Crystal Structure of the Adduct of Rhenium Tetrachloride Oxide and Rhenium Chloride Trioxide

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Crystals of the title compound are triclinic, space group $P1$, $a = 5.78$, $b = 6.02$, $c = 9.08$ Å, $\alpha = 114.8$, $\beta = 96.2$, $\gamma = 95.0°$. The structure was refined by three-dimensional least-squares methods to R 0.059 for 654 reflections. The $ReOCl_4$ and ReO_3Cl units in the structure have square pyramidal and distorted tetrahedral arrangements respectively. The two molecules are linked through an oxygen atom of the ReO_3Cl unit, which thus completes a distorted octahedral co-ordination for the rhenium atom of the $ReOCl_4$ unit.

DURING the sublimation of single crystals of rhenium tetrachloride oxide,[1] prepared by the interaction of rhenium metal and sulphuryl chloride, a single crystal with a different habit was isolated. The present structure analysis has shown it to be the previously characterised [2] adduct formed by $ReOCl_4$ and ReO_3Cl.

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[1] A. J. Edwards, *J.C.S. Dalton*, 1972, 582.

[2] K. I. Petrov, V. V. Kravchenko, D. V. Drobot, and V. A. Aleksandrova, *Russ. J. Inorg. Chem.*, 1971, **16**, 928; D. V. Drobot, B. G. Korshunov, and V. A. Aleksandrova, *ibid.*, p. 1223.

EXPERIMENTAL

The interaction of rhenium metal and sulphuryl chloride and preparation of single crystals has been described previously.[1] Rhenium tetrachloride oxide formed long dark-red needles, and one other crystal was observed, also dark-red in colour, with an irregular block habit.

Crystal Data.—$Re_2Cl_5O_4$, $M = 613.5$, Triclinic, $a = 5.78(1)$, $b = 6.02(1)$, $c = 8.08(1)$ Å, $\alpha = 114.8(3)$, $\beta = 96.2(3)$, $\gamma = 95.0(3)°$, $U = 224$ Å^3, $Z = 1$, $D_c = 4.55$ g cm^{-3}, $F(000) = 267$. Space group $P1$ (C_1, No. 1). Cu-K_α ($\lambda = 1.5418$ Å) and Mo-K_α [$\lambda = 0.7107$ Å; μ(Mo-K_α) = 310 cm^{-1}] radiation. Single crystal precession and Weissenberg photographs.

Structure Determination.—Integrated intensities were collected about the *a* axis (layers 0—4*kl*) by use of Mo-K_α radiation and a Nonius integrating camera. The relative intensities of 654 reflections were measured with a photometer of similar design to that described by Jeffery[3] and were corrected for Lorentz and polarization factors. Absorption corrections were applied as the absorption coefficient was very high, but these were only approximate due to the difficulty of defining the irregular crystal in the capillary tube.

TABLE 1

Final atomic positional and thermal parameters (× 10^3), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B(Å^2)
Re(1)	0	0	0	
Re(2)	0.345 6(5)	−0.024 7(6)	0.439 1(3)	
Cl(1)	−0.049 2(38)	0.304 9(36)	0.273 3(24)	
Cl(2)	0.154 6(39)	−0.324 5(34)	−0.197 0(22)	
Cl(3)	0.327 6(41)	0.241 9(46)	0.007 7(30)	
Cl(4)	−0.219 2(36)	−0.268 2(39)	0.071 7(27)	
Cl(5)	0.595 6(51)	0.300 0(46)	0.598 1(32)	
O(1)	0.311(10)	−0.050(10)	0.209(7)	5.6(1.2)
O(2)	−0.144(9)	0.061(8)	−0.152(6)	4.5(1.0)
O(3)	0.126(9)	−0.006(9)	0.532(7)	4.7(1.1)
O(4)	0.510(9)	−0.270(9)	0.439(6)	4.4(1.1)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re(1)	15.4(2.2)	26.5(1.6)	30.9(2.1)	1.3(1.3)	1.7(1.4)	17.9(1.5)
Re(2)	51.4(3.4)	60.7(3.1)	18.6(1.8)	20.5(2.3)	9.3(1.8)	18.6(1.8)
Cl(1)	61(15)	63(11)	46(8)	36(9)	26(8)	15(8)
Cl(2)	85(16)	47(10)	36(8)	23(9)	16(8)	14(7)
Cl(3)	59(17)	86(15)	63(12)	−4(11)	21(9)	35(11)
Cl(4)	43(14)	74(13)	62(10)	−5(9)	16(8)	33(9)
Cl(5)	94(21)	68(15)	55(11)	−2(12)	2(10)	16(10)

A three-dimensional Patterson synthesis showed that there were two rhenium atoms in the unit cell, approximately 4 Å apart. Three-dimensional electron-density maps, phased on these two atoms, in either of the space groups $P1$ or $P\bar{1}$ were very difficult to interpret. A solution of the structure was eventually derived in space group $P1$, although the electron density map was almost symmetrical about the rhenium atoms. Structure factors were calculated using scattering factors for neutral atoms[4] with corrections applied to those of chlorine and rhenium for the effects of anomalous dispersion.[5] Initial refinement of the positional and isotropic temperature factors, and layer scale factors, was achieved by full-matrix least-squares methods, minimising the function $\Sigma w(|F_o| - |F_c|)^2$ with unit weights. Refinement was continued with the layer scale factors held constant and with the introduction of anisotropic thermal parameters for the rhenium and chlorine atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. In the final stages of refinement a satisfactory analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing fractions of $|F_o|$ was achieved by applying the weighting scheme $w^{\frac{1}{2}} = |F_o|/40$ when $|F_o| \leqslant 40$, and $w^{\frac{1}{2}} = 40/|F_o|$ when $|F_o| > 40$. Refinement was complete when R was 0.059 and the final parameter shifts were $<0.1\sigma$. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21857 (3 pp., 1 microfiche).* The final positional parameters and temperature factors are listed in Table 1 and interatomic distances in Table 2.

TABLE 2

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

(*a*) Distances			
Re(1)–O(1)	2.46(6)	Re(1)–O(2)	1.60(6)
Re(1)–Cl(1)	2.27(2)	Re(1)–Cl(2)	2.27(2)
Re(1)–Cl(3)	2.26(3)	Re(1)–Cl(4)	2.27(3)
Re(2)–O(1)	1.78(6)	Re(2)–O(3)	1.53(6)
Re(2)–O(4)	1.82(6)	Re(2)–Cl(5)	2.14(3)
O(2) ··· Cl(1)	3.08(5)	O(2) ··· Cl(2)	2.94(6)
O(2) ··· Cl(3)	2.80(5)	O(2) ··· Cl(4)	2.23(7)
O(1) ··· Cl(1)	3.04(7)	O(1) ··· Cl(2)	2.98(5)
O(1) ··· Cl(3)	2.86(8)	O(1) ··· Cl(4)	3.11(6)
Cl(1) ··· Cl(3)	3.16(4)	Cl(1) ··· Cl(4)	3.14(3)
Cl(2) ··· Cl(3)	3.11(3)	Cl(2) ··· Cl(4)	3.16(3)
O(1) ··· O(3)	2.48(8)	O(1) ··· O(4)	2.89(9)
O(1) ··· Cl(5)	3.12(5)	O(3) ··· O(4)	2.82(7)
O(3) ··· Cl(5)	3.01(6)	O(4) ··· Cl(5)	3.09(6)
(*b*) Angles			
O(2)–Re(1)–Cl(1)	104.3(1.7)	O(2)–Re(1)–Cl(2)	97.3(1.7)
O(2)–Re(1)–Cl(3)	91.1(2.0)	O(2)–Re(1)–Cl(4)	112.3(1.9)
O(1)–Re(1)–Cl(1)	80.0(1.1)	O(1)–Re(1)–Cl(2)	78.0(1.1)
O(1)–Re(1)–Cl(3)	74.3(1.2)	O(1)–Re(1)–Cl(4)	82.2(1.2)
Cl(1)–Re(1)–Cl(3)	88.2(8)	Cl(1)–Re(1)–Cl(4)	87.8(8)
Cl(2)–Re(1)–Cl(3)	86.6(8)	Cl(2)–Re(1)–Cl(4)	88.5(8)
O(1)–Re(1)–O(2)	164.8(2.5)	O(1)–Re(2)–O(3)	117.8(2.8)
O(1)–Re(2)–O(4)	106.7(2.4)	O(1)–Re(2)–Cl(5)	105.3(1.9)
O(3)–Re(2)–O(4)	114.4(2.9)	O(3)–Re(2)–Cl(5)	109.0(1.7)
O(4)–Re(2)–Cl(5)	102.3(1.6)	Re(1)–O(1)–Re(2)	136.1(8)
(*c*) Contacts <3.6 Å			
Cl(1) ··· O(3)	3.47(7)	Cl(1) ··· Cl(5$^{\mathrm{I}}$)	3.51(4)
Cl(4) ··· O(1$^{\mathrm{I}}$)	3.22(6)	Cl(4) ··· O(4$^{\mathrm{I}}$)	3.51(6)
O(2) ··· Cl(3$^{\mathrm{I}}$)	3.53(6)	O(4) ··· Cl(3$^{\mathrm{II}}$)	3.46(5)
O(4) ··· Cl(5$^{\mathrm{II}}$)	3.39(7)	Cl(4) ··· Cl(3$^{\mathrm{III}}$)	3.59(4)
Cl(2) ··· O(3$^{\mathrm{IV}}$)	3.46(7)	Cl(3) ··· O(3$^{\mathrm{IV}}$)	3.50(5)
O(2) ··· O(3$^{\mathrm{IV}}$)	3.03(8)	O(2) ··· Cl(5$^{\mathrm{V}}$)	3.25(7)
O(2) ··· O(4$^{\mathrm{V}}$)	3.35(6)	Cl(2) ··· Cl(5$^{\mathrm{VI}}$)	3.57(3)
Cl(4) ··· Cl(5$^{\mathrm{VI}}$)	3.58(3)		

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

I	$-1 + x, y, z$	IV	$x, y, -1 + z$
II	$x, -1 + y, z$	V	$-1 + x, y, -1 + z$
III	$-1 + x, -1 + y, z$	VI	$-1 + x, -1 + y, -1 + z$

DISCUSSION

The structure analysis has shown that the interaction of rhenium metal and sulphuryl chloride gives some rhenium chloride trioxide as well as rhenium tetrachloride oxide as the major product. The interaction of these two chloride oxides has been shown previously[2] to form the congruently melting 1 : 1 complex, characterised by differential thermal, *X*-ray powder diffraction, tensimetric, and elemental analyses.[2] A structure in-

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

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

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

volving bridging through one of the oxygen atoms of the rhenium chloride trioxide was postulated[2] from i.r. measurements and this has been confirmed by the present work.

The atomic arrangement is illustrated in Figure 1.

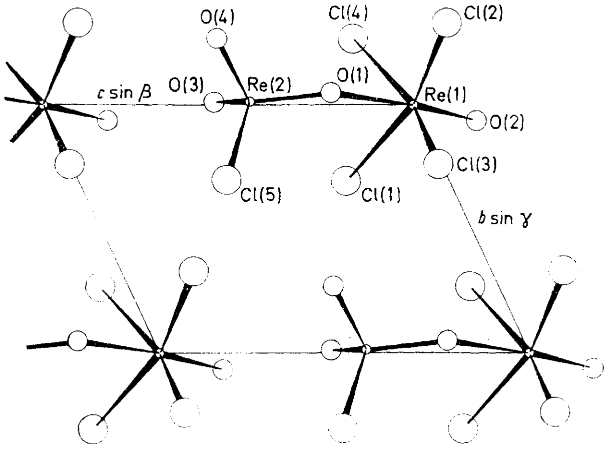

FIGURE 1 Projection of the structure down [100]

The Re(1) atom has a square pyramidal arrangement of four chlorine atoms and the oxygen atom, and completion of a distorted octahedral co-ordination is by an oxygen atom of the rhenium chloride trioxide. This co-ordination is very similar to that in the structures of $ReOCl_4$ itself,[1] and of[6] aquatetrachloro-oxorhenium(VI), $ReOCl_4(OH_2)$, where the sixth co-ordination position is filled by a chlorine atom from another molecular unit, and by the oxygen atom of the water molecule respectively. The Re–O distance of 1.60 Å and the average Re–Cl distance of 2.27 Å are the same as the corresponding distances in $ReOCl_4$ and $ReOCl_4(OH_2)$, but the average O–Re–Cl angle of 100.5° in the adduct is significantly less than the value of 105.1° in the tetrachloride oxide itself and slightly more than the value of 98° for the aqua-compound.

The decrease in angle for the three compounds can be correlated with the increasingly closer co-ordination in the sixth position, with Re ⋯ Cl($ReOCl_4$) 3.60, Re ⋯ O (rhenium chloride trioxide) 2.46, and Re ⋯ O (aqua-compound) 2.27 Å. Although comparison of the systems is difficult, with different atoms involved, the Re ⋯ Cl distance is 1.34 Å larger than the single bond distance, whereas the Re ⋯ O distances are only 0.61 and 0.42 Å greater than the single Re–O bond distance[7] in μ-oxo-bis{trichloro(*O*-chlorotrioxorhenium)oxorhenium(VI)}.

In the ReO_3Cl unit the Re–O distances are rather varied. The Re–O(bridge) distance of 1.78 Å is very similar to that of 1.76 Å in the corresponding unit in μ-oxo-bis{trichloro(*O*-chlorotrioxorhenium)oxorhenium(VI)} and the Re(2)–O(3) distance of 1.53 Å is not significantly different from Re(1)–O(2) at 1.60 Å, at the level of accuracy of this determination. However, the Re(2)–O(4) distance of 1.82 Å is much longer than expected and may be affected by disorder. Figure 2 shows a projection of the molecular unit perpendicular to the plane defined by O(2), Cl(1), and Cl(4). There is an approximate mirror plane through the unit, containing the two rhenium atoms, O(2), O(1), and O(3) and with the non-equivalence of Cl(5) and O(4) alone destroying the mirror symmetry. Thus disorder involving Cl(5) and O(4) appears to be possible and may account for the long Re(2)–O(4) distance, although the accuracy and extent of the data are insufficient to allow a detailed analysis.

The projection in Figure 2 also shows that the molecular unit is so arranged that the chlorine and oxygen atoms lie in positions corresponding to very approximate cubic close packing of these atoms, and therefore the most efficient packing together of the molecular units, with the two rhenium atoms in adjacent octahedral and tetrahedral holes. The Re–O–Re angle of 136° is close to the value of 125° for an idealised close packed array, and very similar to the corresponding angle of 135° in μ-oxo-bis{trichloro(*O*-chlorotrioxorhenium)oxorhenium(VI)}.

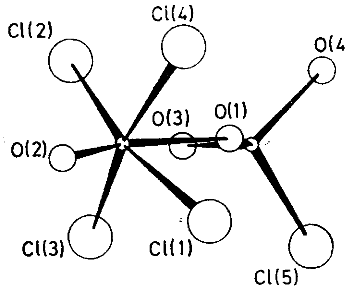

FIGURE 2 The molecular unit seen in projection perpendicular to the plane defined by O(2), Cl(1), and Cl(4)

Most of the calculations were carried out on the University of Manchester Regional Computer Centre's CDC 7600 with the '*X*-Ray '72' system of programmes,[8] and I thank the staff at Birmingham University Computer Centre for their assistance.

[6/818 *Received, 27th April*, 1976]

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[6] P. W. Frais and C. J. L. Lock, *Canad. J. Chem.*, 1972, **50**, 1811.

[7] C. Calvo, P. W. Frais, and C. J. L. Lock, *Canad. J. Chem.*, 1972, **50**, 3607.

[8] '*X*-Ray' System, Technical Report TR 192 of the Computer Science Centre, University of Maryland, June 1972.