

# Room temperature preparations of second and third transition series tetrafluorides and a possible novel structure type for OsF<sub>4</sub> and RhF<sub>4</sub>

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Received 15 June 2001; accepted 31 August 2001

Dedicated to Dr. Karl O. Christe on the occasion of his 65th birthday

## Abstract

The polymeric tetrafluorides, MF<sub>4</sub> (M = Mo, Ru, Pd, Re, and Os) have been precipitated from their MF<sub>6</sub><sup>2-</sup> salts in liquid anhydrous hydrogen fluoride (aHF) at ~20 °C. For M = Ru, Os and Pd, AsF<sub>5</sub> can be used to displace the tetrafluoride, but this strong F<sup>-</sup> acceptor is too strongly oxidizing for use in making MoF<sub>4</sub> and ReF<sub>4</sub>, for which SbF<sub>5</sub> is effective. X-ray powder diffraction photograph (XRDP) show the MF<sub>4</sub> to have the same structures as those from higher temperature preparations, when previously known. XRDP of OsF<sub>4</sub> are very like those of RhF<sub>4</sub> and indicate a close structural relationship of the pair, and a significant structural difference from the PdF<sub>4</sub> type structure adopted by M = Pd, Pt, Ir, and Re. A new, two-dimensional, ‘raft’ structure is proposed for OsF<sub>4</sub> and RhF<sub>4</sub>. © 2001 Published by Elsevier Science B.V.

**Keywords:** Syntheses; Tetrafluorides; Crystal structures; RhF<sub>4</sub>; OsF<sub>4</sub>; ReF<sub>4</sub>

## 1. Introduction

The binary fluorides of the second and third transition series elements provide a wide range of oxidation states for each element, especially for the platinum metals. For Ru, Rh, and Ir the known range is from M<sup>VI</sup> to M<sup>III</sup>. Since the coordination number is commonly six, this means that the structures vary from the three-dimensional F-bridged network of the trifluorides [1], to the molecular hexafluorides [2]. This has provided for investigation of the effect of oxidation state (and the d electron configuration) on M–F bonding in these elements [3].

In the tetrafluorides, the two F ligands that are non-bridging can be *trans* as in NbF<sub>4</sub> [4], and RuF<sub>4</sub> [3] or *cis* as in IrF<sub>4</sub> [5], PtF<sub>4</sub>. (Here, the unit cell given was a pseudo-monoclinic cell with *a* = *b*, this being half the diagonal of the true orthorhombic F cell [6,7], and PdF<sub>4</sub> [8,9]). The M–F–M bridging angle can also vary widely, being nearly linear in NbF<sub>4</sub> [4] and close to 135° in RuF<sub>4</sub> [3] and PdF<sub>4</sub> [8,9]. Indeed such variations, and the absence of a predictively useful explanation for them, prompted efforts to prepare other tetrafluorides, when a convenient new synthetic approach was found [10]. This provided authentic

OsF<sub>4</sub>, and ReF<sub>4</sub>, for the first time and also an easier route to previously known tetrafluorides including MoF<sub>4</sub> [11], RuF<sub>4</sub> [12], RhF<sub>4</sub> [9] and PdF<sub>4</sub> [9].

X-ray powder diffraction photograph (XRDP) of OsF<sub>4</sub> closely resembled those of RhF<sub>4</sub> and were, in important aspects, different from those having the PdF<sub>4</sub> type structure [8,9], i.e. M = Ir, Pt, Pd and Re. This prompted a new evaluation of structural possibilities for RhF<sub>4</sub> and its structural relative OsF<sub>4</sub>. The new preparative method for these tetrafluorides, and a possible structural model for the Rh and OsF<sub>4</sub> are the subjects of this paper.

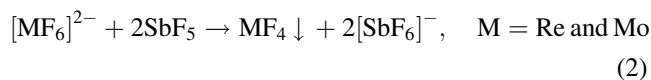
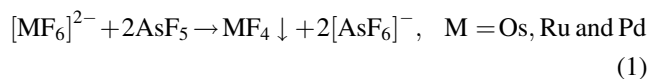
## 2. Results and discussion

The appropriate second and third transition element [MF<sub>6</sub>]<sup>2-</sup> salts were prepared as previously described [13], and the tetrafluorides were derived from them by precipitation, at room temperature, from aHF solutions, using various acids. The choice of acid was determined by (1) convenience, (2) the F<sup>-</sup> acceptor strength of the desired tetrafluoride, and (3) the redox limitations.

Because they are gases, BF<sub>3</sub>, and AsF<sub>5</sub>, are both convenient F<sup>-</sup> acceptors. (GeF<sub>4</sub> is another, which proved to be excellent for AgF<sub>3</sub> precipitation [14], but it was not tried in

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this context.) Unfortunately,  $\text{BF}_3$  is not a very strong  $\text{F}^-$  acceptor [15,16], and for related reasons not very soluble in aHF. It proved to be ineffective in producing the tetrafluorides. With the more easily oxidized tetrafluorides,  $\text{ReF}_4$  and  $\text{MoF}_4$ , the  $\text{AsF}_5$  was too potent an oxidizer and rapidly gave  $\text{M}^{\text{V}}$  products; so for these tetrafluorides it was necessary to employ  $\text{SbF}_5$  as the  $\text{F}^-$  acceptor. The syntheses can therefore be summarized by the following equations:



Because the  $[\text{MF}_6]^{2-}$  salts used in this work were largely potassium salts, deriving from the earlier study [13], these syntheses involved much tedious washing with aHF in which the  $\text{KAsF}_6$  and  $\text{KSbF}_6$  are of low solubility. For any future work it would be worthwhile to prepare the  $\text{Li}_2\text{MF}_6$  salts since  $\text{LiAsF}_6$  and  $\text{LiSbF}_6$  are much more soluble in aHF than their potassium counterparts.

As already noted  $\text{ReF}_4$  and  $\text{MoF}_4$  reduce  $\text{AsF}_5$ , indicating that the  $\text{M}^{\text{IV}}$  oxidation state at the left hand end of each transition series is at least a moderately reducing one. But with the nuclear charge increase along the series we quickly pass to tetrafluorides that are stable with respect to  $\text{AsF}_5$ . In  $\text{PdF}_4$  we have a tetrafluoride capable of oxidizing  $\text{XeF}_2$  to  $\text{XeF}_4$  in aHF at room temperature [17].

Even  $\text{RhF}_4$  is easily reduced. It is pertinent that as Sharpe pointed out long ago,  $[\text{RhF}_6]^{2-}$  salts [18], like those of  $[\text{PdF}_6]^{2-}$  [19], are easily made in solution in  $\text{BrF}_3$  made basic with alkali fluoride. But in neutral  $\text{BrF}_3$  a pink complex is formed ([18] and present work), which is probably  $\text{BrF}_3 \cdot \text{RhF}_3$ , since it is diamagnetic, and its pyrolysis gives the purple–red pyrochlore-form of  $\text{RhF}_3$ . This purple–red product had been identified in Sharpe's early work [18] as  $\text{RhF}_4$ . The pyrochlore-form of  $\text{RhF}_3$  is akin to its  $\text{FeF}_3$  relative reported by dePape and Ferey [20], and to (rhombohedral) pyrochlore-form  $\text{NiF}_3$  which is generated [21] in the slow thermolysis of  $\text{NiF}_4$  above  $-60^\circ\text{C}$ .

XRDP of the tetrafluorides made by this low temperature route showed that the same structures pertained as in those same fluorides made by other methods. These photographs disclosed the variety of structure types set out in Fig. 1.

All of the patterns were indexed except that of  $\text{MoF}_4$  the strong-line pattern of which, however did agree with the d

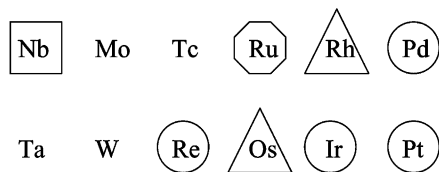


Fig. 1. Observed structure types of the second and third transition series tetrafluorides.  $\text{SnF}_4$  type ( $\square$ ), [4];  $\text{RuF}_4$  type ( $\circ$ ), [3];  $\text{PdF}_4$  type ( $\circ$ ), [8,9]; possible  $\text{OsF}_4$  type ( $\triangle$ ), [9] and this work.

spacings given by Payne and Asprey [11]. Curiously,  $\text{OsF}_4$  showed an almost identical XRDP to that of  $\text{RhF}_4$  and distinctly different from that of its pseudo-isoelectronic relative  $\text{RuF}_4$ . It had been noted in the early work [9] that the XRDP of  $\text{RhF}_4$  exhibited puzzling differences from those of  $\text{IrF}_4$  and its isostructural neighbors  $\text{PdF}_4$  and  $\text{PtF}_4$ . The principal distinguishing features of the  $\text{RhF}_4$  XRDP were the broadness of the diffraction lines (which were broad even in high temperature preparations, which should have favored recrystallization) and the absence of some lines characteristic of the  $\text{PdF}_4$  type pattern [8,9]. The  $\text{OsF}_4$  pattern exhibited the same peculiarities. It was now clear that whatever structural changes set  $\text{RhF}_4$  apart from  $\text{PdF}_4$ , the same also applied to  $\text{OsF}_4$ .

### 2.1. A possible new structure type for $\text{OsF}_4$ and $\text{RhF}_4$

The  $\text{PdF}_4$  type structure is like that of rutile with every other metal atom missing in the stacks of edge-shared  $\text{MF}_6$  or  $\text{F}_6$  octahedra. Fig. 2 represents the (polar) structure as viewed down the stacks of superimposed edge-shared octahedra. Since X-ray scattering, at a particular diffraction angle, is approximately proportional to the atomic number of the atom, the scattering by Os (atomic number = 76) and Rh (atomic number = 45) outweighs that from four F atoms out of phase with the metal atoms ( $4 \times \text{atomic number } 9$ ). We therefore expect that in such a structure 2 2 0 reflections should be observed, and perhaps be even a strong-line in the  $\text{OsF}_4$  case. In the earlier work ([9], Table 3), it was noted that this reflection was very weak (vww) in  $\text{RhF}_4$ , whereas in  $\text{PdF}_4$  the same reflection ([9], Table 1), was strong (s). (In XRDPs of  $\text{RhF}_4$ , also, the 2 2 0 reflection is close to the position of a strong reflection from  $R\text{-RhF}_3$  [1], to which impurity the weak observed line in  $\text{RhF}_4$  could be attributed.) But Rh scattering is not as dominant in  $\text{RhF}_4$  as that of Os in  $\text{OsF}_4$  so the failure to observe a 2 2 0 reflection in the XRDP of the latter provided the decisive indicator that the  $\text{PdF}_4$  type structure was not appropriate for these tetrafluorides.

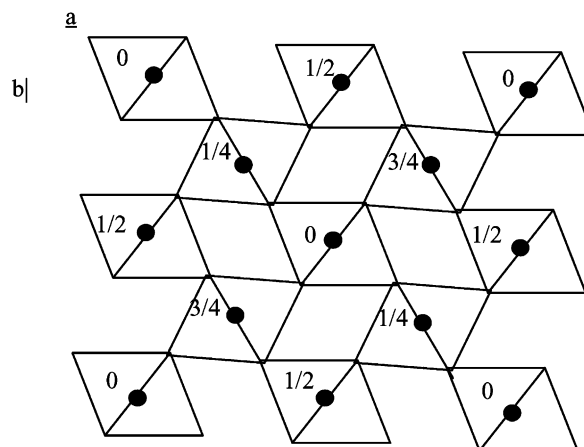


Fig. 2.  $\text{PdF}_4$  type structure—projection in the 0 0 1 plane.

Table 1

Pyrochlore  $\text{RhF}_3$  X-ray powder data (Cu  $K\alpha$ , Ni filter) with a face-centered cubic (probable space group  $Fd\bar{3}m$ ) unit cell,  $a_0 = 10.292(5)$  Å;  $V = 1090$  Å<sup>3</sup>

$hkl$	$1/d^2 \times 10^4$		$hkl$
	Observed	Calculated	
10	287	283	1 1 1
3	793	755	2 2 0
8	1051	1038	3 1 1
9	1142	1133	2 2 2
5	1538	1510	4 0 0
4	1809	1794	3 1 1
3	2235	2266	4 2 2
7	2568	2549	5 1 1; 3 3 3
8	3038	3021	4 4 0
8	3319	3304	5 3 1
5	4068	4059	5 3 3
8	4176	4154	6 2 2
5	4547	4531	4 4 4
7	4837	4814	7 1 1; 5 5 1
8	5591	5570	7 3 1; 5 5 3
4	6077	6042	8 0 0
3	6396	6419	8 2 0; 6 4 4
4	6826	6797	8 2 2; 6 6 0
5	7171	7080	7 5 1; 5 5 5
6	7565	7552	8 4 0
6	7868	7835	9 1 1; 7 5 3
4	8125	8118	9 2 1; 7 6 1; 6 5 5
5	8610	8590	9 3 1
6	9076	9062	8 4 4
5	9355	9346	9 3 5; 7 7 1; 7 5 5
6	10205	10195	10 2 2; 6 6 6
5	10871	10856	9 5 5
4	11600	11611	1 1 1 1; 7 6 6
3	12096	12083	8 8 0
5	12377	12366	1 1 3 1; 9 7 1; 9 5 5
8	13233	13216	10 6 2
3	15112	15104	12 4 0
4	16290	16237	10 6 6
3	16593	16614	12 4 4

Table 2

X-ray powder data (Cu  $K\alpha$  radiation, Ni filter) for  $\text{OsF}_4$ , F orthorhombic cell with  $a = 9.89(1)$  Å,  $b = 9.36(1)$  Å,  $c = 5.70(1)$  Å,  $z = 8$ ,  $V = 528$  Å<sup>3</sup>

$hkl$	$1/d^2 \times 10^4$		$hkl$
	Observed	Calculated	
w	431	409	2 0 0
		456	0 2 0
vs	523	524	1 1 1
		865	2 2 0
w	1351	1341	3 1 1
w	1454	1437	1 3 1
s	1636	1635	4 0 0
		1639	2 0 2
m	1827	1826	0 4 0
m	2099	2092	4 2 0
		2095	2 2 2
w	2969	2983	1 1 3
vw	3269	3262	1 5 1
vs	3473	3461	4 4 0
		3464	2 4 2
vw	3796	3801	3 1 3
vw	3877	3896	1 3 3
w	4699	4690	4 4 2
		4714	3 3 3
ms	4940	4919	0 0 4
		5722	1 5 3
		5743	4 6 0
vw	5758	5746	2 6 2
		5785	2 2 4
m	6579	6539	3 5 3
		6555	4 0 4
m	6748	6745	0 4 4
w	7330	7304	0 8 0
m	8436	8390	4 4 4
m	8977	9027	0 6 4
w	11544	11525	0 2 6
m	12268	12223	0 8 4
m	13362	13379	1 7 5
vw	13900	13855	4 8 4

As has already been noted, the  $\text{RhF}_4$  and  $\text{OsF}_4$  XRDPs are strikingly similar, and not only in the absence (or weakness) of the 2 2 0 reflections, but also in the broadness of the general  $hkl$  reflection lines. The two fluorides evidently share a common structure. Aside from these features that distinguish the XRDPs of these two fluorides from those of

the  $\text{PdF}_4$  type, however, the patterns otherwise exhibit a close relationship. All of the patterns can be indexed on the basis of a face-centered orthorhombic cell (see [9] and Table 2). In the  $\text{PdF}_4$  type structure (see Fig. 3a) each octahedrally coordinated M (i.e.  $[\text{MF}_6]$ ) is edge-shared with an octahedral set of  $[\text{F}_6]$  above and below it in the stack.

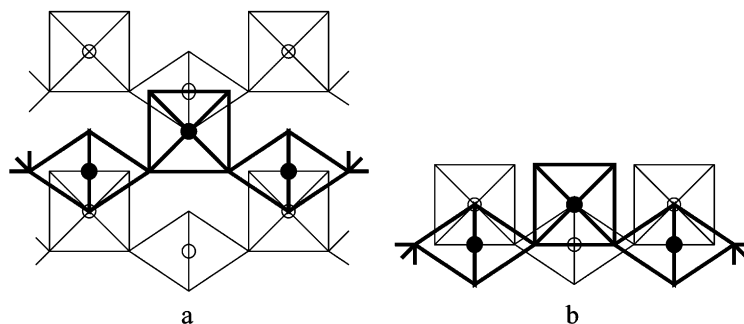


Fig. 3. (a) Polar  $\text{PdF}_4$ : 3D structure; and (b) 2D "raft" structure for  $\text{OsF}_4$  and  $\text{RhF}_4$ .

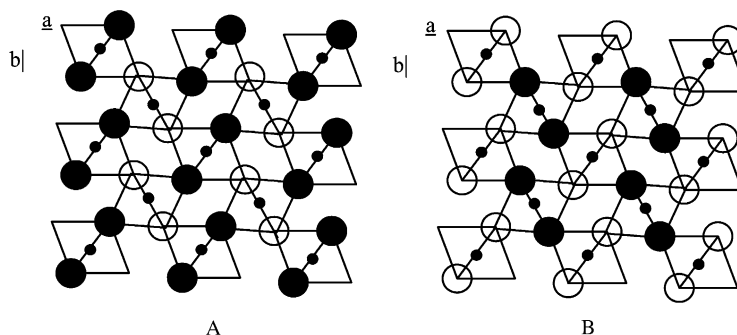


Fig. 4. The two surfaces of the proposed 'raft' structure for  $\text{OsF}_4$  and  $\text{RhF}_4$ : filled circles for non-bridging F on the top surface, open circles for the same on the bottom surface. Reflecting A in the  $ab$  plane converts it to B.

The other two F of the  $[\text{MF}_6]$  (*trans* to each other) are shared with two  $[\text{MF}_6]$  octahedra. These are oriented roughly at right angles with the first,  $[\text{MF}_6]$  and pitched always on the same side (above or below on the  $[\text{MF}_6]$  stacking axis,  $z$ ) to give the three-dimensional polar array represented in Figs. 2 and 3a. This arrangement always has the *cis* non-bridging F of each  $[\text{MF}_6]$  on the same side (up, or down, on the stacking axis,  $z$ ). It will be recognized, from Fig. 3b, that if linkage of the  $[\text{MF}_6]$  is changed, so that the *cis* non-bridging F ligands on adjacent  $[\text{MF}_6]$  are alternately up and down, a two-dimensional ('raft') structure results.

Close-packing of such 'rafts' requires that the non-bridging F of one such 'raft' inter-lock with the adjacent non-bridging F of the adjacent 'raft'. Fig. 4 represents these non-bridging F on the surface of each raft, filled circles for those on one side and open circles for those on the other. For each face-to-face contact there are two stacking possibilities. These can be visualized with the two 'unit cells' of the raft structure labeled A and B. (Reflecting A in the  $ab$  plane produces arrangement B.) Let the filled circles represent up F and the open down F. The up of A is the down of B, and vice versa. If we stack A on A or B on B (filled circles over filled, unfilled over unfilled), we see that the M atoms would be superimposed. To mesh A with B it is necessary to translate A or B by  $\pm 1/4a$ . If we mesh A with B or vice versa, we therefore see that the M do not superimpose. For the latter arrangements the projection of the M atom array into the  $ab$  plane is represented by a simple rectangle of sides quarter  $a$ , quarter  $b$ .

The consequence of randomly stacking 'rafts' A and B therefore satisfies our need to have no significant diffraction from the  $2\ 2\ 0$  planes. Also, since the fit A on A (or B on B) is not exactly the same as A with B, the inter-raft separation will not be exactly the same for both. That accounts, at least partially, for the line broadening in the XRDP.

## 2.2. Why the structural variety?

It is clear from the non-equivalence of the  $\text{RuF}_4$  and  $\text{OsF}_4$  structures on the one hand, and the  $\text{RhF}_4$  and  $\text{IrF}_4$  on the other, that the number of electrons in the d electron configuration has no important influence on which structure is adopted.

Certainly, the effective nuclear charge increases from left to right in each transition series. Also, that increase with atomic number is more dramatic for the second series than for the first, as the molecular instability and oxidizing patterns of the hexafluorides indicate [22]. We therefore expect the F ligands to be more highly polarized in the second series, by the nuclear charge of M, than in the third. This should render the F ligands of the second series fluorides smaller than those of their third series relatives. Certainly  $\text{PdF}_4$  [8,9] has a smaller formula-unit volume than isostructural  $\text{PtF}_4$  [6,7], 63.20 versus 63.57  $\text{\AA}^3$ , which is almost the same as the difference in the formula-unit volumes of the metals themselves (14.71 versus 15.09  $\text{\AA}^3$ ) [23]. The degree of covalency in  $\text{RhF}_4$  is therefore likely to be greater than in  $\text{IrF}_4$ , and greater in  $\text{RuF}_4$  than in  $\text{OsF}_4$ . But, if so, the degree of covalency in the M–F bonding does not determine the structure type, since  $\text{PdF}_4$  should have higher M–F covalency than  $\text{RhF}_4$ , which should be more covalent than  $\text{IrF}_4$ , which has the same structure as

Table 3

X-ray powder data (Cu  $K\alpha$  radiation, Ni filter) for  $\text{ReF}_4$  (F orthorhombic, pseudo-tetragonal, with  $a = b = 9.61(2)$   $\text{\AA}$ ,  $c = 5.66(1)$   $\text{\AA}$ ,  $z = 8$ ,  $V = 522$   $\text{\AA}^3$ , possible space group  $Fdd2$ )

$hkl$	$1/d^2 \times 10^4$		$hkl$
	Observed	Calculated	
s	537	529	1 1 1
w(br)	867	866	2 2 0
m(br)	1401	1395	3 1 1; 1 3 1
s	1696	1683	2 0 2; 0 2 2
–	–	1732	4 0 0; 0 4 0
vw	2138	2116	2 2 2
–	–	2165	4 2 0; 2 4 0
vw	2240	2261	3 3 1
w(br)	3048	3029	1 1 3
–	–	3127	5 1 1; 1 5 1
vs(br)	3450	3414	4 2 2; 2 4 2
–	–	3465	4 4 0
w(br)	3920	3892	3 1 3; 1 3 3
–	–	3994	5 3 1; 3 5 1
–	–	4331	6 2 0; 2 6 0
vvw	4723	4758	3 3 3
w(br)	4999	4994	0 0 4

$\text{PdF}_4$ ! Moreover,  $\text{ReF}_4$ , on the left in the third transition series appears to have the  $\text{PdF}_4$  structure type (see Fig. 2, and Table 3). If this is established, there will be no clear trend for the structure type dependence on Periodic Table location. Here we have a puzzle for future workers to sort out!

### 3. Experimental

Apparatus and methods for the work using liquid HF were as described in [21] and references therein.

For the aHF-based work the reaction vessels routinely used were of three types. Single armed reaction vessels consisting of a FEP tube sealed at one end and joined to a Teflon valve and two armed reactors consisting of two such FEP tubes, joined to a Teflon valve by means of a Swagelok Teflon tee piece. Such apparatus was used for reactions involving aHF in which pressures would not exceed 2 atm FEP tubes were sealed by heating one end over a flame, pinching it shut with pliers when it had softened as signaled by increased transparency. Teflon valves, Fig. 5, consisted of a Teflon valve body, a Kel-F stem containing an inserted Teflon stem tip, and Teflon packing washers. These valves were always attached to the apparatus with the seat side of the valve exposed to vapors from highly acidic oxidizing solutions, which could only contact the Teflon tip of the stem, when the valve was closed. The Teflon packing nuts were pressed against the stem and valve body, to make a seal, by means of an aluminum backing washer and a screw tightened nut. Connections were made to the inlet and outlet of the valve by means of 1/4" Swagelok fittings, or through 1/4" FEP tubing sweated on to a knurled inlet tube at the seat side of the valve.

#### 3.1. Drybox

Involatile, air-sensitive materials were handled in the dry Ar atmosphere of a Vacuum Atmospheres Corp., DRILAB. Freedom of the atmosphere from significant oxygen, or water contamination was judged by the continued burning of an incandescent filament.

#### 3.2. Reagents

Anhydrous hydrogen fluoride (aHF) 98% or better, as obtained from Matheson (Newark, CA) was dried using either dioxygenyl salts [24] ( $\text{O}_2\text{SbF}_6$ , or  $\text{O}_2\text{Sb}_2\text{F}_{11}$ ), or  $\text{K}_2\text{NiF}_6$  (Ozark–Mahoning–Pennwalt).

The commonly used reagent gases  $\text{BF}_3$  (Matheson),  $\text{PF}_5$ , and  $\text{AsF}_5$  (Ozark–Mahoning–Pennwalt, Tulsa, OK) were each checked before use by IR spectroscopy and when found to be free of major volatile impurities were used without further purification. The much less volatile liquids  $\text{BrF}_3$  (Matheson) and  $\text{SbF}_5$  (Ozark–Mahoning) were generally distilled out of their cylinders directly into reaction vessels. Bromine usually accompanied  $\text{BrF}_3$  distillation, however, since this served as a useful diluent and was a by-product of  $\text{BrF}_3$  oxidations, further purification was not carried out. When small amounts of volatile  $\text{O}_2\text{SbF}_6$  impurity in the  $\text{SbF}_5$  could not be tolerated, it was removed by exposing the distilled  $\text{SbF}_5$  to  $\text{C}_6\text{F}_6$  (PCR, Gainesville, FL) which was oxidized to  $\text{C}_6\text{F}_6^+$  by any  $\text{O}_2^+$  present [25].

#### 3.3. X-ray powder diffraction photograph (XRDP)

Debye–Scherrer photographs were taken on General Electric Precision Powder cameras (45 cm circumference) using Ni filtered, Cu  $K\alpha$  radiation. Powder samples for

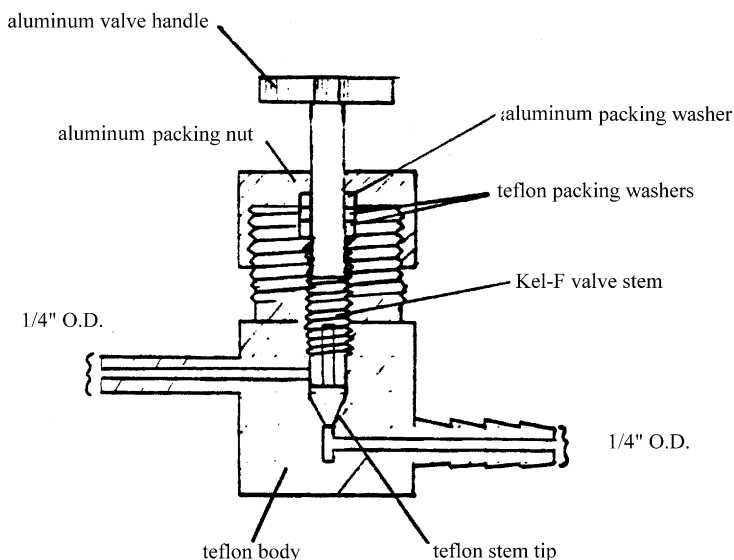


Fig. 5. Teflon valve schematic.

XRDP were loaded into 0.3 or 0.5 mm diameter quartz capillaries (Charles Supper Co., Natick, MA) inside the DRILAB and temporarily sealed with Kel-F grease (Halocarbon Product Corp., N. Augusta, SC). The capillaries were finally sealed outside the DRILAB by drawing down using a micro-torch.

### 3.4. Magnetic measurements

Variable temperature magnetic susceptibility data were collected on a SQUID magnetometer (S.H.E. Corp., and Quantum Dynamics). Samples were held in cylindrical containers made of two Kel-F caps, one fitting inside the other. These were passivated with 2 atm of a  $F_2/AsF_5$ , or  $F_2/BF_3$  mixture overnight before use. Samples were made up in the DRILAB. Typically measurements were taken at 5 and 40 kG between 6 and 280 K.

### 3.5. Specific syntheses

#### 3.5.1. Pyrochlore-form $RhF_3$

The preparation of the  $BrF_3$  adduct  $RhF_3$  (which was shown to be diamagnetic in this work) and its decomposition to purple–red pyrochlore-form  $RhF_3$  followed the method described by Sharpe [18] for ‘ $RhF_4$ ’. Table 1 gives the indexing of the XRDP for this material.

#### 3.5.2. Preparation of $OsF_4$

$K_2OsF_6$  [13] (600 mg, 1.5 mmol) in a T assembly was dissolved in aHF (6 ml) at room temperature. Addition of  $AsF_5$  gave an immediate precipitate of a dense yellow–brown solid. When the solution was colorless,  $AsF_5$  addition was stopped. ( $KAsF_6$  side product has low solubility in the presence of dissolved  $AsF_5$ .) Decantation and back distillation [21] was repeated 10 times to remove  $KAsF_6$  from the  $OsF_4$ . The aHF and any  $AsF_5$  were evacuated through a soda-lime scrubber dedicated to arsenic waste. A nearly quantitative yield of  $OsF_4$  was obtained, there being some loss in the decantation steps. X-ray powder data, Table 2, were indexed completely on the basis of an F orthorhombic unit cell. Variable temperature magnetic susceptibility measurements indicated a low, approximately temperature independent paramagnetism, consistent with known octahedral, third transition series  $d^4$  systems.

#### 3.5.3. $K_2OsF_6$ with $BF_3$

$BF_3$  added to a solution of  $K_2OsF_6$  (492 mg, 1.3 mmol, in 5 ml aHF) gave an orange insoluble solid (207 mg). This was amorphous to X-rays. Addition of  $AsF_5$  in aHF converted this to yellow–brown  $OsF_4$ , as indicated by XRDP.

#### 3.5.4. $K_2RuF_6$ with $BF_3$

Interaction of  $K_2RuF_6$  (600 mg, 2.0 mmol) with  $BF_3$  gave an insoluble orange solid with no XRDP. Interaction of this with  $AsF_5$  in aHF produced deep pink  $RuF_4$ , proved by XRDP [3].

#### 3.5.5. $K_2ReF_6$ with $AsF_5$

Addition of  $AsF_5$  to a pale pink solution of  $K_2ReF_6$  [13] in aHF precipitated a pale pink solid. It quickly dissolved ( $\sim 5$  min) in  $AsF_5$ -rich aHF to a green solution, indicating that oxidation of  $ReF_4$  to green  $ReF_5$  by  $AsF_5$  had occurred [26].

#### 3.5.6. Preparation of $ReF_4$

Excess of  $SbF_5$  (1 ml, 14 mmol) in aHF was poured into an aHF solution of  $K_2ReF_6$  (295 mg, 0.78 mmol) to give a pink precipitate. In  $\sim 30$  min some of the pink solid dissolved in the  $SbF_5$ -rich solution and gave a pale blue solution. The remaining solid was washed in the usual way to leave 110 mg (0.32 mmol, 42% yield based on  $ReF_4$ ). The XRDP data (Table 3) were indexed on the basis of a of  $PdF_4$  type cell.

#### 3.5.7. Preparation of $MoF_4$

$MoF_4$  was made in the same manner as  $ReF_4$ . To a green solution of  $K_2MoF_6$  [13] (410 mg 1.4 mmol) in aHF, in a T reactor, a solution of  $SbF_5$  in aHF was slowly decanted to produce a pale green precipitate. Addition of the  $SbF_5$ /aHF solution, beyond the point at which the supernatant became colorless, caused some dissolution of the green solid, producing a pale green solution. This product was washed and dried in the usual way [21]. The green solid (110 mg, 0.58 mmol, 41% yield based on  $MoF_4$ ) proved to be very poorly crystalline, but the X-ray powder data matched the strongest lines in the pattern described by Payne and Asprey [11] for their  $MoF_4$ . It was not indexed.

#### 3.5.8. $K_2MoF_6$ with $AsF_5$

Addition of  $AsF_5$  to a solution of  $K_2MoF_6$  in aHF produced a green solid which on standing in  $AsF_5$ /aHF solution quickly became pale, tan, indicative of  $MoF_5$  formation [27].

#### 3.5.9. Preparation of $PdF_4$

$K_2PdF_6$  (prepared by the method of Sharpe [19]) gave a yellow–orange solution in aHF. Addition of excess  $AsF_5$ , with rapid stirring of the solution, quickly produced a brown solid. With the reactor continuously agitated and a high  $AsF_5$  concentration maintained ( $\sim 12$  h) in the aHF, the brown solid gradually took on the pink to red color typical of  $PdF_4$  [9]. XRDP of the pale red solid showed it to be identical to those of  $PdF_4$  prepared by high-pressure fluorination.

## Acknowledgements

The authors gratefully acknowledge the support of the bulk of this work by the Director, Office of Basic Energy Sciences, and Chemical Sciences Division of the US Department of Energy under contract number DE-AC-03-76SF00098. The pyrochlore-form  $RhF_3$  (previously believed to be  $RhF_4$ ) was prepared at U.B.C. with support from the National Research Council of Canada.

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