [Re(1)] and 0·58 Å [Re(2)]. The O–Re–Cl angles are the same, within experimental error, 105·0°, and the units have $C_{4v}$ symmetry, although no symmetry is required for their general positions in the space-group.

Although the structure can be described in terms of these monomer units, and previous experimental evidence, particularly the i.r. spectrum[3], has been correlated with such a description, there is evidence for extremely weak interactions between the monomers in the solid state. Thus the monomer units are arranged so that one of the basal chlorine atoms in one unit completes a distorted octahedral arrangement around the rhenium atom in another unit. This association occurs in two ways: to form either dimer or endless-chain arrangements for Re(2) and Re(1) respectively. In the dimer the units are related by the centre of symmetry, and in the endless chain by the screw axis in the space-group (Figure 1). The Re $\cdots$ Cl contacts are very long (3·55 in the dimers and 3·65 Å in the endless chain) and the interactions must be extremely weak. There is no significant lengthening of the Re–Cl distance for the chlorine atoms involved in this bridging in either case, and no significant deviations from $C_{4v}$ symmetry for the monomer units.

The structure is completely different from that of tungsten oxide tetrachloride,[2] where there is relatively strong bonding through *trans*-bridging oxygen atoms between the monomer units and W–O distances of 1·81 and 2·18 Å. The angle O–W–Cl (for the oxygen atom at 1·81 Å) is 97·9°. The much weaker interaction in the rhenium compound is in agreement with the much lower melting point.

The dimer units in rhenium oxide tetrachloride are very similar to those established recently for tungsten sulphide tetrachloride and tungsten sulphide tetrabromide.[9] In the dimer units in $WSCl_4$ the association is stronger, with a lengthening of the W–Cl bond involved in the dimerisation by 0·09 Å, and a W $\cdots$ Cl distance of 3·05 Å. The mean S–W–Cl angle is 100·7°.

If the compounds $ReOCl_4$, $WSCl_4$, and $WOCl_4$ are compared, then the interaction in the solid state increases, as shown by the decreasing contacts between the monomer units, Re $\cdots$ Cl 3·60, W $\cdots$ Cl 3·05, and W $\cdots$ O 2·18 Å (although the W–O distance is not really comparable with the other two distances because of the smaller size of the oxygen atom). This increase in interaction may also be correlated with the decrease in the apical-atom–metal–basal-atom angle from 105·0 through 100·7 to 97·9°.

Although the chain arrangement in rhenium oxide tetrachloride is quite different from that in the corresponding tungsten compound, it is similar to that in rhenium oxide tetrafluoride.[7] In the oxide tetrafluoride the linking between the monomer units is much stronger, and the ratio of the Re–F(bridge) distances is 1·16 compared with 1·59 for the ratio of the Re–Cl(bridge) distances in the oxide tetrachloride. The angle at the bridging atom is 139 for the fluoride and 134° for the chloride, but despite this similarity the relative orientations of the monomer units in the chain are quite different.

Since the monomer units in solid rhenium oxide tetrachloride are extremely weakly linked together into polymers, it seems probable that in the gas phase the molecule will retain the solid-state configuration and thus have a square-pyramidal structure.

By comparison with molybdenum pentachloride, which has a trigonal-bipyramidal structure in the vapour phase,[10] it has been postulated that tungsten oxide tetrachloride and tungsten sulphide tetrachloride have similar configurations,[9] with the sulphur and oxygen atoms in equatorial positions. Although a distorted trigonal-bipyramidal arrangement, with oxygen in an equatorial position, and a square-pyramidal arrangement, are easily interconverted, the evidence of the present structure determination does favour the square-pyramidal configuration in the vapour state. This configuration, with $C_{4v}$ symmetry, has been assigned previously to molybdenum and tungsten oxide tetrafluorides on the basis of i.r. measurements.[11]

I thank Dr. T. A. Hamor for his amended versions of the computer programmes, FORDAP, ORFLS, ORFFE, and ABSCOR. All calculations were carried out on an English Electric KDF 9 computer and I thank the staff of Birmingham University Computer Centre for their assistance.

[1/1831 *Received, 7th October*, 1971]

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[11] S. Blanchard, Commissariat à l'Énergie Atomique Report CEA-R 3194, 1967.