Crystal Structure of *abcde*-Pentacarbonyl-*f*-μ-fluoro-*ghijk*-pentafluoro-rhenium(ı)rhenium(v)

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Crystals of the title compound are orange, orthorhombic, and have space group *Pbca*, $a = 22.34(3)$, $b = 15.51(1)$, and $c = 13.67(1)$Å. The structure has been refined by least-squares methods to R 0.061 for 1 969 reflections measured by diffractometer. The atomic arrangement is consistent with a covalent fluorine-bridged formulation comprising two almost identical $[Re(CO)_5F]\cdot ReF_5$ molecules in the asymmetric unit. Both rhenium atoms have approximately octahedral co-ordination and are linked by a bent fluorine bridge.

THE title compound has been prepared by the reaction of $[Re_2(CO)_{10}]$ with ReF_6 in anhydrous HF,[1] and by room-temperature fluorination of $[Re_2(CO)_{10}]$ with xenon difluoride in Genetron 113 (1,1,2-trichloro-1,2,2-trifluoroethane) or anhydrous hydrogen fluoride solvents.[2] In an earlier investigation of the former reaction [1] in which ReF_6 was condensed stepwise on to $[Re_2(CO)_{10}]$ in anhydrous hydrogen fluoride,† a green solution was produced which gave approximately equal amounts of two solids which separated as orange prisms and green platelets. A preliminary report of the crystal structures of these two solids has been published;[1] we now describe the structure of $[Re(CO)_5F]\cdot ReF_5$ in greater detail. A subsequent paper [3] will describe the structure of α-$[Re(CO)_6][Re_2F_{11}]$ and the results of a detailed study of the $[Re_2(CO)_{10}]$–$[ReF_6]$–HF system.

EXPERIMENTAL

Mixtures of orange and green crystals from the $[Re_2(CO)_{10}]$–ReF_6 reaction in anhydrous hydrogen fluoride were pumped dry after decanting the bulk of the green HF solution. The crystals were transferred to a Pyrex multicapillary apparatus, previously dried and seasoned with ClF_3, in a recirculating nitrogen-filled dry-box (Lintott Engineering Ltd., Horsham, Essex). The apparatus was evacuated and individual crystals of the orange compound were sealed into short lengths of capillary for the crystallographic examination. No noticeable decomposition or attack on the Pyrex occurred during the data collection.

Crystal Data—$C_5F_6O_5Re_2$, $M = 624.4$, Orthorhombic, $a = 22.34(3)$, $b = 15.51(1)$, $c = 13.67(1)$ Å, $U = 4737$ Å³, $Z = 16$, $D_c = 3.51$ g cm⁻³, $F(000) = 4384$, $\lambda(Mo\text{-}K_\alpha) = 0.710\ 7$ Å, $\mu(Mo\text{-}K_\alpha) = 216.8$ cm⁻¹. Space group *Pbca* from systematic absences.

D_m was not measured, but the cell volume is consistent with $Z = 16$ if the structure is assumed to be a close-packed lattice of carbon, oxygen, and fluorine atoms having atomic values of 21, 19, and 17 Å³ respectively [2] (calculated on the basis of covalent radii).[4] This method correctly reproduces the cell volumes for the related compounds $[\{Ru(CO)_3F_2\}_4]$ [5] and $[Re_2(CO)_{10}]$.[6] Accurate unit-cell dimensions

were obtained from zero-layer precession photographs recorded by Mo-K_α radiation.

Intensities of reflections with $(\sin \theta)/\lambda < 0.7$ Å⁻¹ were collected about the c axis (layers $hk0$—12) at 23 °C on a Stoe–Güttinger–Weissenberg diffractometer with monochromatic Mo-K_α radiation and an ω-scan technique. The crystal was a pentagonal plate on {100} having thickness 0.014 5 cm, and other dimensions *ca.* 0.08 × 0.06 cm. The 1 981 reflections having $I \geqslant 3\sigma(I)$ were corrected for Lorentz, polarisation, and absorption effects.[7] Scattering factors for neutral atoms were taken from ref. 8, and the structure was solved by conventional Patterson and difference-Fourier techniques. Block-diagonal least-squares refinement (each block contained the parameters of one atom) of positional and isotropic thermal parameters for all the atoms, and individual layer scale factors, reduced R to 0.075. Further cycles of refinement using anisotropic thermal parameters for rhenium atoms, a single overall scale factor, and including corrections for anomalous scattering by rhenium [9] gave a final R of 0.061. In the final cycles 12 reflections with large discrepancies between $|F_o|$ and $|F_c|$ were excluded. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, with $w = (10 + |F_o|)^{-1}$ in the final cycles. A final difference-Fourier revealed no significant features and an analysis of the weighting scheme over F_o and $(\sin \theta)/\lambda$ was satisfactory.

The computer programs used were written locally except for ORTEP and ABSCOR.[7] Observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 22150 (5 pp.).‡ Final positional and thermal parameters, with their estimated standard deviations, are listed in Table 1. Interatomic distances and angles are given in Table 2.

DISCUSSION

Each formula unit consists of slightly distorted $[Re(CO)_5F]$ and ReF_6 octahedra, sharing one vertex, forming a bent Re–F–Re linkage. The two crystallographically non-equivalent molecules both approximate closely to C_s symmetry and differ only in the orientation of the $Re(CO)_4$ and ReF_4 equatorial planes, relative to the Re–F–Re plane (Figure 1). The $Re(1)$–$Re(2)$ molecule

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† In ref. 1 the ratio $[ReF_6]:[Re_2(CO)_{10}]$ was stated as 1.08 : 0.75. This is in error, the 0.75 referring to the $Re(CO)_5$ molecular unit.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[1] D. M. Bruce, J. H. Holloway, and D. R. Russell, *J.C.S. Chem. Comm.*, 1973, 321.

[2] D. M. Bruce, A. J. Hewitt, J. H. Holloway, R. D. Peacock, and I. L. Wilson, *J.C.S. Dalton*, 1976, 2230.

[3] D. M. Bruce, J. H. Holloway, and D. R. Russell, *J.C.S. Dalton*, in preparation.

[4] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

[5] C. J. Marshall, R. D. Peacock, D. R. Russell, and I. L. Wilson, *Chem. Comm.*, 1970, 1643.

[6] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.

[7] J. De Meulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014; N. W. Alcock, *ibid.*, **A25**, 518.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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

(A) has the ReF_4 unit eclipsed with respect to the Re–F–Re bridge, and the $Re(CO)_4$ unit staggered. The opposite holds for the Re(3)–Re(4) molecule (B).

TABLE 1

Final positional and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/Å^2$
Re(1)	0.005 08(5)	0.251 51(7)	0.049 28(13)	} see below
Re(2)	0.020 47(7)	0.040 76(8)	0.201 23(14)	
Re(3)	0.258 82(6)	0.069 40(8)	0.285 22(14)	
Re(4)	0.260 04(7)	0.274 30(8)	0.449 96(14)	
C(11)	0.075(2)	0.318(3)	0.097(4)	4.8(9)
C(12)	0.050(1)	0.226(2)	−0.075(3)	2.8(6)
C(13)	−0.065(2)	0.186(2)	−0.003(3)	3.0(6)
C(14)	−0.033(2)	0.272(3)	0.179(4)	4.7(9)
C(15)	−0.025(2)	0.357(2)	−0.004(3)	3.4(7)
O(11)	0.112(1)	0.364(2)	0.124(2)	7.0(7)
O(12)	0.069(1)	0.209(2)	−0.150(3)	4.7(6)
O(13)	−0.106(1)	0.148(2)	−0.032(3)	5.8(7)
O(14)	−0.063(1)	0.286(2)	0.241(2)	6.2(8)
O(15)	−0.044(1)	0.423(1)	−0.029(2)	3.2(5)
F(21)	0.042(1)	0.131(1)	0.109(2)	4.4(5)
F(22)	0.099(1)	0.006(1)	0.205(2)	6.3(6)
F(23)	−0.009(1)	−0.039(2)	0.293(2)	6.0(6)
F(24)	−0.056(1)	0.083(1)	0.193(2)	5.0(5)
F(25)	0.036(1)	0.120(2)	0.299(2)	6.1(6)
F(26)	0.004(1)	−0.034(1)	0.104(2)	5.6(6)
C(31)	0.200(1)	0.149(2)	0.225(3)	2.2(5)
C(32)	0.321(2)	0.123(4)	0.211(4)	6.1(1.1)
C(33)	0.320(2)	−0.007(3)	0.354(4)	5.4(1.0)
C(34)	0.194(2)	0.023(3)	0.375(4)	5.7(1.1)
C(35)	0.244(2)	−0.008(3)	0.185(4)	4.9(9)
O(31)	0.164(1)	0.191(2)	0.195(3)	6.3(8)
O(32)	0.358(2)	0.145(2)	0.156(3)	7.3(9)
O(33)	0.354(1)	−0.052(2)	0.373(3)	5.6(7)
O(34)	0.155(2)	0.005(3)	0.427(4)	10.0(1.3)
O(35)	0.231(2)	−0.059(3)	0.119(4)	9.1(1.1)
F(41)	0.282(1)	0.160(1)	0.397(2)	5.7(6)
F(42)	0.339(1)	0.306(2)	0.444(2)	6.1(6)
F(43)	0.239(1)	0.385(2)	0.507(2)	5.8(6)
F(44)	0.182(1)	0.238(2)	0.456(2)	5.8(6)
F(45)	0.246(1)	0.311(2)	0.328(2)	6.8(7)
F(46)	0.272(1)	0.235(2)	0.574(2)	5.5(6)

Anisotropic rhenium-atom temperature factors ($Å^2$) in the form:

$$\exp[-\tfrac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$$

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Re(1)	2.69(5)	2.05(4)	2.06(7)	0.03(5)	0.31(7)	0.08(4)
Re(2)	4.26(7)	2.03(5)	2.68(9)	−0.04(5)	0.39(8)	−0.36(4)
Re(3)	3.12(5)	2.23(5)	3.67(10)	0.02(6)	0.01(8)	0.14(4)
Re(4)	3.83(6)	2.74(5)	2.90(10)	0.12(6)	−0.22(8)	0.50(5)
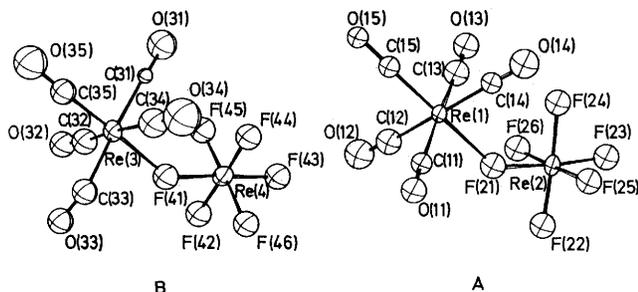
FIGURE 1 A view of the two crystallographically distinct [$Re(CO)_5F$]·ReF_5 molecules showing the atom labelling

TABLE 2

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

(a) Distances

Re(1)–C(11)	1.98(4)	Re(3)–C(31)	1.98(3)
Re(1)–C(12)	2.01(4)	Re(3)–C(32)	1.91(5)
Re(1)–C(13)	2.00(4)	Re(3)–C(33)	2.03(5)
Re(1)–C(14)	1.99(5)	Re(3)–C(34)	2.04(5)
Re(1)–C(15)	1.91(4)	Re(3)–C(35)	1.86(5)
C(11)–O(11)	1.16(5)	C(31)–O(31)	1.10(5)
C(12)–O(12)	1.14(5)	C(32)–O(32)	1.18(7)
C(13)–O(13)	1.16(5)	C(33)–O(33)	1.07(6)
C(14)–O(14)	1.11(6)	C(34)–O(34)	1.15(7)
C(15)–O(15)	1.16(4)	C(35)–O(35)	1.23(7)
Re(1)–F(21)	2.20(2)	Re(3)–F(41)	2.13(3)
Re(2)–F(21)	1.95(2)	Re(4)–F(41)	1.98(2)
Re(2)–F(22)	1.84(3)	Re(4)–F(42)	1.83(3)
Re(2)–F(23)	1.88(3)	Re(4)–F(43)	1.94(3)
Re(2)–F(24)	1.84(2)	Re(4)–F(44)	1.83(3)
Re(2)–F(25)	1.85(3)	Re(4)–F(45)	1.78(3)
Re(2)–F(26)	1.80(3)	Re(4)–F(46)	1.83(3)

(b) Angles

F(21)–Re(1)–C(11)	91.4(1.4)	F(41)–Re(3)–C(31)	92.8(1.2)
F(21)–Re(1)–C(12)	87.3(1.1)	F(41)–Re(3)–C(32)	84.9(1.8)
F(21)–Re(1)–C(13)	89.7(1.2)	F(41)–Re(3)–C(33)	83.5(1.6)
F(21)–Re(1)–C(14)	88.3(1.4)	F(41)–Re(3)–C(34)	88.7(1.7)
F(21)–Re(1)–C(15)	178.5(1.3)	F(41)–Re(3)–C(35)	176.2(1.6)
C(11)–Re(1)–C(12)	89.4(1.7)	C(31)–Re(3)–C(32)	89.3(1.8)
C(11)–Re(1)–C(13)	178.3(1.9)	C(31)–Re(3)–C(33)	176.2(1.8)
C(11)–Re(1)–C(14)	87.5(1.9)	C(31)–Re(3)–C(34)	90.0(1.7)
C(11)–Re(1)–C(15)	87.7(1.7)	C(31)–Re(3)–C(35)	88.8(1.7)
C(12)–Re(1)–C(13)	89.4(1.5)	C(32)–Re(3)–C(33)	91.0(2.1)
C(12)–Re(1)–C(14)	174.6(1.6)	C(32)–Re(3)–C(34)	173.5(2.2)
C(12)–Re(1)–C(15)	91.4(1.6)	C(32)–Re(3)–C(35)	91.6(2.2)
C(13)–Re(1)–C(14)	93.7(1.7)	C(33)–Re(3)–C(34)	89.3(2.0)
C(13)–Re(1)–C(15)	91.1(1.5)	C(33)–Re(3)–C(35)	95.0(2.0)
C(14)–Re(1)–C(15)	93.0(1.8)	C(34)–Re(3)–C(35)	94.8(2.1)
Re(1)–C(11)–O(11)	173.9(3.7)	Re(3)–C(31)–O(31)	175.2(3.1)
Re(1)–C(12)–O(12)	171.5(3.0)	Re(3)–C(32)–O(32)	169.1(4.5)
Re(1)–C(13)–O(13)	179.2(3.8)	Re(3)–C(33)–O(33)	166.1(4.9)
Re(1)–C(14)–O(14)	167.5(4.1)	Re(3)–C(34)–O(34)	172.8(4.2)
Re(1)–C(15)–O(15)	174.7(3.7)	Re(3)–C(35)–O(35)	177.5(4.0)
Re(1)–F(21)–Re(2)	138.8(1.2)	Re(3)–F(41)–Re(4)	142.0(1.4)
F(21)–Re(2)–F(22)	89.0(1.1)	F(41)–Re(4)–F(42)	88.8(1.1)
F(21)–Re(2)–F(23)	173.5(1.0)	F(41)–Re(4)–F(43)	177.5(1.2)
F(21)–Re(2)–F(24)	86.6(1.0)	F(41)–Re(4)–F(44)	88.9(1.1)
F(21)–Re(2)–F(25)	87.0(1.1)	F(41)–Re(4)–F(45)	88.9(1.3)
F(21)–Re(2)–F(26)	91.8(1.1)	F(41)–Re(4)–F(46)	90.4(1.1)
F(22)–Re(2)–F(23)	97.3(1.2)	F(42)–Re(4)–F(43)	90.7(1.1)
F(22)–Re(2)–F(24)	175.3(1.1)	F(42)–Re(4)–F(44)	177.5(1.1)
F(22)–Re(2)–F(25)	89.4(1.2)	F(42)–Re(4)–F(45)	92.2(1.3)
F(22)–Re(2)–F(26)	91.6(1.2)	F(42)–Re(4)–F(46)	89.1(1.2)
F(23)–Re(2)–F(24)	87.1(1.1)	F(43)–Re(4)–F(44)	91.6(1.1)
F(23)–Re(2)–F(25)	91.2(1.2)	F(43)–Re(4)–F(45)	93.5(1.3)
F(23)–Re(2)–F(26)	90.0(1.2)	F(43)–Re(4)–F(46)	87.2(1.1)
F(24)–Re(2)–F(25)	89.0(1.2)	F(44)–Re(4)–F(45)	88.9(1.3)
F(24)–Re(2)–F(26)	90.0(1.2)	F(44)–Re(4)–F(46)	89.8(1.2)
F(25)–Re(2)–F(26)	178.4(1.2)	F(45)–Re(4)–F(46)	178.6(1.2)

(c) Selected non-bonded contacts

Re(1) · · · Re(2)	3.89	Re(2) · · · Re(3)	5.46
Re(1) · · · Re(4)	7.91	Re(3) · · · Re(4)	3.89
Re(1) · · · F(25)	4.04	Re(3) · · · F(46)	4.72
Re(1) · · · F(44)	6.84	Re(3) · · · F(22)	3.85
Re(1) · · · F(41)	7.94	Re(3) · · · F(21)	5.49
Re(2) · · · F(41)	6.69	Re(4) · · · F(21)	7.10
Re(2) · · · C(31)	4.36	Re(4) · · · C(11)	6.39
Re(2) · · · O(31)	3.97	Re(4) · · · O(11)	5.72
F(22) · · · C(31)	3.17	F(44) · · · C(11)	5.61
F(22) · · · O(31)	3.21	F(44) · · · O(11)	5.18
F(22) · · · C(34)	3.15		
F(22) · · · O(34)	3.27		
F(21) · · · O(31)	3.11 (the closest non-bonding approach)		

Figure 2 shows how the two molecules are orientated relative to one another in the crystal. A molecule has as nearest neighbours four A molecules and ' one and two halves ' B molecules and *vice versa* for each B molecule.

There are thus two distinct types of interaction between molecules A and B (Figure 3). In one, the $Re(CO)_5$ half of a B molecule is near to the ReF_5 half of its asymmetric A molecule relative, lying slightly below it in c [Re(3) $\cdots$
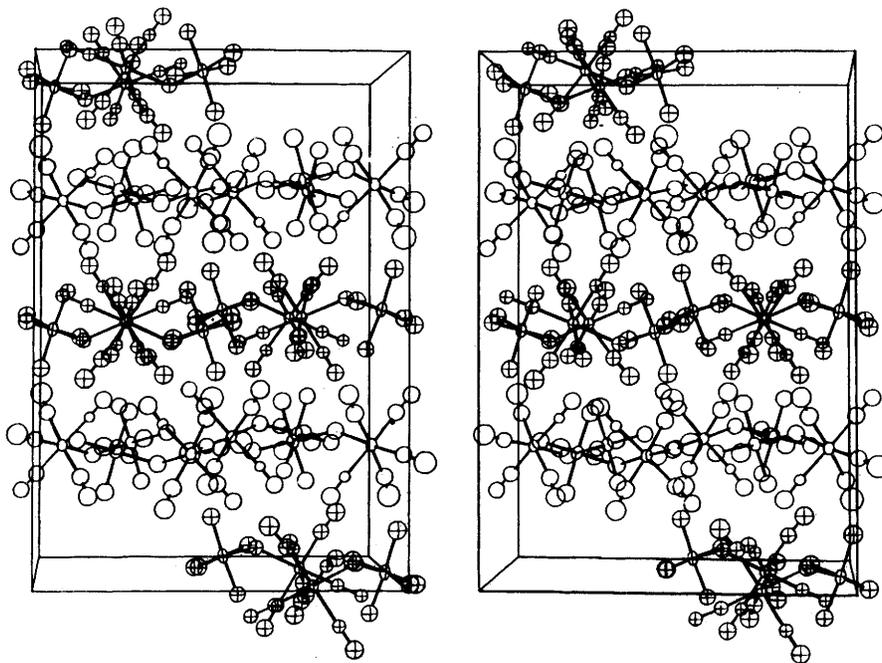
FIGURE 2 A stereoscopic view of the unit-cell contents approximately along the c direction
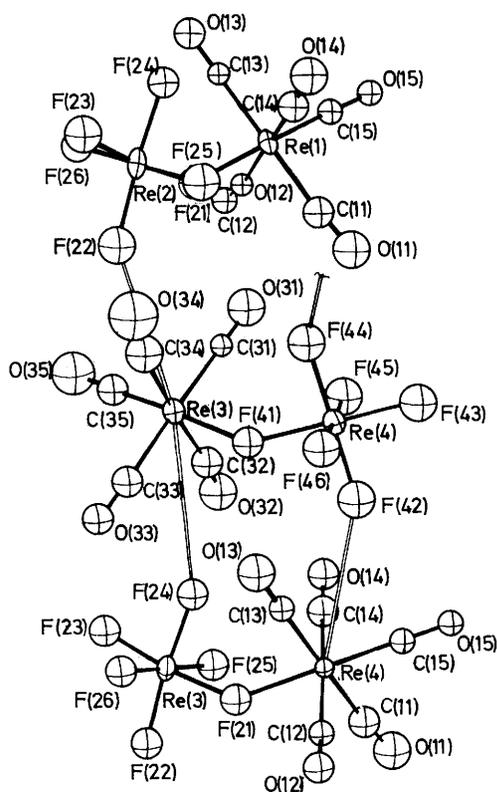
FIGURE 3 A view of part of the unit-cell contents showing the spatial relation between the two different molecules

$F(22)-Re(2)$ 3.85 Å]. The ReF_5 half of B is near to the $Re(CO)_5$ half of a different molecule A'', lying slightly *above* it in c [Re(4)–F(44) $\cdots$ Re(1) 4.16 Å]. The other interaction involves a ' broadside-on ' orientation between *complete* molecules of B and A', thus forming a pseudo-dimeric, eight-membered, ring arrangement, which bears some resemblance to the eight-membered ring in [{Ru(CO)$_3$F$_2$}$_4$].[5] The size of the two inter-molecular Re $\cdots$ F contacts [Re(3) $\cdots$ F(24) 4.14, Re(1) $\cdots$ F(42) 3.80 Å], however, shows that there is no significant bonding between the $[Re(CO)_5] \cdot ReF_5$ molecules. Similar loose oligomeric units are found in $[XeF_5][AsF_6]$ (dimers)[10] and $[SeF_3][NbF_6]$ (tetramers in a cuboid arrangement).[11]

The detailed geometry within the $[Re(CO)_5F] \cdot ReF_5$ molecules is of particular interest with respect to the continuing discussion of the nature of fluorine-bridged interactions.[12] The average bond lengths of the two asymmetric molecules are given in Figure 4, where they are divided into statistically equivalent sets. The

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standard deviations of these sets in each case are no greater than the estimated standard deviations of their individual members. Values for mean Re^V–F bond distances [1.84(2) (terminal) and 2.01(1) Å (bridging)] may be taken from the $[Re_2F_{11}]^-$ anion of $[Re(CO)_6]$-$[Re_2F_{11}]$,[1,3] a discrete centrosymmetric anion with no close interatomic contacts. Thus the equatorial Re^V–F bond lengths of $[Re(CO)_5F]\cdot ReF_5$, b, can be regarded as typical.

The bridging Re^V–F distance, c, is scarcely less than Re–F(bridging) in $[Re_2F_{11}]^-$, which is surprising as it
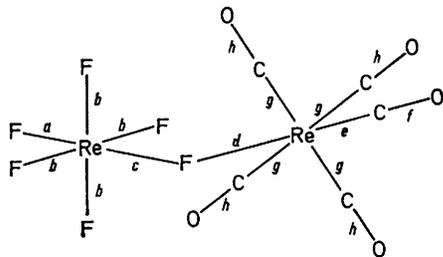
FIGURE 4 Average molecular geometry of $[Re(CO)_5F]\cdot ReF_5$. Average bond lengths (Å) with estimated standard deviations, taken from the two non-equivalent molecules: $a = 1.91(3)$, $b = 1.83(3)$, $c = 1.97(2)$, $d = 2.17(4)$, $e = 1.89(3)$, $f = 1.19(4)$, $g = 1.99(4)$, and $h = 1.13(3)$. The estimated standard deviations of the individual bonds are: Re–F 0.03, Re–C 0.05, and C–O 0.07 Å. The average Re–F–Re angle is 141(1)°

suggests that $[Re(CO)_5]^+$ competes equally with ReF_5 for the bridging fluoride ion. There are no directly comparable data for the Re^I–F (bridging) bond, but an estimate of 2.16 Å for a terminal Re^I–F bond length can be obtained from the covalent radius of fluorine [4] (0.64 Å) and the estimated covalent radius (1.52 Å) of Re^I.[13] This Re–F estimate is close to the distance d involving a bridging fluorine atom, but comparisons with metal–halogen distances in other carbonyl halides and their derivatives,[14] including the only comparable carbonyl fluoride, $[\{Ru(CO)_3F_2\}_4]$,[5] show that there is often little or no difference between terminal and bridging distances where metals are in low oxidation states. The rhenium–fluorine bridge bond lengths, therefore, suggest that $[Re(CO)_5F]\cdot ReF_5$ is essentially a covalent fluorine-bridged adduct, with only minimal

contribution of ionic forms such as $[Re(CO)_6][ReF_6]$. The latter structure would be unlikely in any event, since the $[Re(CO)_5]^+$ cation does not obey the inert-gas rule. The adduct therefore differs from many other fluorine-bridged molecules, such as $XeF_2\cdot 2SbF_5$,[15] where an alternative ionic formulation $[XeF][Sb_2F_{11}]$ must also contribute significantly to the bonding description to be consistent with the observed structural geometry. The best chemical interpretation of the molecular structure is therefore to represent it as $[Re(CO)_5F]\cdot ReF_5$, $i.e.$ an ReF_5 adduct of $[Re(CO)_5F]$ where $[Re(CO)_5F]$ acts as a $partial$ fluoride-ion donor.

Related compounds include $2[Re(CO)_5Cl]\cdot SbCl_5$,[16] whose structure is at present unknown; structures have been determined of two $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]\cdot SbCl_3$ compounds,[17] but these involve only very weak interactions more akin to those of molecular adducts such as $XeF_2\cdot IF_5$.[18] On the other hand the compound $[(Ph_3P)_3Cu(FBF_3)]$ seems to be an example of an adduct much closer to the ionic formulation $[Cu(PPh_3)_3][BF_4]$. The Cu–F distance [19] (average value 2 31 Å) is much greater than the value (1 84 Å) found in CuF,[20] and may result from steric crowding between phenyl rings and the BF_4 unit.

Within the $[Re(CO)_5F]$ unit there is a distinct probability that the Re–C distance $trans$ to fluorine is shorter than Re–C(equatorial). This shortening is frequently noticed in $[Re(CO)_5X]$ compounds [21] although it is generally not significant. A greater range of examples of this $trans$ shortening is available from $[Mn(CO)_5X]$ compounds; [22,23] it is believed that the shortening results from a greater back donation from the metal to carbonyl when the latter is $trans$ to X, X generally being a poorer π acceptor than CO. In $[Re(CO)_5F]\cdot ReF_5$, where the bridging fluorine atom is a particularly poor acceptor (possibly even π donating), the $trans$ Re–C shortening would be enhanced.

The determination of the structure of $[Re(CO)_5F]\cdot ReF_5$ gives credence to earlier postulated structures of related species.[24]

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