High Oxidation State Fluoro–Rhenium Species: Preparation and Characterization of $[ReF_6]^+$, $[ReF_4O]^+$, and $[Re_2F_9O_2]^+$, and the Crystal Structure of $[Re_2F_9O_2]^+[Sb_2F_{11}]^-$ †

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The fluoride ion donor properties of ReF_7 and ReF_5O have been demonstrated by the preparation of the adducts $[ReF_6]^+[Sb_2F_{11}]^-$, $[ReF_6]^+[Sb_3F_{16}]^-$, $[ReF_4O]^+[AsF_6]^-$, and $[Re_2F_9O_2]^+[Sb_2F_{11}]^-$, which have been characterized by vibrational spectroscopy, mass spectrometry, and chemical analysis. The crystal structure of $[Re_2F_9O_2]^+[Sb_2F_{11}]^-$ consists of discrete fluorine-bridged dimeric anions, both of which consist of two bridged octahedra.

Work on oxidation of xenon to XeF_6,[1] iodine to IF_7,[1] and metallic gold to AuF_5[2] using KrF_2, and oxygen to O_2^+, xenon to XeF_5^+,[3] and BrF_5 to BrF_6^+ [3,4] with KrF^+ or $Kr_2F_3^+$, stimulated us to examine the fluoride-ion donor properties of the high oxidation state metal fluoride, ReF_7, and oxide fluoride, ReF_5O, in 1974. Compounds with empirical formulae $ReF_7{\cdot}2SbF_5$, $ReF_7{\cdot}3SbF_5$, $ReF_5O{\cdot}AsF_5$, and $ReF_5O{\cdot}SbF_5$ were obtained. Uncertainties about the exact nature of the oxide fluoride species, especially $ReF_5O{\cdot}SbF_5$, made a single-crystal structure determination mandatory.

We now report details of the preparations and characterizations, including the full structural investigation of '$ReF_5O{\cdot}SbF_5$' which has shown that it consists of discrete $[Re_2F_9O_2]^+$ and $[Sb_2F_{11}]^-$ ions packed in a CsCl-type lattice.

Experimental

Apparatus and Materials.—All manipulations were carried out under anhydrous conditions on a vacuum manifold constructed from 316-stainless-steel, nickel, Teflon, and FEP (Teflon-perfluoropropylene copolymer) and in an inert (nitrogen) atmosphere glove-box. All the preparative work involving ReF_7 and ReF_5O was carried out in 7-mm and 3.5-mm outside diameter (o.d.) lengths of FEP spaghetti tubing. The tubing was heat-sealed at one end and connected to Kel-F or Teflon valves to form the reaction vessel.

Rhenium pentafluoride oxide was prepared by the reaction of ReO_2 with a 10% excess of fluorine in a nickel reactor at 250 °C.[5] The ReO_2 was obtained by thermal decomposition of Re_2O_7 (made by reaction of rhenium metal with oxygen in a dynamic system) at 600 °C and its purity was monitored by *X*-ray powder diffraction. The pentafluorides, AsF_5 and SbF_5, were prepared by direct fluorination of the metals. The purities of ReF_5O and AsF_5 were monitored by i.r. spectroscopy. Commercial anhydrous hydrogen fluoride (research grade, I.C.I.) was thoroughly dried by allowing it to stand under several atmospheres (excess) of F_2 for several weeks prior to distillation and subsequent use.

The adducts $ReF_7{\cdot}2SbF_5$ and $ReF_7{\cdot}3SbF_5$ were obtained as white solids by reaction of stoicheiometric amounts of the compounds at room temperature (Found: F, 43.6; Re, 24.05; Sb, 32.8. $ReF_7{\cdot}2SbF_5$ requires F, 42.9; Re, 24.75; Sb, 32.35%. Found: F, 43.35; Re, 19.0; Sb, 37.7. $ReF_7{\cdot}3SbF_5$ requires F, 43.1; Re, 19.2; Sb, 37.7%). The $ReF_5O{\cdot}AsF_5$ adduct was obtained by direct combination of ReF_5O and excess of AsF_5 in an inert atmosphere or in anhydrous HF solution at room temperature. In a typical preparation, 0.3770 g (1.269 mmol) of ReF_5O absorbed 0.1977 g (1.168 mmol) of AsF_5 yielding a $ReF_5O{:}AsF_5$ ratio of 1.09 : 1.00. The related adduct $2ReF_5O{\cdot}2SbF_5$ was prepared by reaction of the component fluoride and excess of pentafluoride oxide at room temperature, and its empirical formula was confirmed by analysis (Found: F, 37.55; Re, 35.75; Sb, 23.75. $ReF_5O{\cdot}SbF_5$ requires F, 36.95; Re, 36.25; Sb, 23.65%). In typical preparations, 1—3 mmol of ReF_7 or ReF_5O were employed.

Characterizations.—Infrared spectra were recorded with a Perkin-Elmer 580 spectrometer on the powdered solids pressed between KBr discs. The Raman spectra of the solid compounds were recorded in the FEP reactors or in Pyrex Lindemann capillaries using a Coderg model T800 spectrophotometer and the 514.5-nm line of a Spectra Physics model 164 laser filtered with a Coderg premonochromator. Mass spectra were recorded on a VG Micromass 16B spectrometer, the samples being introduced directly into the ionization chamber. Fluorine-19 n.m.r. spectra were recorded on a JEOL JNM-PS-100 instrument operating at 94.08 MHz. Samples were contained in seasoned 3.5-mm o.d. FEP tubes inserted into 5-mm o.d. glass n.m.r. tubes. 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_α filtered radiation. Chemical analyses were performed by the Pascher Microanalytical Laboratory, Bonn. For the single-crystal *X*-ray structure determination, crystals were transferred into short lengths of Pyrex glass capillaries previously dried under vacuum and seasoned (pre-treated) with F_2 (1 atm) for crystallographic examination.[6]

Crystal Data.—$F_{20}O_2Re_2Sb_2$, M = 1 027.9, monoclinic, a = 7.945(8), b = 6.519(7), c = 7.91(2) Å, β = 94.2(1)°, U = 408.6 Å^3, Z = 1, D_c = 4.18 g cm^{-3}, $F(000)$ = 448, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 174 cm^{-1}. Possible space groups consistent with the lack of systematic absences are $P2/m$, $P2$, or Pm; $P2$ was chosen as the most probable from the structure determination. Cell dimensions were obtained from oscillation photographs (c) and from diffractometer setting angles for zero and upper layer reflections (a, b, and β). Intensities of reflections with $\sin\theta/\lambda < 0.7$ Å^{-1} were collected from a crystal

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† μ-Fluoro-bis[tetrafluoro-oxorhenium(VII)] μ-fluoro-bis[pentafluoroantimonate(V)].

Supplementary data available (No. SUP 23911, 7 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: atm = 101 325 Pa, mmHg ≈ 133 Pa.

Table 1. Final positional parameters for the *P*2 refinement of $[Re_2F_9O_2][Sb_2F_{11}]$ with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re	−0.190 11(8)	0	−0.190 16(8)
Sb	0.328 43(15)	−0.495 7(6)	−0.328 33(15)
F(1)	0	−0.027(7)	0
F(2)	−0.322(2)	0.033(8)	−0.018(3)
O	−0.343(3)	0.038(2)	−0.337(3)
F(4)	−0.013(2)	0.022(8)	−0.313(3)
F(5)	−0.162(6)	−0.269(6)	−0.178(4)
F(6)	−0.154(6)	0.270(6)	−0.156(6)
F(11)	0.5	−0.492(22)	−0.5
F(12)	0.169(3)	−0.482(10)	−0.177(3)
F(13)	0.481(5)	−0.306(12)	−0.199(8)
F(14)	0.201(5)	−0.653(9)	−0.488(3)
F(15)	0.249(6)	−0.268(7)	−0.434(4)
F(16)	0.423(5)	−0.721(7)	−0.248(6)

Table 2. Interatomic distances (Å) and angies (°) for $[Re_2F_9O_2]$-$[Sb_2F_{11}]$ with estimated standard deviations in parentheses

(*a*) Distances

Re–F(1)	2.060(4)	Sb–F(11)	1.994(2)
Re–F(2)	1.79(2)	Sb–F(12)	1.81(2)
Re–O	1.63(2)	Sb–F(13)	1.97(5)
Re–F(4)	1.77(2)	Sb–F(14)	1.87(3)
Re–F(5)	1.77(4)	Sb–F(15)	1.79(3)
Re–F(6)	1.80(3)	Sb–F(16)	1.75(3)

(*b*) Angles

F(1)–Re–O	176(1)	F(11)–Sb–F(12)	176(4)
F(1)–Re–F(2)	84(1)	F(11)–Sb–F(13)	86(3)
F(2)–Re–F(4)	81(1)	F(11)–Sb–F(14)	85(3)
F(1)–Re–F(5)	78(2)	F(11)–Sb–F(15)	85(4)
F(1)–Re–F(6)	83(2)	F(11)–Sb–F(16)	88(4)
O–Re–F(2)	94(1)	F(12)–Sb–F(13)	93(2)
O–Re–F(4)	100(1)	F(12)–Sb–F(14)	96(2)
O–Re–F(5)	106(1)	F(12)–Sb–F(15)	92(3)
O–Re–F(6)	94(2)	F(12)–Sb–F(16)	96(3)
F(2)–Re–F(4)	160(2)	F(13)–Sb–F(14)	169(2)
F(2)–Re–F(5)	99(2)	F(13)–Sb–F(15)	85(3)
F(2)–Re–F(6)	82(2)	F(13)–Sb–F(16)	96(2)
F(4)–Re–F(5)	90(2)	F(14)–Sb–F(15)	89(2)
F(4)–Re–F(6)	83(2)	F(14)–Sb–F(16)	89(3)
F(5)–Re–F(6)	161(1)	F(15)–Sb–F(16)	172(2)
Re–F(1)–Re′	170(3)	Sb–F(11)–Sb′	179(5)

(approximate dimensions 0.28 × 0.3 × 0.25 mm) mounted about the *c* axis (layers ± *hk*0—10) at 20 °C using a Stoe–Güttinger Weissenberg diffractometer with graphite-monochromated Mo-K_α radiation and a variable ω-scan technique.[7] The 1 172 reflections having $I \geqslant 3\sigma(I)$ were corrected for Lorentz, polarization, and absorption effects (maximum and minimum transmission factors were 0.0837 and 0.0174), and were averaged to 1 042 unique reflections.

The compound was originally thought to be the F-bridged adduct $ReF_5O{\cdot}SbF_5$ but this structure was inconsistent with the Patterson map which instead pointed to the presence of two separate F-bridged dimeric ions $[Re_2F_9O_2]^+$ and $[Sb_2F_{11}]^-$. A difference-Fourier map calculated with space group *P*2/*m* with Re atoms on special position *m*, $\pm(x, 0, z)$, and Sb on *n*, $\pm(x, \frac{1}{2}, z)$,[8] revealed all the light atoms and confirmed that both dimeric ions consisted of two bridged octahedra. Space group *P*2/*m* requires both dimers to have overall symmetry 2/*m* (C_{2h}), which appeared correct for the $[Re_2F_9O_2]^+$ cation; four of the six light atoms about each rhenium were in the crystallographic mirror plane at $y = 0$. However, each Sb atom was surrounded by ten peaks, eight of which corresponded to half-weight F atoms, suggesting that four out of six F atoms are disordered across the mirror plane at $y = \frac{1}{2}$ in *P*2/*m*. Alternatively, an ordered structure for the six F atoms about each Sb atom is possible if the space group symmetry is lowered to *P*2 which only requires the $[Sb_2F_{11}]^-$ ion to have 2 (C_2) symmetry. Both models were tested by least-squares refinement and both converged to similar reliability indices [$R_G = 0.082$ for the *P*2/*m* structure with 70 parameters (anisotropic thermal parameters for all atoms except the four 'disordered' F atoms), $R_G = 0.078$ for *P*2 with 118 parameters (all atoms anisotropic)], this is to be expected as only four F atoms out of a total of 14 independent atoms, including Re and Sb, break the *m* symmetry of *P*2/*m*. However, the ordered *P*2 structure is preferred as the derived $[Sb_2F_{11}]^-$ geometry is consistent with other examples of this anion.[9]

In the final cycle of least-squares refinement [5] all atoms were given anisotropic thermal parameters, the origin on the *y* axis was fixed by the Re atom, the oxygen atom was identified by the shortness of its distance to Re. Two low-angle reflections (111 and −111) with large discrepencies were removed from the data set, the remaining 1 040 reflections had $R = 0.0609$, $R' = 0.0612$ with weights calculated from $w = 1.0/[\sigma^2(F) + 0.008 F^2]$. Neutral-atom scattering factors with full correction for anomalous dispersion were used.[10] As *P*2 is a polar space group the inverse structure was investigated and rejected as it gave higher reliability indices ($R = 0.0613$, $R' = 0.0619$), and some F atom thermal amplitudes refined to very large values.[11] A final difference-Fourier map was featureless apart from several maxima and minima, < 3 e Å^{-3}, close to the Re and Sb atoms.

The final atomic co-ordinates are listed in Table 1, interatomic distances and angles are given in Table 2.

Table 3. Raman spectra (cm^{-1}) of $[ReF_6][Sb_2F_{11}]$ and $[ReF_6]$-$[Sb_3F_{16}]$ *

$[ReF_6][Sb_2F_{11}]$	Assignment	$[ReF_6][Sb_3F_{16}]$	Assignment
801.0 (100)	$\nu_1(a_{1g})[ReF_6]^+$	801.5 (100)	$\nu_1(a_{1g})[ReF_6]^+$
		772.0 (1)	$\nu_3(t_{1u})[ReF_6]^+$
737.0 (22)	$\nu_2(e_g)[ReF_6]^+$	736.0 (52)	$\nu_2(e_g)[ReF_6]^+$
730.0 (25)			
		716.5 (3)	$\nu([Sb_3F_{16}]^-)$
680.0 (37)	$\nu([Sb_2F_{11}]^-)$	706.0 (2)	
671.0 (9)		692.0 (37)	
657.5 (13)		682.0 (4)	
648.0 (14)		666.0 (38)	
605.5 (8)		628.5 (2)	
579.0 (3.1)		614.0 (6)	
358.0 (18)	$\nu_5(t_{1g})[ReF_6]^+$	359.5 (12)	$\nu_5(t_{2g})[ReF_6]^+$
		304.5 (6)	$\nu([Sb_3F_{16}]^-)$
306.0 (4)	$\nu([Sb_2F_{11}]^-)$	299.0 (sh)	
278.0 (3)		292.0 (sh)	
231.0 (4)		271.0 (2)	
136.0 (1)		223.0 (6)	
		146.0 (2)	
		110.0 (2)	
104 (1.3)	lattice mode	49.0 (2)	lattice mode

* Relative intensities (0—100) are given in parentheses. FEP lines have been deleted.

Results and Discussion

Rhenium heptafluoride, like IF_7, is expected [12] to behave as a fluoride ion donor. It reacts with stoicheiometric amounts of SbF_5 to form solids having the compositions $ReF_7{\cdot}2SbF_5$ and $ReF_7{\cdot}3SbF_5$. Both decompose under dynamic vacuum at room temperature and can be pumped away in the form of

Table 4. Raman and i.r. spectra (cm^{-1}) of [ReF$_4$O][AsF$_6$] and ReF$_4$O and ReF$_5$O vapours

[ReF$_4$O][AsF$_6$]			ReF$_4$O [a]	ReF$_5$O [b]		
Raman [c]	I.r. [d]	Assignment [e]	I.r. [d]	Raman [c]	I.r. [d]	Assignment [e]
					1 975	$2\nu_1$
	1 455w	comb.			1 450	$\nu_2 + \nu_8$
	1 420w	comb.				
					1 370	$\nu_2 + \nu_3$
					1 280	$2\nu_3$
			1 086		998	
1 060.0 (54)	1 052mw	$\nu_1(a_1)[\mathrm{ReF_4O}]^+$	1 077.0	989.8	990.8	ν_1
			1 067		984	
	1 021s	comb.			961	$\nu_8 + \nu_9$
	992vs				916	
					865	$\nu_2 + \nu_{11}$
					747	
765.5 (100)		$\nu_2(a_1)[\mathrm{ReF_4O}]^+$	731	737.6	737.7	ν_2
733.0 (29.6) [f]		$\nu_3(t_{1u})[\mathrm{AsF_6}]^-$	722.3			
					719	ν_8
					713	
			706.5			
696.0 (34.2)	698vs	$\nu_7(e)[\mathrm{ReF_4O}]^+$	700.2			$\nu_7(\mathrm{ReF_4O})$ [a]
	690m		693	652		ν_5
687.0 (42.8)	670m	$\nu_1(a_1)[\mathrm{AsF_6}]^-$				
	665m					
					651	
				640	643	ν_3
					635	
609.0 (9.5)		$\nu_2(e_g)[\mathrm{AsF_6}]^-$				
389.0 (13.4) [f]	385vs	$\nu_4(t_{1u})[\mathrm{AsF_6}]^-$				
				367	365	ν_{10}
340.0 (56.5)		$\nu_8(e)[\mathrm{ReF_4O}]^+$		334		ν_7
303.5 (7.9)		$\nu_5(t_{2g})[\mathrm{AsF_6}]^-$		309	309	ν_4
294.0 (9.1) [f]		$\nu_4(a_1)[\mathrm{ReF_4O}]^+$				
					260	ν_9
232.0 (9.7)		$\nu_9(a_1)[\mathrm{ReF_4O}]^+$		234		ν_6
212.5 (9.3)		$\nu_6(e)[\mathrm{ReF_4O}]^+$				
147.5 (3.6)				125		ν_{11}

[a] Ref. 23. [b] Ref. 5. [c] Relative intensities (0—100) are given in parentheses. [d] w = Weak, m = medium, s = strong, v = very. [e] comb. = Combination band. [f] Seriously overlapped by an FEP line.

their volatile components ReF$_7$ and SbF$_5$. Sample mixtures containing a higher proportion of ReF$_7$ lose ReF$_7$ in dynamic vacuum until the ReF$_7$·2SbF$_5$ composition is reached. The Raman spectra of the adducts indicate that they are best formulated as the ionic species [ReF$_6$]$^+$[Sb$_2$F$_{11}$]$^-$ and [ReF$_6$]$^+$-[Sb$_3$F$_{16}$]$^-$ (Table 3). Three Raman-active modes are expected for an [ReF$_6$]$^+$ cation possessing O_h symmetry and these occur at ν_1 (a_{1g}) 801 (relative intensity 100), ν_2 (e_g) 737 (22) and 730 (25), and ν_5 (t_{2g}) 358 (18) cm^{-1} for the [Sb$_2$F$_{11}$]$^-$ salt, in accord with the results of Jacob and Fähnle;[12] and at ν_1 (a_{1g}) 801.5 (100), ν_2 (e_g) 736 (52), and ν_5 (t_{2g}) 359.5 (12) cm^{-1} for the [Sb$_3$F$_{16}$]$^-$ salt. Owing to the formal positive charge on [ReF$_6$]$^+$, these modes are significantly higher in frequency than the corresponding modes of ReF$_6$, which occur at ν_1 (a_{1g}) 754, ν_2 (e_g), 671, and ν_5 (t_{2g}) 295 cm^{-1} in the gas phase,[13] and [ReF$_6$]$^-$ (in [NO]$^+$[ReF$_6$]$^-$) which appear at even lower frequency, ν_1 (a_{1g}) 695, ν_2 (e_g) 602, and ν_5 (t_{2g}) 254 and 245 cm^{-1} in the solid.[14] The Raman bands associated with the antimony pentafluoride components of the two compounds are similar, but not identical. Those associated with the ReF$_7$·2SbF$_5$ adduct are comparable with those of [Sb$_2$F$_{11}$]$^-$ in a number of other species [15-18] whereas those in the ReF$_7$·3SbF$_5$ adduct are much more closely analogous to those assigned to [Sb$_3$F$_{16}$]$^-$ in [PF$_4$]$^+$[Sb$_3$F$_{16}$]$^-$.[19]

The ^{19}F n.m.r. spectrum of molten [ReF$_6$]$^+$[Sb$_3$F$_{16}$]$^-$ was recorded at -78 °C. In addition to a strong broad line at -114 p.p.m. (with respect to neat CFCl$_3$), assignable to fluorine on antimony, a strong singlet due to [ReF$_6$]$^+$ was observed at 271 p.p.m. This can be compared to the chemical shift of ReF$_7$ which is 324 p.p.m. in HF solution.[20] The change in chemical shift between the parent molecule and the cation is in the same direction as the difference reported for IF$_7$ and [IF$_6$]$^+$.[21]

Rhenium heptafluoride did not interact with an excess of AsF$_5$ at room temperature. However, ReF$_5$O reacts with excess AsF$_5$ either by direct combination in an inert atmosphere or in anhydrous HF solution at room temperature. The solid obtained is unstable at room temperature over periods in excess of 1 h and, having a vapour pressure of *ca.* 10 mmHg, can be pumped away in dynamic vacuum at room temperature. Monitoring the reaction by weight showed that the adduct formed has a 1 : 1 composition and the vibrational spectra of the solid (Table 4) shows that it is best formulated as an ionic species, [ReF$_4$O]$^+$[AsF$_6$]$^-$. In addition to the anion modes associated with octahedral [AsF$_6$]$^-$, which correlate closely with those observed in the Raman spectra of [BrF$_6$]$^+$[AsF$_6$]$^-$,[4] [XeF]$^+$[AsF$_6$]$^-$,[17] and [Xe$_2$F$_3$]$^+$[AsF$_6$]$^-$,[17] ν(Re=O) in both the i.r. and the Raman spectra is shifted to higher frequency than in ReF$_5$O itself (Table 4) indicating a decrease in Re=O bond length which is consistent with the formation of a species with cationic character. In fact, the vibrational spectrum of the cationic component is in accord with the monomer spectra of the MoF$_4$O, WF$_4$O, and ReF$_4$O series which have one M=O stretch, ν_1, near 1 050 cm^{-1} and

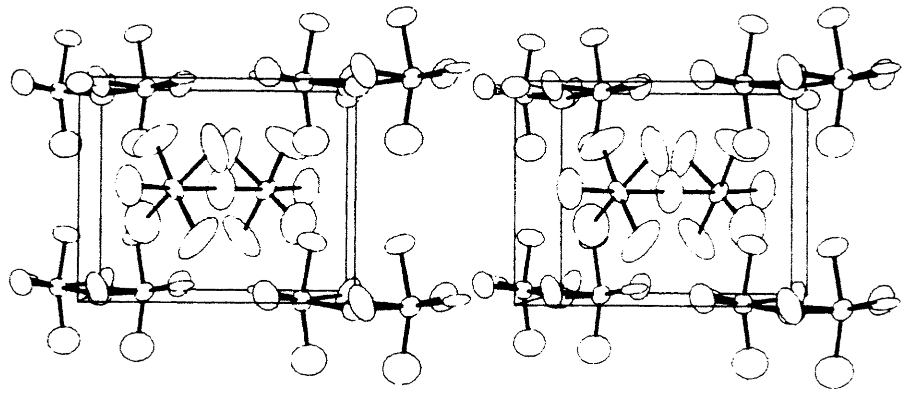

Figure 1. Stereoscopic view of the unit-cell contents of $[Re_2F_9O_2][Sb_2F_{11}]$ viewed approximately along *c*. Only four of the eight cations at the cell corners are drawn

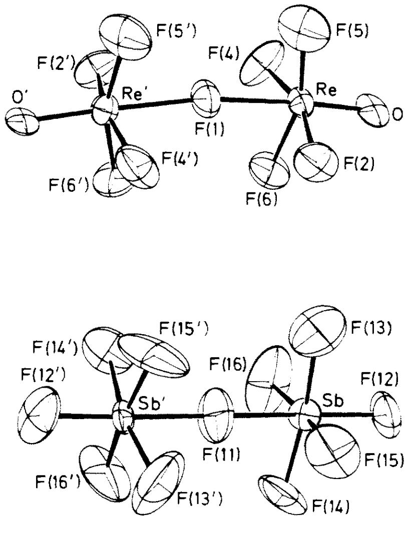

Figure 2. ORTEP views (50% probability) of the $[Re_2F_9O_2]^+$ cation and $[Sb_2F_{11}]^-$ anion showing atomic labelling. The two halves of each ion are related by a two-fold rotation axis

Table 5. Raman spectra of $[Re_2F_9O_2][Sb_2F_{11}]$ and ReF_5O vapour

$[Re_2F_9O_2][Sb_2F_{11}]$		ReF_5O [a]	
Raman	Assignment [b]	Raman	Assignment
1 059.0 (53)	$\nu_1(a_1)$, ν(ReO)	989.8s	$\nu_1(a_1)$
762.0 (100)	$\nu_2(a_1)$, ν_{sym}(in-plane ReF_4)	737.6vs	$\nu_2(a_1)$
698.0 (18)	$\nu_8(e)$,	719vs	$\nu_8(e)$
691.0 (31)	ν_{asym}(in-plane ReF_4)	713vs	
656.5 (39)		652m	$\nu_5(b_1)$
606.0 (9)	$\nu([Sb_2F_{11}]^-)$	640m	$\nu_3(a_1)$
579.0 (4)br			
340.5 (48)	$\nu_9(e)$, $\delta(ReF_4O)$ or $\nu_{10}(e)$, $\delta(FReF_4)$	367s	$\nu_{10}(a_1)$
		334s	$\nu_7(b_2)$
304.0 (8) [c]		309vw	$\nu_4(a_1)$
283.0 (6) [c]	$\nu([Sb_2F_{11}]^-)$		
272.0 (4)			
229.5 (14)		234vw	$\nu_6(b_1)$
212.0 (7)			
134.0 (2)br	δ(F−Re−F/F−Sb−F)	125vw	$\nu_{11}(e)$
106.0 (2)			

[a] Ref. 5. [b] Ref. 26. [c] These peaks are seriously overlapped by an FEP line.

two M−F stretches, ν_2 and ν_7, near 700 cm^{-1}.[22,23] Such a correlation strongly supports the existence of a $[ReF_4O]^+$ ion. Mass spectrometric examination of the solid also strongly supports the 1 : 1 formulation. Fragmentation patterns associated with $[ReF_4O]^+$, $[ReF_3O]^+$, $[ReF_2O]^+$, $[ReFO]^+$, $[ReO]^+$, Re^+, $[ReF_4]^+$, $[ReF_3]^+$, $[ReF_2]^+$, $[ReF]^+$, $[AsF_4]^+$, $[AsF_3]^+$, $[AsF_2]^+$, $[AsF]^+$, and As^+ were found, but no evidence for the dimeric cation, $[Re_2F_9O_2]^+$, or its fragmentation could be detected.

The product of the reaction of equimolar quantities of ReF_5O and SbF_5 at room temperature was, at first, thought to be the simple fluorine-bridged adduct $ReF_5O{\cdot}SbF_5$. There is, after all, little evidence of dimerized ReF_4O or ReF_5O ions and, unlike MoF_4O and WF_4O, ReF_4O shows no evidence for gaseous oligomers in the vapour, even at the 1 in 10^3 detection level.[24,25] The Raman spectrum, however, is more complex than expected. Examination of single crystals of the compound by *X*-ray methods has shown that the crystal structure of $[Re_2F_9O_2]^+[Sb_2F_{11}]^-$ consists of discrete anions packed in a CsCl-type lattice (Figure 1). The symmetry of both ions, shown separately in Figure 2, is required crystallographically to be 2 (C_2). The cation symmetry is close to $2/m$ (C_{2h}), and resembles closely that found for the anion in $[Re(CO)_6]^+[Re_2F_{11}]^-$ [9] although the large limits of error preclude detailed analysis. The shortness of the bond *trans* to the bridging F atom strongly points to this atom being oxygen in accordance with the subsequent Raman spectroscopic data. The cation is essentially linear with the equatorial F atoms eclipsed and bent away from the oxygen atom, the average F−Re−O angle is 98°. The $[Sb_2F_{11}]^-$ anion adopts a similar linear-bridged structure, but the two groups of equatorial F atoms are rotated by 20° relative to each other.*

The closest contact between fluorine atoms of the anion and rhenium is 3.28 Å [to F(13)], confirming the ionic formulation of the compound.

Subsequent examination of the Raman data has shown that this can be assigned on the basis of the $[Re_2F_9O_2]^+[Sb_2F_{11}]^-$ formulation. Bands associated with $[Sb_2F_{11}]^-$ are rather easily distinguished by comparison with earlier work [15–18] and the residue can be correlated with the partial assignments on a number of $[M_2F_9O_2]^-$ anions [26,27] and ReF_5O itself (Table 5).

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* The dihedral angle between planes Sb,F(11),F(12),F(13),F(14) and Sb',F(11),F(12'),F(15'),F(16') is 20.4°.

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