# Transition-metal Tetrafluoride Oxide–Antimony Pentafluoride Adducts; Preparation and Characterization of the Adducts $MF_4O{\cdot}SbF_5$ (M = Mo, W, or Re) and Crystal Structures of $MoF_4O{\cdot}SbF_5$ and $ReF_4O{\cdot}SbF_5$

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The adducts $MF_4O{\cdot}SbF_5$ (M = Mo, W, or Re) have been obtained as colourless (Mo, W) or pale blue (Re) solids from the reaction of the appropriate tetrafluoride oxide with excess of $SbF_5$. The solid adducts have been characterized by observation of reaction stoicheiometries, Raman and mass spectra, and by *X*-ray diffraction. Crystals of $MoF_4O{\cdot}SbF_5$ are monoclinic, space group $P2_1/n$, with unit-cell dimensions $a$ = 7.470(8), $b$ = 10.40(2), $c$ = 9.606(9) Å, β = 93.13(30)°, and $Z$ = 4; those of $ReF_4O{\cdot}SbF_5$ are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a$ = 5.561(10), $b$ = 10.198(8), $c$ = 12.622(9) Å, β = 99.37(20)°, and $Z$ = 4. Both structures have been refined by three-dimensional least-squares methods to $R$ = 0.041 3 for 1 123 reflections for $MoF_4O{\cdot}SbF_5$ and $R$ = 0.057 6 for 1 062 reflections for $ReF_4O{\cdot}SbF_5$. The molybdenum adduct is best regarded as a polymeric zig-zag chain in which alternate Sb and Mo atoms are linked through fluorine bridges. The rhenium adduct, on the other hand, contains dimers, with two Re atoms and two Sb atoms, linked through fluorine bridges into distorted, essentially covalent eight-membered rings. Evidence has also been obtained for a second adduct of molybdenum, $MoF_4O{\cdot}2SbF_5$. An estimate of the ionic contribution to bonding in the adducts is made.

COMPARATIVE studies of the acid properties of the tetrafluoride oxides of molybdenum, tungsten,[1,2] rhenium,[1] and uranium [2] have been carried out. Conductimetric measurements [1] gave an order of Lewis-acid strength, $ReF_4O > WF_4O > MoF_4O$, while an investigation based on equilibrium-constant data [2] for the molybdenum, tungsten, and uranium compounds showed $WF_4O > MoF_4O > UF_4O$. In all cases complexes containing the $[MF_5O]^-$ ion are readily prepared [2-13] and in the $MF_4O$–NOF–HF (M = Mo or W) systems the anions $[M_2F_9O_2]^-$ and $[MF_6O]^{2-}$ can also be obtained.[2]

Some of the tetrafluoride oxides also form fluorine-bridged adducts with noble-gas fluorides. Xenon difluoride and tungsten tetrafluoride oxide form the adducts $XeF_2{\cdot}nWF_4O$ ($n$ = 1 or 2) which, in the solid state [14,15] and in solution,[14] are covalent with xenon–fluorine–tungsten bridges with no appreciable contribution to the bonding from ionic formulations such as $[XeF][WF_5O]$ or $[XeF][W_2F_9O_2]$. Recent detailed investigations of the reactions of $XeF_2$ [16] and $KrF_2$ [17] with $WF_4O$ and $MoF_4O$ have shown not only that adducts analogous to $XeF_2{\cdot}nWF_4O$ ($n$ = 1 or 2) also occur with $XeF_2$ and $MoF_4O$, but that similar krypton compounds can be prepared.

Following work on the uranium tetrafluoride oxide–antimony pentafluoride system, in which adducts with the compositions $UF_4O{\cdot}nSbF_5$ ($n$ = 1—3) were successfully prepared and characterized and the single-crystal structure of $UF_4O{\cdot}2SbF_5$ was determined by *X*-ray analysis,[18] it seemed appropriate to attempt the analogous reactions with $MoF_4O$, $WF_4O$, and $ReF_4O$. The *X*-ray study of $UF_4O{\cdot}2SbF_5$ revealed a fluorine-bridged structure with some tendency towards the ionic formulation $[UF_2O][SbF_6]_2$. Antimony(V) fluoride is a far stronger Lewis acid than the tetrafluoride oxides, which should favour ionic formulations, and the relative Lewis acidities of $MoF_4O$, $WF_4O$, and $ReF_4O$ [1,2] imply that the rhenium adduct should have the least ionic character, and perhaps be the least stable.

## RESULTS

*Preparations and Characterizations.*—Reactions between molybdenum tetrafluoride oxide and antimony pentafluoride were carried out by dissolution of $MoF_4O$ in a five-fold excess of $SbF_5$. Removal of excess of $SbF_5$ under dynamic vacuum revealed the existence of adducts of 1 : 2 and 1 : 1 compositions, the latter of which is stable under dynamic vacuum at room temperature (Figure 1).

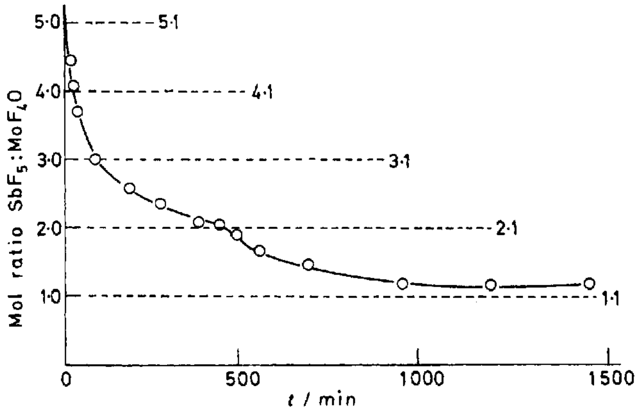

FIGURE 1 Curve of weight loss *versus* time of pumping for $MoF_4O{\cdot}nSbF_5$

The mass spectrum of a sample of the residual solid revealed the species $[SbF_6]^+$, $[SbF_5]^+$, $[SbF_4]^+$, $[SbF_3]^+$, $[SbF_2]^+$, $[SbF]^+$, $Sb^+$, $[MoF_2O]^+$, $[MoFO_2]^+$, $[MoF_2O_2]^+$, and $[MoF_3O]^+$. The fluoride dioxide species might be attributed to impurities in the sample, but more likely arises from reaction of $MoF_4O{\cdot}SbF_5$ in the mass spectrometer. The Raman spectrum of a powdered sample is shown in Table 1 along with spectra of $MoF_4O$ and $SbF_5$. The increase in the metal–oxygen stretching frequency of 5(±1) $cm^{-1}$ implies an increased positive charge on the molybdenum due to a slight contribution from an ionic formulation such as $[MoF_3O][SbF_6]$.

Reactions between tungsten tetrafluoride oxide and antimony pentafluoride were carried out in the same way as for $MoF_4O$. However, no point of inflection at the 1 : 2

TABLE 1

Raman spectra (cm$^{-1}$) of the adducts $WF_4O{\cdot}SbF_5$ and $MoF_4O{\cdot}SbF_5$ compared with those of pure $WF_4O$, $MoF_4O$, and $SbF_5$

| $WF_4O{\cdot}SbF_5$ | $WF_4O$ | $MoF_4O{\cdot}SbF_5$ | $MoF_4O$ | $SbF_5$ |
|---|---|---|---|---|
| 1 061vs | 1 058vs | | | |
| | | 1 047s | 1 042s | |
| 758mw | 744m | | | |
| | | 766mw | 740m | |
| 710s | 728w | | | |
| | | 704m | 721mw | 718s |
| | 687vw | | | |
| | | 675s | 688s | 670vs |
| 670s | 669vw,sh | | | |
| | | 621w | | |
| | 663mw | | | |
| | | 578w | 571w | |
| 556vw | 563w | | | |
| | | | 529w | |
| | 532vw | | | |
| | | | 506vw | |
| | 523w | | | |
| | | 338w | 333m | 349vw |
| | 388w | | | |
| | | 314w | 309ms | |
| | 367vw | | | |
| | | | 275w | 268m |
| 334w | 330mw | | | |
| | | 233w | 222mw | 231mw |
| | 318m,sh | | | |
| | | | | 189mw |
| 312w | 314s | | | |
| 279w | 265w | | | |
| 242vw | 242mw | | | |
| | 215mw | | | |
| | 151mw | | | |
| 133vw | 135w | | | |

composition was observed. It was also clear, in all cases, that, although only solid was present at the 1 : 1 composition, $SbF_5$ was still being slowly lost in dynamic vacuum.

The mass spectrum of the solid residue revealed only fragmentation patterns associated with $[SbF_4]^+$, $[SbF_3]^+$, $[SbF_2]^+$, $[SbF]^+$, $Sb^+$, $[WF_3O]^+$, $[WF_2O]^+$, $[WF_3]^+$, $[WFO]^+$, and $[WF_2]^+$. No distinction is possible between the solid being $WF_4O{\cdot}SbF_5$ or a $WF_4O$–$SbF_5$ mixture. The Raman spectrum of the solid (Table 1) is similarly inconclusive. The $\nu_1$(Sb–F) band at 670 cm$^{-1}$ is consistent with the fundamental Sb–F frequency for $SbF_5$ rather than for $[SbF_6]^-$ (662 cm$^{-1}$),[19] and the metal–oxygen stretch at 1 061 cm$^{-1}$ is close to that found for $WF_4O$ (1 058 cm$^{-1}$).[20] An *X*-ray powder-diffraction pattern shows differences in intensity for the reflections {130} and {040} in $WF_4O$, but, in all other respects, is identical.

A white solid obtained by fusing stoicheiometric quantities of $WF_4O$ and $SbF_5$ gave Raman spectra and an *X*-ray powder diffraction pattern identical with those from the reactions where excess of $SbF_5$ was used.

These data suggest that if an adduct of 1 : 1 composition is produced the $SbF_5$ fits into the $WF_4O$ structure without significant alteration of unit-cell size. The possibility that the ' adduct ' consists of a mixture of $WF_4O$ and $SbF_5$ cannot be dismissed.

Reaction between rhenium tetrafluoride oxide and antimony pentafluoride was carried out by dissolution of $ReF_4O$ in a 12-fold excess of $SbF_5$. The curve of weight loss *versus* time of pumping was similar to that observed with the $WF_4O$–$SbF_5$ system, $SbF_5$ continuing to be lost rapidly as the 1 : 2 stoicheiometry was passed. Attempts to powder the pale blue crystals remaining after pumping resulted in chemical decomposition. However, collections of single crystals isolated in Pyrex capillaries gave *X*-ray powder photographs of sufficiently good quality to confirm that the bulk material was $ReF_4O{\cdot}SbF_5$, the same compound as the crystal used in the single-crystal structure investigation. Mass spectra of the single crystal used for the *X*-ray analysis and the bulk material (Figure 2) were identical.

*Single-crystal Structure Determinations.*—Single-crystal *X*-ray studies were carried out on crystals of colourless $MoF_4O{\cdot}SbF_5$ and pale blue $ReF_4O{\cdot}SbF_5$ obtained from the reactions of the respective tetrafluoride oxides with excess of $SbF_5$.

The structure of $MoF_4O{\cdot}SbF_5$ is related to that of $MoF_4O$,[21]

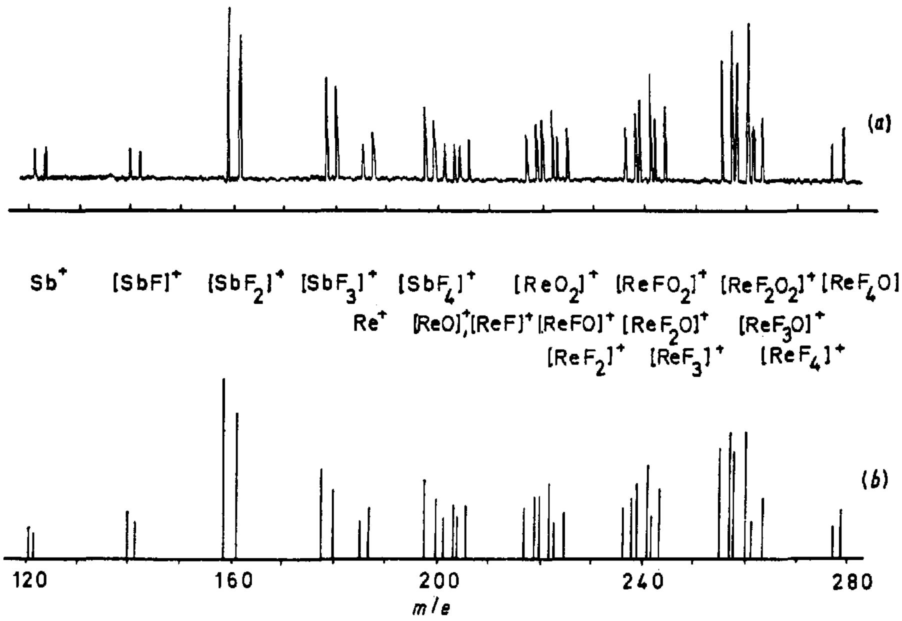

FIGURE 2 Recorded (*a*) and calculated (*b*) mass spectrum of $ReF_4O{\cdot}SbF_5$

with alternate antimony and molybdenum atoms linked through fluorine bridges into a polymeric zigzag chain (Figure 3). Equivalent atoms of each chain are aligned in the *ab* plane. The arrangement of the pairs of bridging fluorine atoms about the molybdenum atom is *cis*, and *trans* for the antimony atom. The light atoms are approximately octahedrally arranged about the antimony atom but the octahedron is elongated in the direction of the *trans*-fluorine bridges. The light-atom array about molybdenum is less regular, due to the presence of the oxygen atom and the *cis*-fluorine bridging arrangement. The molybdenum atom is effectively displaced away from the adjacent bridging fluorine atoms and towards the two light atoms in the same plane (Figure 4).

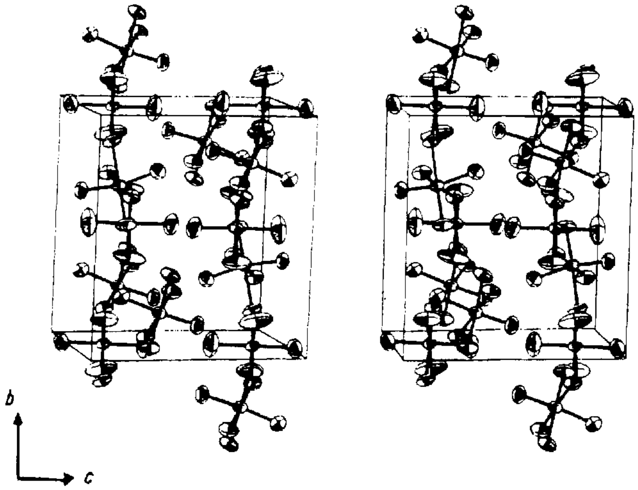

FIGURE 3 Stereoscopic view of the unit-cell contents of $MoF_4O{\cdot}SbF_5$ approximately down the *a* axis

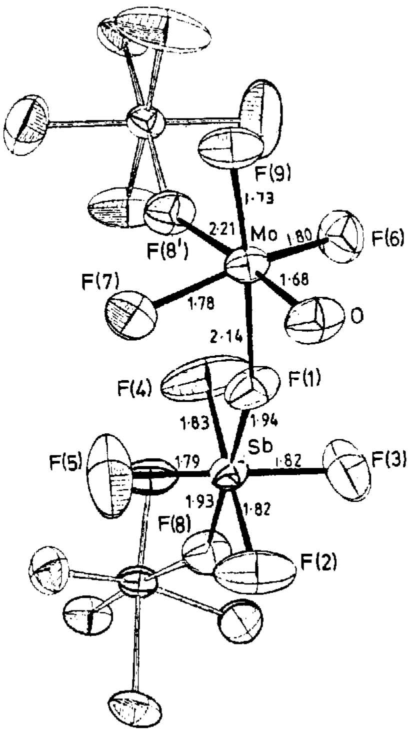

FIGURE 4 The asymmetric unit of $MoF_4O{\cdot}SbF_5$

The structure of $ReF_4O{\cdot}SbF_5$ consists of dimers of the adduct linked through fluorine bridges into distorted eight-membered rings (Figure 5). The structure is, therefore, more closely related to that of the solid-state tetrameric structure of $SbF_5$ [19] than to $ReF_4O$,[22] which forms endless chains. However, the dimer ring is less planar than that of $SbF_5$, and approximates to the tetrameric ring arrangements of $RhF_5$ [23] and $RuF_5$ [24] which have average bridge-bond angles of 135 and 132° respectively.

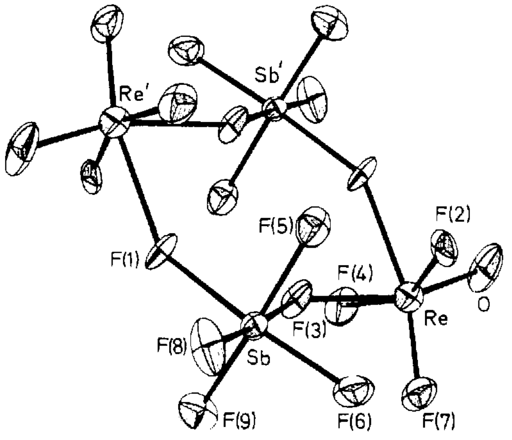

FIGURE 5 The dimer ring unit $(ReF_4O{\cdot}SbF_5)_2$

## DISCUSSION

Unlike uranium tetrafluoride oxide, the tetrafluoride oxides of molybdenum, tungsten, and rhenium apparently only form adducts of 1 : 1 composition with antimony pentafluoride which are stable at room temperature. As expected the $WF_4O$ adducts are less stable than those of $MoF_4O$; for $WF_4O$ no evidence of a 1 : 2 adduct could be found, but in the $MoF_4O$–$SbF_5$ system there is a point of inflection at a 1 : 2 composition in the curve of weight loss *versus* time of pumping. Single crystals of $MoF_4O{\cdot}SbF_5$ were readily obtained, but $WF_4O{\cdot}SbF_5$ continued slowly to lose $SbF_5$ at room temperature.

As pointed out previously, the zigzag chain structure of $MoF_4O{\cdot}SbF_5$ is related to that of $MoF_4O$ itself but, unlike $MoF_4O$, which has asymmetric molybdenum-fluorine bridge bonds [1.94(1) and 2.29(2) Å], the bridging distances to molybdenum in the $SbF_5$ adduct are approximately equal at 2.15(1) and 2.21(1) Å. The possibility that the bridging atoms could be alternately oxygen and fluorine was rejected on the evidence of vibrational spectroscopic data and the equivalence of the bridging bonds. The terminal atoms perpendicular to the bridging plane were assigned to fluorine, the bond distances to molybdenum [1.78(1) and 1.80(1) Å] being typical of metal–fluorine (terminal) bond lengths. The assignment of the oxygen atom to one of the two light atoms equatorial to the bridging atoms is not conclusive, but has been made on the basis of the shortest molybdenum–light atom bond length. In the structure of $MoF_4O$, the light atom opposite the longer fluorine bridge has a bond distance of 1.65(1) Å, compared with 1.82(1) Å for the light atom *trans* to the short fluorine bridge, and the oxygen atom was thus fixed unequivocally. However, the equivalent atoms of the $SbF_5$ adduct have bond lengths of 1.68(1) and 1.73(1) Å, and although this indicates a preference for placing the oxygen atom at the co-ordinates 1.68(1) Å from molybdenum this distance is longer than expected for a metal–oxygen bond, and the length of 1.73(1) Å is short for a metal–fluorine bond, which suggests a degree of disorder between these positions.

The zigzag chain structure of the adduct is in contrast with the solid-state structure of $SbF_5$,[25] which consists of tetrameric fluorine-bridged rings with alternate antimony–fluorine–antimony angles of 141 and 170°. It is, therefore, intermediate between the linear-bridged tetramer exhibited by $NbF_5$ [26] and the tetrameric structure typified by $RhF_5$ [23] and $RuF_5$ [24] with M–F–M angles near 135°.

Since in $MoF_4O{\cdot}SbF_5$ the fluorine atoms are closer to the antimony than to the molybdenum atoms, it can be argued that there is a contribution from the ionic formulation $[MoF_3O][SbF_6]$. The average Sb–F bridge distance [1.94(1) Å] in the adduct is less than the average fluorine-bridge distance [2.02(3) Å] found in the tetrameric $SbF_5$ structure.[25] The average Mo–F bridge distance [2.18(1) Å] in the adduct is greater than the average of the equivalent bonds in the $MoF_4O$ structure [2.12(1) Å].[21] This reflects the greater affinity of antimony for fluorine, but the Raman spectrum with an almost insignificant shift to higher frequency of the Mo=O bond-stretching vibration suggests only a slight ionic contribution.

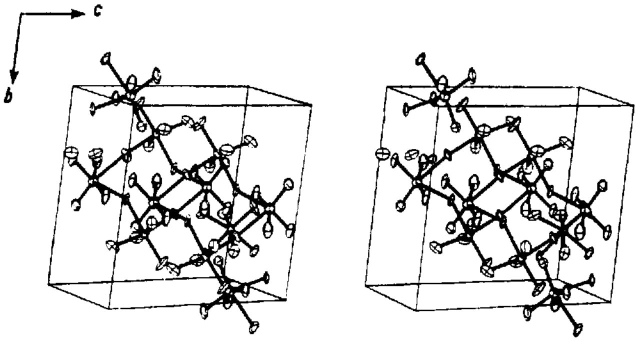

FIGURE 6 Stereoscopic view of the unit-cell contents of $ReF_4O{\cdot}SbF_5$ approximately down the *a* axis

Unlike $MoF_4O{\cdot}SbF_5$ and $ReF_4O$ which have chain-type structures, the structure of $ReF_4O{\cdot}SbF_5$ contains pairs of adduct units linked *via* fluorine bridges into distorted ruthenium pentafluoride-like tetramers. Figure 6 shows a stereoscopic view of the tetramers lying across the {010} faces of the unit cell. The antimony and rhenium atoms are both displaced from the centre of the bonded light-atom arrays, away from the *cis*-fluorine bridge atoms. The displacement is less apparent in the antimony environment where angles between adjacent fluorine atoms about the Sb atom are between 84.2(7) and 97.1(8)°. The average Sb–F (terminal) distance (1.84 Å) is close to the distance (1.82 Å) found in the $SbF_5$ tetramer. The average of the two Sb–F(bridge) distances (2.00 Å) is also much nearer to the distance found in $SbF_5$ than in the uranium and molybdenum adducts. The light-atom array about rhenium is less regular, with angles between adjacent light atoms about the rhenium varying from 81.7(6) to 106.5(9)°. The oxygen-atom position, in the plane of the *cis* bridges, was chosen entirely by bond-length considerations. Vibrational spectra of the adduct were not obtained due to the instability of the material to grinding, and oxygen bridging could not, therefore, be ruled out as was possible for the uranium and molybdenum adducts. However, the light-atom distance [1.66(2) Å] from Re and the distance [1.72(2) Å] of the other terminal atom in the bridging plane are similar to the bond lengths in the molybdenum adduct and on this basis the oxygen position can be assigned for this adduct, with the same probability of disorder. The Re–O bond distance compares with the distance [1.63(4) Å] found in the monoclinic form of $ReF_4O$, and is less than the average terminal-oxygen distance (1.695 Å), found in the $Re_2O_7$ structure.[27] The remaining two terminal atoms, axial to the *cis*-bridging plane, have an average bond length to Re of 1.84 Å. The fluorine-bridge distances (2.08 and 2.23 Å) are, within the limits of error, equivalent to the distances found in $ReF_4O$.

In an attempt to quantify the relative degree of ionic character in $MF_x{\cdot}SbF_5$ adducts, an ionicity value $\mathscr{I}$ has been derived using the Sb–F(bridging) bond length $D_a$ in a given adduct; $\mathscr{I}$ is given by equation (1) where $D_c$

$$\mathscr{I} = (D_c - D_a)/(D_c - D_i) \qquad (1)$$

(=2.02 Å) is the 'covalent' Sb–F bridging distance and $D_i$ is the Sb–F distance in the ion $[SbF_6]^-$ [=1.845(10) Å] taken from the structure of $K[SbF_6]$.[28] The value chosen for $D_c$ is based on the average Sb–F (bridging) distance in $(SbF_5)_4$ [25] [=2.025(34) Å] and the average of 2.024(50) Å from eight crystal-structure determinations containing the $Sb_2F_{11}$ unit. The quotient $\mathscr{I}$ should therefore range from 0.0 in a 'covalent' adduct, to 1.0 in an ionic adduct $[MF_{x-1}][SbF_6]$. Although the Sb–F(bridging) distance is not expected to vary linearly with ionic character, the variation should be monotonic. Values of $\mathscr{I}$ for a number of adducts are collected in Table 2; the overall trend is in line with other evidence, *e.g.* bond-stretching frequencies, although there is a general shortage of other data. The similar ionicity values for $MoF_4O{\cdot}SbF_5$ and $UF_4O{\cdot}2SbF_5$ appear to conflict with the much smaller increase in ν(Mo=O) of 5 $cm^{-1}$ compared with that for ν(U=O) of *ca.* 20 $cm^{-1}$ on adduct formation, but there are of course two $SbF_5$ units sharing the increased negative charge in the case of the uranium adduct. The much smaller ionicity value of 0.11 for $ReF_4O{\cdot}SbF_5$ is in line with the higher Lewis acidity of $ReF_4O$ compared with $UF_4O$ and $MoF_4O$. The low ionicity value indicates that considerable ionic contribution to the bonding is not a requirement for the formation of a stable and ordered adduct. Thus the solid obtained from the $WF_4O$–$SbF_5$ reaction at 1 : 1 molar composition may yet prove to be an adduct in spite of the lack of other supporting evidence.

TABLE 2

Calculated ionicity values, $\mathscr{I}$,[a] of some antimony pentafluoride compounds

| Compound | Average Sb–F/Å | $\mathscr{I}$ | Ref. |
|---|---|---|---|
| $(SbF_5)_4$ | 2.020 | 0.00 | 25 |
| $ReF_4O{\cdot}SbF_5$ | 2.000 | 0.11 | |
| $UF_4O{\cdot}2SbF_5$ | 1.949 | 0.40 | 18 |
| $NbF_5{\cdot}SbF_5$ | 1.945 | 0.43 | *b* |
| $MoF_4O{\cdot}SbF_5$ | 1.936 | 0.48 | |
| $BrF_3{\cdot}SbF_5$ | 1.91 | 0.63 | *c* |
| $ClF_3{\cdot}SbF_5$ | 1.905 | 0.66 | *d* |
| $K[SbF_6]$ | 1.845 | 1.00 | 28 |

[a] Defined in text. [b] A. J. Edwards, *J. Chem. Soc., Dalton Trans.*, 1972, 2325. [c] A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1969, 1467. [d] A. J. Edwards and R. J. C. Sills, *J. Chem. Soc. A*, 1970, 2697.

## EXPERIMENTAL

*Starting Materials.*—Molybdenum and tungsten tetrafluoride oxides were prepared in quartz systems by passing a mixture of $F_2$ and $O_2$ (*ca.* 5 : 1) over metal powders (99.9%, BDH Chemicals Ltd.) in nickel boats heated to *ca.* 400 °C. The $MoF_4O$ and $WF_4O$ produced were purified by sublimation in Pyrex vessels and stored in and dispensed from Kel-F containers in a nitrogen-filled dry-box (Vacuum Atmospheres, U.S.A.). Rhenium tetrafluoride oxide was prepared in a closed Kel-F reactor by the controlled hydrolysis of $ReF_6$ dissolved in anhydrous hydrogen fluoride. The rhenium hexafluoride was prepared in a nickel pressure vessel by the direct fluorination of a slight excess of rhenium powder (99.9%, BDH), antimony pentafluoride by passing $F_2$ over antimony powder (Technical grade, BDH) in a nickel boat in a quartz system. The crude $SbF_5$ was purified by sublimation in a Pyrex system by trap-to-trap sublimation under vacuum.

TABLE 3

Atomic positional parameters for $MoF_4O{\cdot}SbF_5$, with estimated standard deviations in parentheses

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Sb | 0.289 09(9) | 0.018 61(6) | 0.191 83(7) |
| Mo | 0.626 17(12) | 0.320 94(9) | 0.169 27(9) |
| O | 0.790 2(11) | 0.251 4(8) | 0.082 8(8) |
| F(1) | 0.469 3(9) | 0.148 1(6) | 0.159 4(7) |
| F(2) | 0.455 5(10) | −0.105 0(7) | 0.159 7(10) |
| F(3) | 0.224 1(12) | 0.016 0(8) | 0.006 0(8) |
| F(4) | 0.123 7(12) | 0.144 2(8) | 0.219 7(13) |
| F(5) | 0.352 9(15) | 0.019 9(11) | 0.374 4(8) |
| F(6) | 0.471 3(10) | 0.354 4(7) | 0.024 1(6) |
| F(7) | 0.670 3(10) | 0.257 4(7) | 0.339 3(6) |
| F(8) | 0.390 1(9) | 0.389 5(6) | 0.276 9(7) |
| F(9) | 0.708 5(10) | 0.475 2(7) | 0.192 5(8) |

Vibrational spectroscopy and *X*-ray powder-diffraction photographs attested to the purity of the products.

*Characterizations.*—Reaction stoicheiometries were monitored by weighing the reaction tubes and their contents on a modified Stanton Unimatic CL41 microanalytical balance. Raman spectra were recorded using a Coderg

TABLE 4

Atomic positional parameters for $ReF_4O{\cdot}SbF_5$, with estimated standard deviations in parentheses

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Re | 0.325 7(18) | 0.016 6(11) | 0.209 4(9) |
| Sb | −0.015 9(3) | 0.255 4(16) | 0.001 7(14) |
| O | 0.482(4) | 0.154(2) | 0.242 1(17) |
| F(1) | 0.188(3) | 0.097 0(16) | 0.060 5(13) |
| F(2) | 0.021(3) | 0.059 4(18) | 0.235 9(12) |
| F(3) | −0.097(3) | 0.147 8(17) | −0.127 7(12) |
| F(4) | 0.535(2) | −0.068 0(19) | 0.132 0(13) |
| F(5) | −0.263(3) | 0.170 9(18) | 0.056 2(13) |
| F(6) | −0.203(3) | 0.390 7(20) | −0.052 7(14) |
| F(7) | 0.386(3) | −0.086 0(19) | 0.319 2(14) |
| F(8) | 0.100(3) | 0.330 1(17) | 0.134 7(13) |
| F(9) | 0.256(3) | 0.307 7(18) | −0.052 3(13) |

TABLE 5

Interatomic distances (Å) and angles (°) for $MoF_4O{\cdot}SbF_5$ with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| (*a*) Distances | | | |
| Sb–F(1) | 1.942(6) | Mo–O | 1.681(7) |
| Sb–F(2) | 1.826(7) | Mo–F(1) | 2.145(6) |
| Sb–F(3) | 1.824(7) | Mo–F(6) | 1.797(6) |
| Sb–F(4) | 1.827(8) | Mo–F(7) | 1.776(6) |
| Sb–F(5) | 1.792(8) | Mo–F(8) | 2.210(6) |
| Sb–F(8) | 1.931(6) | Mo–F(9) | 1.728(7) |
| (*b*) Angles | | | |
| F(2)–Sb–F(1) | 88.7(3) | F(7)–Mo–O | 101.0(4) |
| F(3)–Sb–F(1) | 90.2(3) | F(7)–Mo–F(1) | 78.6(3) |
| F(3)–Sb–F(2) | 88.4(4) | F(7)–Mo–F(6) | 149.9(3) |
| F(4)–Sb–F(1) | 90.5(4) | F(8)–Mo–O | 172.5(3) |
| F(4)–Sb–F(2) | 178.5(5) | F(8)–Mo–F(1) | 81.0(2) |
| F(4)–Sb–F(3) | 90.5(5) | F(8)–Mo–F(6) | 78.7(3) |
| F(5)–Sb–F(1) | 90.1(4) | F(8)–Mo–F(7) | 78.6(3) |
| F(5)–Sb–F(2) | 91.4(5) | F(9)–Mo–O | 101.5(4) |
| F(5)–Sb–F(3) | 179.6(3) | F(9)–Mo–F(1) | 166.7(3) |
| F(5)–Sb–F(4) | 89.8(6) | F(9)–Mo–F(6) | 97.5(3) |
| F(1)–Mo–O | 91.6(3) | F(9)–Mo–F(7) | 100.4(4) |
| F(6)–Mo–O | 98.9(4) | F(9)–Mo–F(8) | 85.8(3) |
| F(6)–Mo–F(1) | 78.5(3) | Mo–F(1)–Sb | 163.0(4) |
| | | Mo–F(8)–Sb | 161.6(4) |

TABLE 6

Interatomic distances (Å) and angles (°) for $ReF_4O{\cdot}SbF_5$ with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| (*a*) Distances | | | |
| Re–F(1) | 2.079(15) | Sb–F(1) | 2.043(15) |
| Re–F(2) | 1.832(15) | Sb–F(3) | 1.959(15) |
| Re–F(4) | 1.850(15) | Sb–F(5) | 1.845(14) |
| Re–F(7) | 1.725(17) | Sb–F(6) | 1.797(16) |
| Re–F(3) | 2.231(15) | Sb–F(8) | 1.860(16) |
| Re–O | 1.660(20) | Sb–F(9) | 1.835(15) |
| (*b*) Angles | | | |
| F(2)–Re–F(1) | 81.7(6) | F(6)–Sb–F(1) | 177.9(7) |
| F(4)–Re–F(1) | 82.9(7) | F(6)–Sb–F(3) | 94.0(8) |
| F(4)–Re–F(2) | 152.5(7) | F(6)–Sb–F(5) | 94.6(8) |
| F(7)–Re–F(1) | 163.8(7) | F(8)–Sb–F(1) | 84.6(7) |
| F(7)–Re–F(2) | 93.6(8) | F(8)–Sb–F(3) | 168.8(7) |
| F(7)–Re–F(4) | 94.9(8) | F(8)–Sb–F(5) | 91.4(8) |
| O–Re–F(1) | 89.7(9) | F(8)–Sb–F(6) | 97.1(8) |
| O–Re–F(2) | 102.6(9) | F(9)–Sb–F(1) | 85.6(7) |
| O–Re–F(4) | 100.0(9) | F(9)–Sb–F(3) | 86.9(7) |
| O–Re–F(7) | 106.5(9) | F(9)–Sb–F(5) | 168.9(8) |
| F(3)–Sb–F(1) | 84.2(7) | F(9)–Sb–F(6) | 95.5(7) |
| F(5)–Sb–F(1) | 84.2(7) | F(9)–Sb–F(8) | 91.8(7) |
| F(5)–Sb–F(3) | 87.9(7) | Sb–F(1)–Re | 137.8(9) |
| | | Sb–F(3)–Re | 148.0(9) |

T800 spectrometer. The exciting radiation was the blue line (4 880 Å) of a model 52 Coherent Radiation Laboratories argon-ion laser. Mass spectra were obtained on a VG Micromass 16B spectrometer, the samples being introduced directly into the ionization chamber. Specimens for *X*-ray powder-diffraction measurement were mounted in evacuated Pyrex capillaries and their diffraction patterns recorded photographically on a Philips camera (diameter 11.46 cm) with Cu-$K_\alpha$ filtered radiation.

*Preparations*.—$MoF_4O{\cdot}SbF_5$. In a typical reaction $MoF_4O$ (1.336 mmol) was dissolved in a five-fold excess (6.645 mmol) of $SbF_5$ in a preseasoned and weighed Kel-F reactor. The reaction mixture was warmed (40—50 °C) until all the $MoF_4O$ had dissolved. After cooling to room temperature the homogeneous solution was pumped and the loss of $SbF_5$ was monitored by weighing (Figure 1). The rate of loss of material decreased until no observable weight loss occurred over 5 h. At this stage the weight of the colourless solid residue corresponded to a $MoF_4O : SbF_5$ mol ratio of 1 : 1.15.

Some stability for the adduct $MoF_4O{\cdot}2SbF_5$ is indicated by the change of slope at the 1 : 2 composition. Interruption of pumping during one preparation resulted in the appearance after 12 h of well defined crystals. However, after 4 d only 30% of the reaction mixture was crystalline and cooling did not promote further crystallization.

$WF_4O{\cdot}SbF_5$. The reaction conditions used for the $WF_4O$–$SbF_5$ reaction were the same as in the $MoF_4O$–$SbF_5$ case. Typically, *ca.* 1.5 mmol of $WF_4O$ was used with a five-fold excess of $SbF_5$ (Figure 1). In these reactions $SbF_5$ was still being removed under vacuum when the 1 : 1 composition had been reached, and the rate of loss varied in each experiment.

$ReF_4O{\cdot}SbF_5$. The same procedure was adopted as in the previous experiments. However, a larger excess of $SbF_5$ was usually employed. In a typical reaction, $ReF_4O$ (0.315 mmol) was dissolved in $SbF_5$ (3.694 mmol) with gentle warming until a dark blue homogeneous solution was obtained.

*Single-crystal Examination*.—Crystals of the $MoF_4O{\cdot}SbF_5$ and $ReF_4O{\cdot}SbF_5$ adducts were transferred in a dry-box to preseasoned Pyrex capillaries. Their identities were established by comparison of the single-crystal data with *X*-ray powder data from the bulk products. The dimensions of the two crystals were: $MoF_4O{\cdot}SbF_5$, 0.07 × 0.2 × 0.1 mm with edges parallel to *a*, *b*, and *c* respectively; $ReF_4O{\cdot}SbF_5$, 0.26 × 0.1 × 0.1 mm with edges parallel to *a*, [011], and $[0\bar{1}1]$ respectively.

*Crystal data for* $MoF_4O{\cdot}SbF_5$. $F_9MoOSb$, $M = 404.75$, Colourless, monoclinic, $a = 7.470(8)$, $b = 10.40(2)$, $c = 9.606(9)$ Å, $\beta = 93.13(30)°$, $U = 745.06$ Å$^3$, $Z = 4$, $D_c = 3.61$ g cm$^{-3}$, $\mu(\text{Mo-}K_\alpha) = 50.12$ cm$^{-1}$, $F(000) = 727.82$, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14).

Cell dimensions were determined from precession photographs and from optimised counter angles for zero- and upper-layer reflections on a Weissenberg diffractometer. The intensities of reflections with $0.09 < (\sin\theta)/\lambda < 0.7$ Å$^{-1}$ were collected at 22—25 °C from layers $h0l$ to $h10l$ using a Stadi-2 diffractometer, equipped with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.710\,7$ Å) and an $\omega$-scan technique. The 1 123 reflections having $I \geqslant 3\sigma(I)$ were corrected for Lorentz, polarization, and absorption effects. Monitoring of check reflections for each layer indicated no significant deterioration of the crystal during data collection.

All subsequent computations were carried out using the computer program SHELX written by Dr. G. Sheldrick. Scattering factors for neutral atoms were taken from ref. 29 and the structure was solved by conventional Patterson and difference-Fourier techniques. The oxygen atom was chosen from the shortest molybdenum–light atom bond length. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave an *R* factor of 0.11. Further cycles of refinement using anisotropic thermal parameters for all atoms reduced *R* to 0.043. Final cycles employed a weighting parameter *g* (0.000 76) in $w \propto 1/[\sigma^2(F) + gF^2]$ where *F* is the observed amplitude, and an isotropic extinction parameter *x* (0.000 45) in $F_{\text{cor.}} = F(1 - xF^2/\sin\theta)$ where *F* is the calculated amplitude. The final difference Fourier revealed no significant features and an analysis of the weighting scheme over $|F_o|$ and $(\sin\theta)/\lambda$ was satisfactory. The final residual indices were $R = 0.041\,3$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.040\,8$.

*Crystal data for* $ReF_4O{\cdot}SbF_5$. $F_9OReSb$, $M = 494.93$, Blue, monoclinic, $a = 5.561(10)$, $b = 10.198(8)$, $c = 12.622(9)$ Å, $\beta = 99.37(20)°$, $U = 706.26$ Å$^3$, $Z = 4$, $D_c = 4.66$ g cm$^{-3}$, $\mu(\text{Mo-}K_\alpha) = 200.95$ cm$^{-1}$, $F(000) = 859.80$, space group $P2_1/c$ ($C^5_{2h}$, no. 14).

Preliminary and final cell dimensions were determined as for $MoF_4O{\cdot}SbF_5$ but the crystal was set about *a* as the rotation axis. The intensities of reflections with $0.06 < (\sin\theta)/\lambda < 0.7$ Å$^{-1}$ were collected at 22—25 °C from layers $0kl$ to $7kl$ using a Stadi-2 diffractometer as described above. The 1 075 unique reflections having $I \geqslant 3\sigma(I)$ were corrected for Lorentz, polarization, and absorption effects and the crystal was monitored for deterioration as previously.

The structure was solved as for the molybdenum compound, but solution of the Patterson map was complicated by the approximate zero values for the fractional coordinates $x/a$ and $z/c$ of the antimony atom and $y/b$ for the rhenium. The oxygen atom was chosen to correspond with the shortest rhenium–light atom distance, and three cycles of refinement with all atoms included with isotropic thermal parameters gave $R = 0.071$. An analysis of the weighting scheme over $|F_o|$ and $(\sin\theta)/\lambda$ with various values of weighting parameter, *g* in $w \propto 1/[\sigma^2(F) + gF^2]$, proved unsatisfactory. Poor agreement between reflections $h(2n)l$ and $h(2n + 1)l$ was obtained and several reflections with deviations greater than $2\sigma$ occurred for reflections with $k = 1$ and 3. Convergence was improved by repeating the absorption correction with a reduced value for the absorption coefficient ($\mu$), which effectively decreased all measured crystal dimensions.

Final cycles, for which all atoms were refined anisotropically, employed a weighting parameter $g = 0.001$ and 13 deviant reflections were omitted. The final difference Fourier revealed no significant features and an analysis of the weighting scheme over $|F_o|$ and $(\sin\theta)/\lambda$ was now satisfactory. The final residual indices for 1 062 reflections were $R = 0.057\,6$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.061\,2$.

Observed and calculated structure factors and atomic and thermal parameters for $MoF_4O{\cdot}SbF_5$ and $ReF_4O{\cdot}SbF_5$ have been deposited as Supplementary Publication No. SUP 23015 (10 pp.).* Final positional co-ordinates with their estimated standard deviations are listed in Tables 3 (Mo)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

and 4 (Re), interaction distances and angles in Tables 5 (Mo) and 6 (Re).

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