The Crystal Structures of Tungsten, Molybdenum, Rhenium, and Technetium Oxide Tetrafluorides

By A. J. EDWARDS,* G. R. JONES, and B. R. STEVENTON
(*Department of Chemistry, University of Birmingham, P.O. Box* 363, *Edgbaston, Birmingham,* 15)

TRANSITION-METAL oxide tetrafluorides have similar physical properties to the corresponding pentafluorides[1] and we have found that their structures are also similar, with replacement of fluorine by oxygen atoms. However, for the molybdenum and rhenium compounds, detailed crystallographic examination suggests that, contrary to expectation, the oxygen atoms are bonded to the metal in terminal rather than in bridging positions. Linking between units is by fluorine atoms, as in the pentafluorides.

Unit-cell dimensions, determined from *X*-ray single-crystal measurements, are compared with those of corresponding pentafluorides in the Table.

Compound	Crystal class	*a*	*b*	*c* (Å)	*β*°	*V* (Å^3)	*Z*	Space group
NbF_5[2]	Monoclinic	9·62	14·43	5·12	96·1	706	8	*C*2/*m*
WOF_4	„	9·65	14·42	5·15	95·4	713	8	*C*2/*m*
TcF_5[3]	Orthorhombic	7·75	17·01	5·76	—	759	—	—
$MoOF_4$	Monoclinic	7·84	16·98	5·49	92·5	731	8	$P2_1/a$
$ReOF_4$	„	19·01	5·57	14·72	114·0	1431	16	*C*2/*c*
$TcOF_4$	„	18·83	5·49	14·43	114·0	1366	16	—

Tungsten oxide tetrafluoride has been shown by a complete crystallographic analysis to have the niobium pentafluoride structure, with tetrameric units in the solid state.[4] Molybdenum oxide tetrafluoride is not isostructural with its tungsten analogue, but has a monoclinic unit cell, very similar to the orthorhombic technetium pentafluoride cell. This orthorhombic cell has also been found for chromium,[5] vanadium, and rhenium[4] pentafluorides but the molecular structure of these compounds has not been elucidated.

The detailed molecular structure of molybdenum oxide tetrafluoride has now been determined from three-dimensional data, collected photographically, using Mo-K_α radiation. A comparison of its unit-cell volume with those of the pentafluorides showed that there are eight $MoOF_4$ units in the cell. Atom positions were determined initially by the usual "heavy-atom" methods and atomic parameters refined by several full-matrix, least-squares cycles. The discrepancy factor, *R*, for 1850 observed reflections is 0·10.

The structure consists of distorted octahedral groups, linked into endless chains parallel to the *c*-axis by *cis*-bridging atoms. This is the alternative linking arrangement, for *cis*-bridged octahedra, to the closed tetramers found for niobium[2] and ruthenium[6] pentafluorides.

Although rhenium oxide tetrafluoride has very different unit-cell dimensions from the molybdenum compound, the molecular structural unit has been found to be very similar with chains parallel to the *b*-axis. Technetium oxide tetrafluoride has also been shown to have this structural unit, by a preliminary two-dimensional analysis.[4] A three-dimensional structure refinement for $ReOF_4$ similar to that described above, has given a value of R, for 950 observations, of 0·11. The difference between the structures lies only in the angle at which the two octahedra in the chain are linked together, (151° for $MoOF_4$ and 139° for $ReOF_4$) and in the packing of the chains.

The structural unit for the two compounds consists of two crystallographically distinct octahedra, in which the bond lengths and angles are very similar. This unit is illustrated in the Figure, where the oxygen atom position is determined from the stereochemistry (see below), since we could not distinguish oxygen from fluorine by X-ray methods in the presence of heavy atoms.

The most significant feature of the structure is the single, very short, terminal bond-length of 1·65 Å in each octahedron, which we suggest is due to a multiple bond to oxygen. The bridge bond-length opposite to this oxygen atom is considerably longer than that opposite to a fluorine atom. The total effect can be described by considering the metal atom drawn 0·3 Å towards the oxygen atom, above the plane defined by F(1), F(2), F(3), F(4), inside a relatively undistorted octahedron of light atoms.

The arrangement is very similar to that found in some compounds containing $[ReBr_4OL]^-$ ions, ($L = H_2O$, MeCN)[7] where there is a short Re–O bond, with a long Re–L bond *trans* to it. It has also been suggested[8] that there is a general tendency for bonds *trans* to Mo–O multiple bonds to be weakened and hence lengthened, and the present result for $MoOF_4$ agrees well with this.

The infrared spectra of molybdenum and tungsten oxide tetrafluorides, in the vapour phase, have been recorded between 4000 and 400 cm.$^{-1}$ and are very similar:—

$MoOF_4$; 1045sh, w; 1032, 1025, 1020vs; 750sh, w; 725, 718vs; 630m; 540vw.

WOF_4; 1055s; 1040sh, m; 735m; 705, 700, 690vs; 630m; 555vw. These results suggest a simple, monomeric structure in the vapour phase for the two compounds.

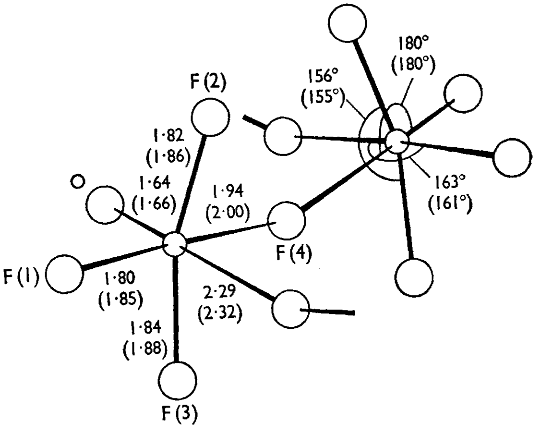

FIGURE. *Unbracketed numbers refer to* $MoOF_4$, *those bracketed to* $ReOF_4$. *Values averaged for the two octahedra are given, estimated standard deviations are* ±0·02 Å *for* $MoOF_4$ *and* ±0·04 Å *for* $ReOF_4$.

(*Received, March* 15*th*, 1967; *Com.* 253.)

---

[1] R. D. Peacock, *Progr. Inorg. Chem.*, 1960, **2**, 193.
[2] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.
[3] A. J. Edwards, D. Hugill, and R. D. Peacock, *Nature*, 1963, **200**, 672.
[4] A. J. Edwards and G. R. Jones, unpublished results.
[5] A. J. Edwards, *Proc. Chem. Soc.*, 1963, 205.
[6] J. H. Holloway, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 1964, 644.
[7] F. A. Cotton and S. J. Lippard, *Chem. Comm.*, 1965, 245; *Inorg. Chem.*, 1965, **4**, 1621; 1966, **5**, 416.
[8] F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1603.