Thermodynamically Unstable Fluorides of Nickel: NiF4 and NiF₃ Syntheses and Some Properties[§]

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Abstract: F^- acceptors (BF₃, AsF₅, SbF₅, or BiF₅) added to solutions of NiF₆²⁻ salts in anhydrous hydrogen fluoride (aHF) below -65 °C precipitate the tan solid NiF₄. This solid, preserved at ≤ -65 °C, is quantitatively converted, by 2 equiv of F^- donor (XeF₆ or KF) in aHF, to dissolved NiF₆²⁻. Dry NiF₄ loses F₂ above -60 °C, the decomposition to nearly black NiF₃ becoming rapid at ~ 0 °C. When the dry NiF₄ is prepared from K₂NiF₆, inclusion of some K⁺ leads, on thermolysis at 0 °C, to a pyrochlore form of NiF₃ (P-NiF₃). P-NiF₃ contains K^+ in the open channels, with K_xNiF₃, $x \approx 0.1$. The nearly cubic *P*-NiF₃ unit cell is rhombohedral: $a_0 = 9.933(3)$ Å, $\alpha = 91.01(3)^\circ$, V = 980 Å³, z = 16, with absent reflections coincident with those of the cubic space group O_h^7 -Fd3m, appropriate for pyrochlore. Decomposition of NiF₄ in aHF begins at -65 °C and is rapid at 0 °C, giving black rhombohedral NiF₃ (*R*-NiF₃) with $a_0 = 5.168(2)$ Å, $\alpha = 55.46(3)^\circ$, V = 87.3 Å³, z = 2. When the NiF₄ is made and decomposed at ~20 °C, with K⁺ present, a hexagonal tungsten bronze form of NiF₃ is precipated (H-NiF₃), with $a_0 = 7.074(6)$ Å, $c_0 = 7.193(6)$ Å, V = 312Å³, z = 6. R- and H-NiF₃ can also be made by mixing solutions of Ni²⁺ salts [e.g., Ni(AsF₆)₂] with NiF₆²⁻ salts (e.g. K₂NiF₆) in aHF. All forms of the trifluoride (R, H, and P) lose F₂ on warming ($R > 39^\circ$, $H > 72^\circ$ and P > 138 °C) to yield NiF₂, but an intermediate red-brown phase is observed for R-NiF₃. R-NiF₃ at ~20 °C, oxidizes Xe to Xe(VI), perfluoropropene, C_3F_6 , to perfluoropropane, C_3F_8 , and solid LiCl with incandescence. H-NiF₃ and P-NiF₃ interact similarly but less energetically.

Introduction

At the centennial celebrations for the discovery of fluorine, Christe described¹ the first chemical route to fluorine. This was achieved via the release of thermally unstable MnF4 from K2-MnF₆ with the strong fluoride ion acceptor SbF₅. It occurred to one of us (N.B.) that a modification of this approach to the synthesis of binary fluorides of low thermal stability, using the low melting solvent, liquid anhydrous hydrogen fluoride (aHF), might give, at low temperatures, from such a solution, access to binary fluorides that are thermodynamically unstable with respect to F_2 and a lower fluoride. The syntheses of the thermodynamically unstable fluorides AgF₃, NiF₄, and NiF₃ were quickly achieved as a result of that approach.^{2,3}

The idea was not new however. Court and Dove in 1971 had described⁴ both the precipitation, at 20 °C, of MnF₄ from solutions of K₂MnF₆ in aHF, and a black precipitate, claimed to be NiF₃, from a like solution of K_2NiF_6 , using AsF₅ as the F⁻ acceptor. This black NiF₃ was described as decomposing to NiF₂ when the AsF_6^- salt produced along with it was extracted with aHF at 20 °C. In addition they remarked explicity that NiF₄ was not produced from the K₂NiF₆ with AsF₅ reaction.

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It is clear from their later detailed descriptions⁵ that they had indeed achieved a preparation of NiF₃, but their materials were always heavily contaminated with the coproduced potassium salts (KBF₄ or KAsF₆) and the oxidation state in their (mostly brown) precipitates was never as high as +3. Unfortunately they did not succeed in obtaining meaningful X-ray powder diffraction patterns for their novel solid products. In the light of the work described in this paper, it is difficult to understand why Court and Dove failed to observe NiF4, or isolate the relatively long-lived NiF₃, which is thermally stable at 20 °C, when dry.

The interest in nickel fluorides higher than NiF₂ had been much stimulated by the development, by Simons, of the process^{6,7} for the anodic fluorination of organic compounds. Simons had found that this was particularly efficient with a nickel anode and this had prompted Haszeldine and his co-workers,⁸ and Burdon and Tatlow, in their review⁹ of the Simons process chemistry, to conjecture on the possible role of a higher fluoride of nickel at the Ni anode, in that chemistry. Both Page¹⁰ and Stein¹¹ carried out electrochemical oxidation studies with attention to the possibility of preparing a higher nickel fluoride. Stein convincingly demonstrated that a brown solid, formed using a nickel anode in aHF (with KF or NH₄F electrolyte) had "appreciable oxidizing power (0.30-0.48 equiv of iodine per mole of nickel)". Stein noted similar brown

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precipitates from K_3NiF_6 in aHF. He did not report black solids (appropriate for NiF₃ forms) nor was he able to obtain any X-ray powder diffraction information from any of his brown solids. Although Page claimed¹⁰ a red impure nickel "perfluoride" from the electrolysis of a KF•3HF melt, with nickel electrodes, this material was otherwise uncharacterized.

In this paper, we provide evidence for the existence of NiF₄, which can be kept indefinitely as a dry solid at -55 °C and below. In addition, three forms of NiF₃ have been prepared, their structures identified, these related to other first transition series trifluoride structures, and the oxidizing properties briefly described. NiF₄ and the three known forms of NiF₃ are seen to be thermodynamically unstable with respect to loss of F₂ at 20 °C.

Results and Discussion

Nickel Tetrafluoride Synthesis. The precipitation of a tan solid on introduction of BF₃ to an aHF solution of K₂NiF₆ at -65 °C was the first indication of the possible existence of NiF₄. Since F_2 was evolved from this solid well below 0 °C (the tan solid then becoming black) experiments to settle the composition of the solid were carried out initially on solutions of the salt, $(Xe_2F_{11})_2NiF_6$, in aHF at -65 °C.¹² This system provided for the easy removal of XeF5AsF6, which is highly soluble in aHF even at -65 °C. In this set of experiments, AsF₅ was employed as the F⁻ acceptor and was measured out tensimetrically for delivery to the solution of $(Xe_2F_{11})_2NiF_6$ in aHF. As AsF₅ was added to the solution a tan precipitate was formed at the gas-solution interface, but this rapidly disappeared on agitation of the solution. At the point where 2 equiv of AsF₅ had been added, this dissolution needed vigorous mixing and the next AsF₅ addition resulted in a permanent tan precipitate. Clearly, the first 2 equiv of AsF₅ merely neutralized the second XeF_6 molecule of the complex cation:

$$(Xe_2F_{11})_2NiF_6 + 2AsF_5 \rightarrow (XeF_5)_2NiF_6 + 2XeF_5AsF_6$$
(1)

An additional AsF₅ was added, and more tan precipitate formed, the red solution color, characteristic of NiF_6^{2-} , paled, and at the point where 4 equiv of AsF₅ had been added, the supernatant solution had only a pale-straw color, typical for solutions of XeF₅AsF₆ in aHF:

$$(XeF_5)_2NiF_6 + 2AsF_5 \rightarrow NiF_4 \downarrow + 2XeF_5AsF_6 \qquad (2)$$

Quenching this system to -196 °C showed that there was no F_2 present. The solution of XeF₅AsF₆ in aHF was removed by decantation from the precipitate, which was then washed twice with aHF, all of these operations being carried out at -65 °C. Removal of remaining aHF under dynamic vacuum at -55 °C left a tan powder. This powder did not lose F_2 or discolor during several hours at -60 °C. With the powder again in suspension in aHF, XeF₆ was added tensimetrically. Addition of 2 equiv of XeF₆ dissolved all of the tan solid to a red solution, from which (XeF₅)₂NiF₆ was recovered:

$$NiF_4 + 2XeF_6 \rightarrow (XeF_5)_2NiF_6$$
(3)

This established that the tan solid is NiF₄ and that it retains its integrity at -60 °C, since NiF₂ does not interact with XeF₆ in aHF, nor dissolve in that solution.¹² This did not prove, however, that the tan precipitate, obtained from interaction of K₂NiF₆ with BF₃ in aHF, was also NiF₄, since earlier studies

of the K_2PdF_6/BF_3 in aHF system,¹³ had shown the existence of KPdF₅ as a precursor to PdF₄.

Precipitation of the tan solid at -65 °C, with BF₃, from a K₂NiF₆ solution in aHF, has established, from gravimetry, that 2 mol of KBF₄ are formed from 1 mol of K₂NiF₆:

$$K_2 NiF_6 + 2BF_3 \rightarrow NiF_4 \downarrow + 2KBF_4$$
 (4)

The tan solid, mixed with colorless KBF₄, obtained from this preparation, was found to lose F_2 slowly above -55 °C but very rapidly at ~ -1 °C.

The low kinetic stability of NiF₄ has hampered the structural and magnetic investigations of the material, but as its ready liberation of F₂ implies, it is a powerful oxidizer and fluorinator. It has already been shown¹⁴ to dissolve in aHF in the presence of excess acid to give yellow-brown solutions of cationic Ni(IV) which are able to electron-oxidize PtF_6^- or RuF_6^- to form the neutral hexafluorides:

$$NiF_3^{+} + MF_6^{-} \rightarrow NiF_3 + MF_6$$
 (5)

It is therefore, with cationic Ag^{III} ,¹⁴ the most powerful electron oxidizer known to date.

Nickel Trifluoride Syntheses. As a dry solid, NiF₄ decomposed to produce a dark brown (nearly black) material which gave an X-ray powder diffraction pattern which showed it to have a rhombohedral variant of the pyrochlore structure (see below and Table 1):

$$\operatorname{NiF}_{4} \operatorname{solid} \xrightarrow{>-55 \, ^{\circ} \mathrm{C}} P \operatorname{-NiF}_{3} + \frac{1}{2} F_{2} \tag{6}$$

A pyrochlore form of FeF₃ is known,¹⁵ having been obtained by topotactic oxidation of NH₄Fe₂F₆ with Br₂ in CH₃CN, the product being cubic, with $a_0 = 10.325(2)$ Å. In the instance of *P*-NiF₃, this poorly packed structure probably arises as a consequence of the release of F₂ from its dry NiF₄ precursor, there being no solvent to provide for recrystallization to a more thermodynamically stable form.

The decomposition of NiF₄ in aHF at 0 °C proceeds smoothly, in several hours (in the presence of a F^- acceptor), to a black solid which has the approximately hexagonally close-packed structure (*R*-NiF₃, Table 2) common to the late transition series element trifluorides:

$$\operatorname{NiF}_{4} \xrightarrow{\operatorname{aHF, 0 °C}} R \operatorname{-NiF}_{3} + \frac{1}{2}F_{2}$$
(7)

Suspensions of *R*-NiF₃ at 20 °C slowly evolve F_2 over several days to give yellow-brown NiF₂. This loss of F_2 in aHF at 20 °C may be the cause of the formation of a hexagonal tungsten bronze form¹⁶ of the trifluoride (*H*-NiF₃) when the tetrafluoride is decomposed, in aHF, at 20 °C rather than at 0 °C:

NiF₄
$$\xrightarrow{aHF, 20 °C}_{K^+}$$
 H-NiF₃ + ¹/₂F₂ (8)

This form of the trifluoride is not made when potassium salts are absent from solution. Moreover analytical and other data (see below) indicate that there is K⁺ in the hexagonal tunnels of the structure, with a composition close to $K_{0.12}$ NiF₃. This requires some additional Ni^{II} (~0.12 per mole of Ni) in the lattice, above that required to balance any Ni^{IV}. The formation

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Table 1. X-ray Powder Diffraction Data (Cu K α radiation, Ni filter) for Pyrochlore NiF₃ (Unit cell: $a_0 = 9.933(3)$ Å; $\alpha = 91.01(3)^\circ$; V = 980(2) Å³; Z = 16; V/Z = 61.25(13) Å³)

	$1/d_{hkl}^2$	$\times 10^4$			
I/I _o	obsd	calcd	h	k	l
100	300	300	1	1	ī
100	317	315	1	1	1
20	408	405	2	0	0
w ^a	803	b			-
70	1104	∫ 1097	3	$\frac{1}{1}$	1
			3	l	1
30	1141	1140	$\frac{3}{2}$	1	1
80	1197	1202	2	2	2
30	1257	1260	2	2	2
-	_	1893	3	3	1
_		1937	3	3	1
5	1993	1980	3	3	1
VW ^a	2246		-	_	_
20	2403	[2389	4	2	2
20	2105	L2418	4	2	2
5	2510	2505	4	2	2
50	2701	2704	3	3	3
20	2841	2835	<u>3</u>	3	3
60	3181	3185	4	4	0
60	3307	3302	4	4	0
20	3485	∫3485	5	<u>3</u>	1
20	5405	L3500	5	3	<u>1</u>
10	3564	3573	5	3	1
10	3632	3631	<u>5</u>	3	1
5	4020	4010	6	2	0
5	4112	4098	6	2	0
10	4290	4281	5	<u>3</u>	3
-	_	4325	5	3	3
_	_	4386	6	2	2
20	4446	4445	6	2	2
10	1562	∫ 4501	5	3	3
10	4002	14562	<u>6</u>	2	2
10	4812	4806	4	4	4
20	5069	15078	4 5	5	4
-	-	5121	Ī	<u>1</u>	1
5	5212	5165	7	1	1
-	J 44 1 44	L5224	7	1	1
5	5295	5297	5	5	1
20	5896	5888	7	3	1
5	6030	∫ 5918	7	3	$\frac{1}{1}$
0	0020	L6020	7	3	1
_		6093	7	3	1
10	6481	6486	8	0	0

^a Line due to a small R-NiF₃ impurity. ^b Systematic absences obey F with *hkl*: *h*, *k*, l = 2n + 1, or *h*, *k*, l = 4n + 2, or *h*, *k*, l = 4n.

of some Ni^{II} in the presence of K^+ (the latter accommodating well with the *H*-NiF₃ structure), may combine to favor the precipitation of this form of the trifluoride.

In order to provide a simple and direct approach to the synthesis of NiF₃, a Ni²⁺ salt in aHF was added to a solution of K₂NiF₆ in aHF. At 0 °C, with slow mixing, this gives predominantly *R*-NiF₃, but when the solutions are mixed at 20 °C the dominant phase is *H*-NiF₃:

$$Ni(MF_6)_2 (M = As, Sb, Bi) + K_2NiF_6 \rightarrow 2NiF_3 + 2KMF_6$$
(9)

The relatively high solubility of $KBiF_6$ in aHF eases the purification of the NiF₃ prepared using Ni(BiF₆)₂.

Thermal and Solution Stability of R-, H-, and P-NiF₃. All forms of dry solid NiF₃ (R, H, and P) lose F₂ when the solids are warmed (R- > 39 °C, H- > 72 °C, and P-NiF₃, > 138 °C) and there is X-ray powder diffraction evidence for the red-brown solid, derived from the pyrolysis of R-NiF₃ at 83 °C being similar to that remaining from the reduction of solid R-NiF₃ by

Table 2. X-ray Powder Diffraction Data (Cu K α radiation, Ni Filter) for Rhombohedral NiF₃ (Unit cell: $a_0 = 5.168(2)$ Å; $\alpha = 55.46(3)^\circ$; V = 87.3(2) Å³; Z = 2)

	$1/d_{hkl}^2$	× 10 ⁴			
<i>I/I</i> 0	obsd	calcd	h	k	l
vs	810	810	· 1	1	0
m	1515	1512	2	1	<u>1</u>
vw	1728	1729	1	0	1
S	2257	2256	2	0	1^a
vvw	2538	2540	2	0	0
w	3243	3242	2	2	0
s	3843	3835	3	2	1
w	4265	4269	2	1	ī
w	4314	4320	3	3	2
vw	4987	4971	3	1	0
w	5178	5188	2	ī	ī
vvw	6036	6049	4	2	2
vw	6455	{ 6425	4	3	3
	CO14	L0407	4	3	ž
vvw	0914	091/	2	0	$\frac{2}{1a}$
vvw	/412	7444	3	1	<u>1</u> "
vw	7767	1//28	3	0	1
		L///8 [9420	4	2	$\frac{1}{1}$
vvw	8411	18430	3	2 4	1
vvw	9031	9023	4	2	ō
vvw	9463	9457	2	$\overline{2}$	ž
vvw	9891	9884	5	3	2

^a F-only reflections; these also obey h + k + l = 3(2n + 1). The hexagonal cell has $a_0 = 4.809(4)$ Å; $c_0 = 13.076(2)$ Å; V = 261.9(5) Å³; Z = 6; V/Z = 43.65(8) Å³; c/a = 2.72.

gaseous xenon at 20 °C. The composition of this phase is not known, but lies between NiF_3 and NiF_2 .

In suspension in liquid aHF at ~ 20 °C all forms of NiF₃ are observed to evolve F₂ over several days to finally produce NiF₂:

R-, *H*-, and *P*-NiF₃
$$\xrightarrow{\text{aHF, 20 °C}}$$
 NiF₂ + $\frac{1}{2}$ F₂ (10)

the *R*-NiF₃ decomposing most rapidly and *P*-NiF₃ least. When a good F^- donor is also present (e.g. KF or XeF₆)¹⁷ in the aHF, NiF₃ is partially converted in a disproportionation reaction to the appropriate NiF₆²⁻ salt:

$$2\mathrm{NiF}_{3} + 2\mathrm{F}^{-\frac{\mathrm{aHF}, 20\,^{\circ}\mathrm{C}}{-}} \mathrm{NiF}_{6}^{2-} + \mathrm{NiF}_{2} \qquad (11)$$

but this reaction is slow, and the decomposition represented in eq 10 competes with it. The greatest yield of NiF_6^{2-} occurs with *R*-NiF₃ (approximately two-thirds of that expected for eq 11) and the least with *P*-NiF₃.

Some Oxidizing Properties of R-, H-, and P-NiF₃. An instance of both the oxidizing power of R-NiF₃ and the disproportionation reaction indicated by eq 11 is seen in the interaction of a multimolar excess of R-NiF₃ in aHF, at ~20 °C, with xenon. The xenon is oxidized, by the abundant oxidizer, to XeF₆, which, acting as a F⁻ donor (eq 11), converts the remaining R-NiF₃ to (XeF₅)₂NiF₆ and NiF₂:

$$14R-\mathrm{NiF}_3 + 2\mathrm{Xe} \xrightarrow{\mathrm{aHF}, 20\,^{\circ}\mathrm{C}} (\mathrm{XeF}_5)_2\mathrm{NiF}_6 + 13\mathrm{NiF}_2 \quad (12)$$

When excess xenon is used, all forms of NiF₃ yield XeF₂, *H*and *P*-NiF₃ reacting relatively slowly and both *R*-NiF₃ and *H*-NiF₃ also oxidize XeF₂ to XeF₄:

$$2\mathrm{NiF}_3 + \mathrm{Xe} \xrightarrow{\mathrm{aHF, 20 \ °C}} 2\mathrm{NiF}_2 + \mathrm{XeF}_2$$
(13)

⁽¹⁷⁾ Bartlett, N.; Sladky, F. O. J. Am. Chem. Soc. 1968, 90, 5316.

$$XeF_2 + 2R$$
- or H -NiF₃ $\xrightarrow{aHF, 20 \circ C} XeF_4 + 2NiF_2$ (14)

Although R-NiF₃ as a dry solid, is unable to oxidize xenon it does so when it has been exposed to HF vapor (~ 100 Torr). This reaction (to produce XeF_2), unlike the formation of XeF_2 from xenon and F₂, does proceed in the dark. The R-NiF₃ therefore behaves much more like a fluorine atom source. It is of interest that studies¹⁸⁻²¹ in the early 1960s showed that the interaction of xenon with F2 in nickel vessels occurred via a NiF_x intermediate. The red-brown nickel fluoride remaining from the R-NiF₃ reduction by xenon may have a composition Ni_2F_5 . It possesses a distinctive (but unknown) structure; see Table 4.

As expected for such a strong oxidizer, R-NiF₃ was found to be a very effective fluorinator of perfluoropropene, C_3F_6 , and even though the interaction between the solid and the C_3F_6 vapor, at ~ 20 °C, was exothermic, there was only slight carbon-carbon bond cleavage, the great bulk of the product being perfluoropropane. The interaction in aHF solution, at 20 $^{\circ}$ C, was more controlled, with no trace of CF₄:

$$CF_3 \cdot CF = CF_2 + 2R \cdot NiF_3 \xrightarrow{aHF, 20 \circ C} C_3F_8 + 2NiF_2 \quad (15)$$

A more surprising observation was the violence of the interaction of solid R-NiF₃ with solid lithium chloride, which occurred with incandescence when the solids were ground together. In aHF solution the LiCl (HCl present) reacted more placidly with each of the NiF₃ forms to release chlorine and form NiF₂. It was expected that this reaction

LiCl + *R*-, *H*-, and *P*-NiF₃
$$\xrightarrow{\text{aHF, 20 °C}}$$
 LiHF₂ + NiF₂ + $\frac{1}{2}$ Cl₂ (16)

might result in some Li⁺ incorporation into the H- or P-NiF₃ but no evidence for this was found.

Since dry acetonitrile is an effective solvent for many strongly oxidizing materials (e.g. XeF₂) it was tested for use with the nickel fluorides, but was found to be too easily oxidized to be of value. The interaction with R-NiF₃ was violent even at ~ -40 °C, but H- and P-NiF₃ interacted very slowly even at 20 °C, but with eventual reduction of the NiF₃ to NiF₂. In the instance of the reaction with P-NiF₃ this released potassium fluoride, which provided a measure of the potassium content of that fluoride (approximately $K_{0,1}NiF_3$).

The small K^+ content of both H-NiF₃ ($\sim K_{0.12}NiF_3$) and *P*-NiF₃, ($\sim K_{0,1}$ NiF₃) and the attendant requirement of that same amount of Ni^{II}, probably has an important role in the lower oxidizing power of these forms relative to R-NiF₃, in which all of the nickel is formally Ni^{III}. These K_xNiF₃ forms may also have lower solubility in the aHF and lower tendency to disproportionate than does R-NiF3, and these differences could also diminish their oxidizing potency relative to the R-NiF₃.

Structural Features in R-, H-, and P-NiF₃. The three observed forms of NiF₃ have their counterparts in other trifluorides, both those of the transition and non-transition elements.²² Since neither single crystals nor even highly microcrystalline samples of any one of the NiF₃ forms has been



Figure 1. Representation of the hexagonal close-packed F-ligand array in the R-MF₃ typified by NiF₃. M's are located in octahedral hole sites. Heavy shading of interatom connectors shows the puckered eightmembered M₄F₄ rings.

obtained, the F-atom positions and interatomic distances in the structures are not known with precision, but the rough structural outlines at least are clear.

The R-NiF₃ represents the commonly available form of a transition metal trifluoride,²³ usually made under conditions which favor the thermodynamically preferred material. In almost every first transition series case the metal atom resides in octahedral hole sites, in a nearly close-packed F-atom array²⁴ shown in Figure 1. The unit cell parameters of R-NiF₃ are not very different from those of R-CoF₃, but the formula unit volume (FUV) of 43.7 Å is smaller, and the least of any other known trifluoride except²⁵ AlF₃ (FUV = 43.6 Å³). This demonstrates that the effective nuclear charge of the metal atom in R-NiF₃ must be high. The plot of FUV for each of the first transitionseries trifluorides against atomic number is displayed in Figure 2. The simple crystal-field, d orbital configuration is displayed for each M^{III} species, and the FUV is seen to correlate well with that configuration. From ScF3 to CrF3 the FUV decreases sharply and in almost linear relationship with increase in atomic number z of M. This FUV decrease with increase in z must represent the change in effective nuclear charge at M^{III}. Evidently the t_{2g}^* electrons (which have π^* character) have little screening effect on z. With Mn^{III} and Fe^{III} the FUV increases incrementally and this must arise from impact of the antibonding- σ , e_g^* electron population, in these M^{III} species. The decrease in FUV from FeF₃ to CoF₃ is attributable to the eg* population, being the same in both, the additional electron of the Co^{III} d⁶ configuration being placed in the t_{2g}* orbital set. The absence of Jahn-Teller distortion in R-NiF3 and the value of its FUV are in harmony with a Ni^{III} species d electron configuration $t_{2g}^{*5}e_{g}^{*2}$. However the blackness of the material and the magnetic behavior (see below) could indicate a contribution from a mixed-valence formulation Ni^{II}Ni^{IV}F₆.

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Figure 2. Formula unit volume (Å³) for each of the known forms of the first-transition series trifluorides, plotted as a function of atomic number. $\Delta = R$ -MF₃, $\bullet = H$ -MF₃, and $\Box = P$ -MF₃ 491, 199 (1982). References: (R-ScF₃) Lösch, R.; Hebecker, C.; Ranft, Z. Z. Anorg. Chem. 1982, 491, 199. (R-TiF₃) Ehrlich, P.; Pietzka, G. Z. Anorg. Chem. 1954, 275, 121. (R-VF₃) Gutmaun, V.; Jack, K. H. Acta Crystallogr. 1951, 4, 244. (R-CrF₃) Jack, K. H.; Maitland, R. Proc. Chem. Soc. 1957, 232. (MnF₃, monoclinic) Hepworth, M. A.; Jack, K. H. Acta Crystallogr. 1957, 10, 345. (R-FeF₃ and R-CoF₃) ref 24. (H-VF₃ and H-CrF₃) ref 29. (H-FeF₃) ref 28. (P-FeF₃) ref 15.

Although neutron diffraction data for R-NiF₃ have been collected, the sample was not sufficiently crystalline to distinguish unambiguously between $R\overline{3}c$ and $R\overline{3}$. For high-spin electron configurations such as Ni^{III} $t_{2g}^{*5}e_{g}^{*2}$, Ni^{II} $t_{2g}^{*6}e_{g}^{*2}$, and $Ni^{IV} t_{2g}^{*4} e_{g}^{*2}$ there would in any case be only subtle differences in size, since the eg* electron population, which is the same for all, would have prime impact on effective size.²⁶ The lowspin d electron configuration for Ni^{IV} , t_{eg} ^{*6}, would surely signify a smaller Ni species, but it is not certain that the Ni-F interatomic distance in the Ni^{IV}F₆ octahedron would be very much smaller than for the high spin relative, since the FUV for R-NiF₃ is near the lower limit for known close-packed trifluorides. Even in the ruthenium and rhodium fluorides, where the MF_6 octahedra are much larger than here,²⁷ the hard-ligand nature of the F-ligand leads, via cis F-ligand repulsion, to the bridging M-F-M distances being slightly longer in the pentafluorides than in the trifluorides. In R-NiF₃, the F-F repulsive interactions must be highly resistant to further volume diminution. A low-spin Ni^{IV} species $(t_{2g}*6)$ could therefore rattle in its octahedral hole.

The *H*-NiF₃ form has the structure first described¹⁶ by Magneli for the tungsten bronzes, M_xWO_3 (M a heavier alkali metal). As with Magneli's bronzes, *H*-NiF₃ has hexagonal symmetry, as may be seen from the XRPP data in Table 3. A hexagonal tungsten bronze form has also been reported for *H*-FeF₃ derived from (H₂O)_{0.33}FeF₃ by Leblanc *et al.*²⁸ In their study of the hexagonal tungsten bronze forms of CrF₃ and VF₃, however, de Pape *et al.*²⁹ have shown that these particular materials are not hexagonal, but orthorhombic, in space group *Cmcm*, with *b/a* close to $\sqrt{3}$, and therefore pseudo-hexagonal.

Table 3. X-ray Powder Diffraction Data (Cu K α radiation, Ni filter) for the Hexagonal Tungsten Bronze Form of NiF₃ (Unit cell: $a_{\circ} = 7.074(6)$ Å; $c_{\circ} = 7.193(6)$ Å; V = 311.7(8) Å; Z = 6; V/Z = 51.95(13) Å³)

	$1/d_{hk}^2$	$_{l} \times 10^{4}$			
I/I _o a	obsd	calcd	h	k	l
s	264	266	1	0	0
S	772	773	0	0	2
w	806	799	1	1	0
vs (br)	1052	${1040 \\ 1066}$	1 2	0 0	2 0
m	1566	1573	1	1	2
m	1840	1839	2	0	2
m (br)	2019	${2006 \\ 2058}$	1 2	0 1	3 1
w	2390	2398	3	0	0
ms	3096	3093	0	0	4
ms	3179	{3171 {3197	3 2	0 2	2 0
w	3362	3359	1	0	4
vvw	3468	3464	3	1	0
m (—sh)	3943	{3892 3971	1 2	1 2	4 2
ms (+sh)	4151	${4158 \\ 4237}$	2 3	0 1	4 2
-		4263	4	0	0
w (br)	5000	5036	4	0	2
vw (br)	5469	5491	3	0	4
vw (br)	5773	5789	4	1	1
w (br)	6264	6290	2	2	4
vvw	6695	6697	2	1	5

^a For I/I_o , vs > s > ms > m > w > vw > vvw; br = broad line; \pm sh = a shoulder on the high (+) or low (-) angle side.

Table 4. X-ray Powder Diffraction Data (Cu K α radiation, Ni filter) for NiF_x (2 < x < 3) (Heavy Background and Broad Lines Indicative of Small Particle Size in Each Sample)^{*a*}

	$1/d_{hkl}^2 \times 10^4$					$1/d_{hki}^2 \times$: 104	
<i>I/I</i> _o	obsd	calcd ^b	h	k	l	<i>I/I</i> ₀	obsd	calcd ^c
s	780	772	1	0	1	-	_	744
w	1465	1468	1	0	2	-		1412
m	1634	1620	1	1	0	w	1581	1566
vs	2162	2160	2	0	0	m	2088	2088
vw	2395	2392	2	0	1			2310
vw	3187	3088	2	0	2		-	2978
vs	3712	3712	0	0	4	s	3588	3712
m.	4968	${4860 \\ 5092}$	${3 \\ 3}$	0 0	${}^{0}_{1}$	vw	4814	{4698 {4920

^{*a*} The data on the left are from the solids remaining after the thermal decomposition of *R*-NiF₃ up to 83 °C, and the data on the right are from the residue from the reaction of Xe with dry *R*-NiF₃. ^{*b*} Based on a hexagonal cell with $a_0 = 4.97(2)$ Å; $c_0 = 6.57(2)$ Å, V = 140.4 Å³; volume fits ~9 F atoms, with 4 Ni. ^{*c*} Based on a hexagonal cell with $a_0 = 5.05(2)$ Å; $c_0 = 6.71(2)$ Å; V = 148.3 Å³; volume fits ~10 F atoms with 4 Ni.

Since high-quality neutron or X-ray diffraction data have not been available so far for H-NiF₃, because of the relatively poor microcrystallinity of the samples, it has not been possible to establish beyond doubt that the H-NiF₃ is not orthrhombic, and therefore merely pseudo-hexagonal.

The structure of H-NiF₃ must be essentially as represented in Figure 3. Since the value for c_0 is 7.193(6) Å, the unit cell must involve two layers. These are probably related by a mirror plane perpendicular to c, in which the F atoms that link the octahedra along c, are placed. This allows for tilting of the octahedra, but all Ni atoms are likely to remain coplanar in each sheet, nearest-neighbor Ni atoms being $a_0/2$ (i.e. 3.537 Å) apart. The analytical data, and the KH₂F₃ recovered on reduction of H-NiF₃ with Xe, indicate that the K⁺ content, x in K_xNiF₃, \approx 0.12; only abut one third of that allowed by the structure, since

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Figure 3. Representation of a single idealized sheet of the hexagonal tungsten bronze *H*-MF₃ structure. Open circles represent the F ligands close to the plane containing the M atoms (small black spots). MF₆ octahedra represented by the squares, crossed diagonally, are tilted in the direction indicated by the short arrows. Shaded circles indicate K^+ sites at $c_0/4$ above or below the plane of the M atoms.

this could accommodate a composition $K_{1/3}NiF_3$. As the *H*-NiF₃ is formed in the aHF solution it must take HF into the hexagonal cavities as well as K^+ , since on removal of the HF from the precipitated *H*-NiF₃, the particles of that solid rapidly outgas and propel themselves about the evacuated container. The hexagonal cavities are large enough in diameter to accommodate either K^+ or HF. It is probable that in each of the hexagonal channels running parallel to *c* that the K^+ are occupying approximately one-third of the available sites in the center of the channels in the mirror planes perpendicular to *c*. An ordered distribution to maximize their separation would be expected but it is unlikely that this occupancy is correlated with that in other channels in the structure. Therefore the overall distribution would appear to be simply statistical. This fits the small hexagonal unit cell.

If the *H*-NiF₃ is truly hexagonal, the tilting of the octahedra will be as indicated by the arrows in Figure 3. If the octahedra are regular, the a_0 and c_0 dimensions give us both the tilt angle (t) and the Ni-F interatomic distance, since $c_0 = [4 \times \text{Ni}-\text{F}]$ distance $\times \cos t$] and $a_0 = [\sqrt{2} \times \text{Ni}-\text{F}]$ distance $\times (1 + \sqrt{3} \cos t)$]. This requires $t = 17.60^\circ$ (i.e. a Ni-F-Ni bridging angle along c of 145°) and Ni-F = 1.887 Å. Some distortion of the octahedra probably occurs, therefore, these values are only a rough assessment. Indeed, the careful X-ray powder diffraction study of Jack and his co-workers²⁴ had found for *R*-FeF₃ and *R*-CoF₃, the interatomic distances Fe-F = 1.92 and Co-F = 1.89 Å, therefore a somewhat smaller average value than 1.887 Å might be anticipated for Ni-F in each of the NiF₃ forms.

The change in structure from *R*-NiF₃ to *H*-NiF₃ results in a FUV increase of 8.3 Å³, (comparison of Figures 1 and 3 reveals the close ligand packing in *R*- and its absence in *H*-NiF₃) this being associated with the open hexagonal channels of *H*-NiF₃, of effective dinner close to 2.6 Å. This poorly packed arrangement probably arises from the advantageous lattice energy associated with incorporation of xK^+ in the channels, these compensating for additional Ni^{II} over the mixed-valence requirement, in the NiF₃^{x-} network. Dielectric screening of the K⁺ by HF molecules also incorporated into the channels, must further benefit the energetics. It is seen in Figure 2 that this



Figure 4. A tetrahedral cluster of MF_6 octahedra, representative of the *P*-NiF₃ structure. All Ni are linked through F bridges to other Ni in Ni₃F₃ rings. Open hexagonal channels (at ~109° 28' to one another) run through the structure and in *P*-NiF₃ are partially occupied by K⁺.

FUV increase, of *H* over *R* forms, is typical of that reported for other first transition series trifluorides, and it is also seen that the trend in *H*-MF₃ FUV, across the period, is the same as for *R*-MF₃. Although the Ni species in *R*- and *H*-NiF₃ are each octahedrally coordinated by F ligands and each F ligand is shared (bridges) with two Ni species, the structures differ greatly. In the close-packed *R*-NiF₃, the octahedra are linked through bridging F ligands, in 8 membered Ni₄F₄ rings (alternating Ni and F) as seen in Figure 1. As shown in Figure 3 NiF₆ octahedra in *H*-NiF₃ are linked by corner sharing in the *ab* plane, in 3–fold sets. All Ni species in the *ab* plane are therefore in six-membered Ni₃F₃ rings with alternating Ni and F. It is this closer grouping of the octahedra in *H*-NiF₃ that provides for the "open" hexagonal channels that run parallel to *c*.

For the *P*-NiF₃, the clustering of octahedra of NiF₆ is in tetrahedral sets, illustrated in Figure 4. The unit cell must be similar to that of the cubic pyrochlore described for *P*-FeF₃ by dePape *et al.*¹⁵ It is also similar in size to the cell described³⁰ by Cowley and Scott for a hydroxy aluminum fluoride. In such a structure the Ni species are each connected via F ligands to neighboring Ni species in six-membered rings, like those of the networks in *H*-NiF₃ perpendicular to *c*. Because of the small K⁺ content, Ni^{II} must be present in like concentration. If there is a mixed-valence contribution to the *P*-NiF₃, the Ni^{II} will exceed the Ni^{IV} by that same amount. It is not known if there is any ordering of the positioning of these different Ni species. Such ordering could be responsible for the slight departure from cubic symmetry.

The Magnetic Behavior of *R***-**, *H***-**, **and** *P***-NiF**₃. In all three forms of NiF₃, field dependence of the magnetic susceptibility is observed but the ordering temperature below which this occurs is dramatically different, see Figure 5, being ~ 250 K in *R*-NiF₃ but ~ 120 K in *H*-NiF₃ and only ~ 50 K in *P*-NiF₃. This is very like the change in the three-dimensional ordering temperature observed by Ferey and his co-workers,³¹ for the three forms of FeF₃, where the transition temperatures are *R*-FeF₃, 365 K; *H*-FeF₃, 110 K; and *P*-FeF₃, 20 K.

In *R*-NiF₃ like *R*-FeF₃, each metal center is linked by bridging F ligands in eight-membered rings, as illustrated in Figure 1. For the high-spin d⁵ configuration of Fe^{III}, the strong antiferromagnetic coupling, predicted by Goodenough's rules,³² accounts for the observed high magnetic ordering temperature.

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Figure 5. Magnetic susceptibility data at two fields (Δ 5 kg, \blacksquare 40 kg) as a function of temperature (K) for (a) *R*-NiF₃, (b) *H*-NiF₃, and (c) *P*-NiF₃ (a Curie-Weiss plot).

The strong field dependence is due to the canting of the Fe^{III} spins, as established by Ferey and his co-workers.³¹

The qualitative similarity of the magnetic behavior of *R*-NiF₃ to *R*-FeF₃ suggests antiferromagnetic coupling of Ni^{III} species of configuration $t_{2g}s_{eg}^{*2}$, at temperatures below ~250 K, these canted magnets producing the observed field dependence. A mixed-valence formulation Ni^{II} $t_{2g}s_{eg}^{*2}$, Ni^{IV} $t_{2g}s_{eg}^{*0}$ could also contribute, but by itself would merely provide for weak ferromagnetism akin to that discussed³³ by Tressaud and Dance for Pd^{II}Pd^{IV}F₆ and Pt^{II}Pt^{IV}F₆ (the second^{34,35} and third^{36,37} transition series analogues of Ni^{III}Ni^{IV}F₆) where the T_c values are 10 and 16 K, respectively. The magnetic behavior of a high-spin mixed-valence formulation, Ni^{II} $t_{2g}s_{eg}^{*2}$, Ni^{IV} $t_{2g}s_{eg}^{*2}$ would be qualitatively like that of high spin Ni^{III}. But in this case the field dependence below the magnetic ordering temperature would result from the ferrimagnetism deriving from these antiferromagnetically coupled mixed-valence configurations.

The evidence for antiferromagnetically coupled high-spin Ni^{III} being the dominant species in these fluorides is more decisively made by the behavior of *H*- and *P*-NiF₃.

Because, in *H*-NiF₃, the Ni species, in the *ab* plane, are linked via F-ligand bridges to four other Ni species, but always in sixmembered Ni₃F₃ rings (see Figure 3), the antiferromagnetic coupling in these *ab* plane rings must be highly frustrated, as discussed for the general case by Ferey *et al.*³⁸ As a consequence of this, the only antiferromagnetic coupling of the Ni^{III} $t_2g^5e_g^{*2}$ species that would be effective, would be that parallel to *c*. Such a coupling situation occurs^{31,39} in *H*-FeF₃, which exhibits much weaker antiferromagnetic coupling $(T_N = 110 \text{ K})$ than *R*-FeF₃ $(T_N = 365 \text{ K})$. The magnetic behavior of *P*-NiF₃ is also consistent with frustrated coupling of Ni^{III} high-spin species.

As is shown in Figure 5c, by the nearly Curie–Weiss dependence of the reciprocal of susceptibility on temperature, the *P*-NiF₃ is almost a simple paramagnet, field dependence being apparent only below 50 K. This is in accord with the highly frustrated situation associated with antiferromagnetic coupling of Ni species in a pyrochlore structure. The magnetic frustration occurring in the *ab* planes of *H*-NiF₃, is everywhere present in the *P*-NiF₃. This is a consequence of the tetrahedral clustering of the octahedra as illustrated in Figure 4, since each Ni species is now linked to each of its six nearest Ni neighbors, as a component of a six-membered Ni₃F₃ ring.

The magnetic properties of all three forms of NiF₃ are therefore seen to be consistent with high-spin Ni^{III} t_{2g} ⁵ e_g ^{*2} species, although some contribution from mixed-valence Ni^{II}-Ni^{IV}F₆ cannot be ruled out.

Experimental Section

A. Apparatus and Technique. A metal vacuum line, fluorine handling equipment, bomb reactors, and valves were as previously described.⁴⁰ In the experimental work involving aHF, the apparatus was constructed from FEP tubing (CHEMPLAST, Inc., Wayne NJ 07470). The commonly used reactor was constructed from two $1/_2$ in. o.d. FEP tubes, each drawn down to $3/_8$ in. o.d. on one end and sealed at the other. These were joined at right angles by a Teflon Swagelok T compression fitting and joined to a Teflon valve (previously described⁴⁰) by a small section of $3/_8$ in. tubing drawn down to $1/_4$ in. i.d. This entire T-shaped assembly was connected to the gas handling and vacuum system via ~1 ft length $1/_4$ in. o.d. FEP tubing. This facilitated the decanting of the aHF solutions, from one tube to that at right angles to it in the T-assembly. The T-reactors were passivated with F₂ (~2 atm) for several hours, then evacuated before use.

Washing of precipitates, to dissolve aHF - soluble salts, was achieved by back distilling the aHF from the decanted solution, under static vacuum, to the limb containing the precipitate, cooled to -196 °C. The precipitate was mixed, by agitation, with the aHF at a suitable temperature for the washing, and the solution, because of the low surface tension of the aHF solution was usually cleanly decanted into the other limb. This back-distillation and washing could be repeated as many times as needed. All solid starting materials and products were handled in the dry argon atmosphere of a Vacuum Atmosphere DRILAB.

X-ray powder patterns (XRPP) and IR and Raman spectra were obtained as previously described.^{40,41}

Magnetic Susceptibility. Magnetic susceptibility data were obtained on a SQUID magnetometer with a gaseous He cooling jet. The cylindrical sample container, of length 0.8 in. and diameter 0.16 in.,

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Table 5

quired weight for the stated solid products mg	

starting weight of		observed weight for			
K ₂ NiF ₆ , mg (mmol)	(1) $KNiF_5 + KBF_4$	(2) $KNiF_4 + KBF_4$	$(3) \operatorname{NiF}_4 + 2 \operatorname{KBF}_4$	(4) $NiF_3 + 2KBF_4$	the solid product, mg
(a) 383.3 (1.53)	487.6	457.9	591.4	561.5	559.2
(b) 527.5 (2.10)	669.3	630.1	811.7	772.7	761.1

consisted of a Kel-F base with a threaded neck and a screw-in cap. Inside the DRILAB, a known quantity of material was packed into the bucket with a Kel-F packing tool. The screw cap was then tightened down with an aluminum screwdriver to achieve an air-tight seal. The container was immediately transported to the magnetometer, where it was suspended in the He atmosphere by a cotton thread. Prior to their use with the nickel fluorides, both the SQUID container and the packing tool were passivated with ~2 atm of F₂ for 12 h.

B. Materials. K₂NiF₆ (Ozark-Mahoning Pennwalt) was heated in F_2 (20-30 atm) at 300 °C for 1-2 days in a copper-gasket Monel bomb. To extract KF impurity from the K₂NiF₆, enough aHF ($\sim 4-5$ mL) was added to K_2NiF_6 (~2-3 g) in an FEP T-reactor, to dissolve all of it. This solution was reduced to ~ 0.5 mL by vacuum removal of aHF and was then decanted from the crystallized K₂NiF₆. This was repeated twice, and then the K₂NiF₆ was dried under a dynamic vacuum. To remove any insoluble phase from the K₂NiF₆, the tube containing the KF-free K₂NiF₆ was placed on a second Teflon T-reactor with a $5-10 \mu$ porous Teflon filter (Berghof-America) inserted in the neck of the "T". The K₂NiF₆ was dissolved in aHF, any insoluble material being allowed to settle to the bottom of the tube, following which the solution was decanted through the filter to the other arm of the reactor. Removal of aHF gave a XRPP of the solid entirely attributable to K_2NiF_6 (yield ~1.5-2 g). BiF₅ (Ozark-Mahoning Pennwalt) was fluorinated under the same conditions as the K2NiF6, and then recrystallized from aHF following decantation of the solution from any insoluble material. BF3 (Matheson) was used as supplied.

C. Preparation of NiF₄ and Evidence for its Composition. NiF₄ from K_2NiF_6 with BF₃. Solutions of K_2NiF_6 in aHF at -78 °C were exposed to BF3 until the solutions no longer took up the gas. The aHF and remaining BF3 were removed under dynamic vacuum at -45 °C to leave a tan solid mixed with a colorless solid. The mixture of solids was warmed to room temperature. This produced fluorine gas and the tan solid became black. Residual solids were weighed. XRPP of the solids revealed KBF4 and either an amorphous or poorly crystalline P-NiF₃ (q.v.) phase. Two reactions were followed gravimetrically as shown in Table 5. Washing with aHF at ~ 20 °C extracted the KBF₄ to leave poorly crystalline P-NiF₃. NiF₄ from (Xe₂F₁₁)₂NiF₆ with AsF₅. $(Xe_2F_{11})_2NiF_6$ prepared as previously described¹² was dissolved in aHF. AsF₅, measured out tensimetrically, was slowly admitted via a Teflon valve to the red solution at -65 °C. Three separate experiments gave essentially the same observations as described under Results and Discussion.

D. Synthesis of *R*-NiF₃. K₂NiF₆ with BF₃. K₂NiF₆ (790 mg; 3.15 mmol) was dissolved in aHF (4–5 mL) in one arm of an FEP T-reactor, which was cooled to 0 °C. A 2-fold molar excess of BF₃ (measured out tensimetrically) was added to the solution over a span of 2 h. A tan precipitate of NiF₄ settled to the bottom of the reactor, below a clear, slightly yellow-tinted solution. The tan color changed to black as F₂ evolved. Decomposition was considered to be complete when F₂ evolution had ceased (~2 h). The byproduct, KBF₄, was extracted by decantation of its solution in aHF at 0 °C followed by back distillation of the aHF and further washing at 0 °C under dynamic vacuum. This yielded black *R*-NiF₃ (346 mg, 2.99 mmol, 95% yield), represented by the XRPP given in Table 2.

K₂NiF₆ with BiF₅. K₂NiF₆ (309 mg; 1.23 mmol) was loaded into one arm of an FEP T-reactor and BiF₅ (754 mg; 2.48 mmol) into the other. Each reactant was dissolved in aHF (\sim 3 mL each). Both solutions were cooled to 0 °C. The solution of BiF₅ was decanted dropwise into the solution of K₂NiF₆ to precipitate tan NiF₄. When the addition was complete, the supernatant solution was colorless, and the tan color slowly changed to black over 6 h, at 0 °C, with evolution of F₂. Cessation of F₂ evolution signaled completion of the reaction. The byproduct, KBiF₆ was extracted by decantation of its aHF solution at 0 °C (with two back-distillations and washings) and the black residue was dried at 0 °C under dynamic vacuum. This gave R-NiF₃ (142 mg; 1.23 mmol, 99% yield).

E. Synthesis of *H*-NiF₃. The preparation of the hexagonal tungsten bronze form of NiF₃ (designated *H*-NiF₃) involved essentially the same experimental conditions as for the *R*-NiF₃ except that for *H*-NiF₃, the preparation temperature was \sim 20 °C, with slow addition of the acid.

K₂NiF₆ with BF₃. K₂NiF₆ (595 mg; 2.37 mmol) in aHF (4-5 mL) gave 225 mg of nearly black solid, characterized by the XRPP in Table 3 as H-NiF₃ (82% yield).

K₂NiF₆ with BiF₅. K₂NiF₆ (351 mg; 1.40 mmol) and BiF₅ (860 mg; 2.83 mmol), each reactant in aHF (\sim 3 mL) gave 160 mg *H*-NiF₃ (from XRPP in Table 3), a yield of 98%.

F. Synthesis of P-NiF₃. Purified K₂NiF₆ (856.7 mg; 3.41 mmol) in one arm of an FEP T-reactor was dissolved in aHF (8 mL), cooled to -65 °C, and a 2-fold molar excess of BF₃ added to the solution, at that temperature, over 2 h, tan NiF₄ precipitated, the supernatent solution having a pale-yellow tint. The BF3 was removed at -65 °C and the aHF solution became turbid brown as the BF3 was removed. The bulk of the aHF was taken off under dynamic vacuum, at or below -50 °C, over a period of 24 h and to ensure complete aHF removal the temperature was raised to -45 °C for 3 h. The dry solid which resulted was warmed at a rate of ~1 °C per hour over 88 h, to 24 °C. The solid product was dark brown. F_2 (formed from the decomposition of NiF₄) was removed and aHF (8 mL) was added. KBF₄ was extracted at -30 °C with seven washings with the aHF (back-distilled). The brown (nearly black) trifluoride, KBF4 free (XRPP), was characterized by the rhombohedral XRPP (nearly cubic) represented in Table 1, with $a_0 = 9.933(3)$ Å, $\alpha = 9101(3)$, indicative of a pyrochlore type structure, yield P-NiF₃ = 294.9 mg, i.e. 2.47 mmol K_{0.1}NiF₃, 72% yield.

G. Preparation of R- and H-NiF₃ from $Ni(MF_6)_2$ (M = As, Sb, Bi) + K_2NiF_6 in aHF. Ni(MF₆)₂, prepared by dissolving NiF₂ in aHF containing 2 equiv of MF₅ (M = As, Sb, Bi) at 20 °C, was in each case highly soluble in aHF and gave a yellow solution. The Ni(MF₆)₂ salt was loaded in one arm of a T-reactor and an equimolar quantity of purified K₂NiF₆ in the other. The solution of Ni(MF₆)₂ in aHF was poured slowly into a solution of the K₂NiF₆, to produce a black precipitate. When the solutions had been completely mixed the supernatant solution was colorless. When the mixing was carried out slowly at 0 °C the predominant phase was R-NiF3 and when done at 20 °C H-NiF₃ was the major product. The NiF₃ product was in each case washed with back-distilled aHF at 0 °C to minimize NiF2 production. Example: Ni(AsF₆)₂ (1330.3 mg; 3.048 mmol) + K_2NiF_6 $(764.6 \text{ mg}; 3.048 \text{ mmol}) \rightarrow 2H\text{-NiF}_3 \text{ (found: } 700.8 \text{ mg}; 6.058 \text{ mmol})$ + 2KAsF₆ (slightly contaminated by *H*-NiF₃ transferred in the multiple decantations).

H. Thermal Decomposition of *R*-, *H*-, and *P*-NiF₃. *R*-NiF₃. The release of F_2 from *R*-NiF₃ on heating was detected by the formation of I_2 from KI. The KI was incorporated into a column made from 1/4 in. FEP tubing containing a section of NaF (~1 in.) followed by KI (~12 in.), held in place with a plug of quartz wool at each end. This column was evacuated to 10^{-7} Torr before use. The sample was placed in a small Pyrex glass tube connected to this column, heated in an oil bath, with the column opened slightly to a dynamic vacuum. A yellowing of the column occurred near 39 °C, which intensified and coincided with the black solid becoming brown. Rapid formation of I_2 at 52-53 °C signaled major decomposition of the *R*-NiF₃ at that temperature. No further major I_2 release occurred to 83 °C. The remaining solid was dark red-brown and was characterized by low crystallinity (XRPP tabulated in Table 4). This resembles the material remaining after the interaction of solid *R*-NiF₃ with a molar excess of Xe gas (q.v.).

H-NiF₃. The pyrolysis of *H*-NiF₃ was examined similarly. No F_2 was observed until ~72 °C, and that was slight. Much F_2 was formed at ~103 °C, and was especially abundant at 135 °C.

*P***-NiF₃**. F₂ release from *P*-NiF₃ was not seen until \sim 138 °C at which temperature the dark brown solid became lighter in color.

I. Decomposition in aHF at ~20 °C. *R*-NiF₃. When prepared from K₂NiF₆ with BF₃ at 0 °C, the decomposition of *R*-NiF₃ in aHF, at 20 °C, was usually complete within 24 h, but in the instance of the *R*-NiF₃ precipitated by a stoichiometric quantity of BiF₅ the decomposition was much slower as follows: aHF (1.5 mL) agitated with *R*-NiF₃ (83.2 mg; 0.72 mmol) showed little evidence of change for 2 days, but after 9 days, the entire sample was pale tan in color. Highly crystalline NiF₂, identified by XRPP (71.5 mg; 0.74 mmol) was recovered.

H-NiF₃. *H*-NiF₃ (68.7 mg; 0.59 mmol if NiF₃) in aHF (3 mL) became red-brown after 8 days and pale tan after 15 days. The supernatant aHF solution was decanted from the tan residue. XRPP showed it to be NiF₂ (57.3 mg; 0.59 mmol).

P-NiF₃. *P*-NiF₃ (15.8 mg) held at 20 °C in aHF for 10 days gave a colorless supernatant over a yellow-brown solid. The decantate and washings from the yellow-brown NiF₂ (XRPP) on removal of aHF gave KH₂F₃ (1.7 mg) from which the K content of the *P*-NiF₃ is 0.68 mg, indicating composition K_{0.13}NiF₃. The *P*-NiF₃ (0.131 mmol of K_{0.13}NiF₃) should yield 0.131 mmol of NiF₂, 12.6 mg. Found "NiF₂", 13.6 mg.

J. Analysis of NiF₃. Analysis of R-NiF₃. The major difficulty associated with the analysis of samples of R-NiF₃ (most of which were prepared from K₂NiF₆) lay in the removal of the K⁺ salts generated simultaneously with the R-NiF3. Washing with aHF at $\sim 20~^\circ C$ to remove these salts was advantageous in that the K⁺ salt solubility was greater at this temperature than at 0 °C, but the rate of decomposition to F₂ and lower fluoride was also greater at the higher temperature. The R-NiF₃ was therefore usually washed at 0 °C, but removal of the salts was then slow. The complete removal of the salts was often associated with some NiF2 production (as revealed by XRPP). Removal of salts was greatly aided by bringing the entire reaction product (R-NiF₃ and KX) to dryness before washing with aHF. (This probably crystallized K^+ and X^- adsorbed on the R-NiF₃.) For samples for analysis, care was taken to minimize the NiF2 formation, but KX salt removal was in such instances rarely complete. R-NiF₃ (prepared from K₂NiF₆ and BF₃, with XRPP showing only the lines of the rhombohedral phase). Found: F, 49.7, 49.9; Ni, 48.6, 48.6; K, 0.4; B 1.6%. NiF₃, plus 0.04KBF₄ impurity, requires: F, 49.7; Ni, 48.6, K, 1.3; B, 0.4%. NiF₃ requires: F, 49.3; Ni 50.7%. The low K and high B content could signify some NiF BF4 impurity in the case of this analyzed sample but the presence of such an impurity was not otherwise indicated.

Note on Analysis of the *H*- and *P*-NiF₃ Solids. Conventional analysis of the "trifluoride" forms prepared in the presence of potassium salts proved to be ambiguous because of the frequent presence of occluded K⁺ salts (KBF₄, KAsF₆, etc.) produced on addition of the F⁻ acceptor (BF₃, AsF₅, etc.) to the aHF solution of K₂NiF₆. It was found that a more reliable indicator of the K⁺ present in the hexagonal channels of the *H*- or *P*-NiF₃ was given by the formation of KH₂F₃ (highly soluble in aHF) as the trifluoride was reduced. Three sets of observations were employed for this: (1) the decomposition of the trifluoride with xenon (faster); and (3) the reduction of the *P*-NiF₃ with CH₃CN (moderately fast).

Analysis of H-NiF₃. This material decomposed less quickly in 20 °C aHF and was therefore more easily washed than R-NiF₃. Found: F, 47.1; 47.0; Ni, 48.3; 48.3; K 4.07; B, 0.62%. H-NiF₃ (contaminated with 0.0074 mmol KBF₄ impurity) having a composition $K_{0.12}$ -NiF₃·0.0074KBF₄, requires: F, 47.4; Ni, 48.4; K, 4.09; B, 0.07%.

K. Some Chemical Reactions of *R*-, *H*-, or *P*-NiF₃. 1. Interaction of *R*-, *H*- and *P*-NiF₃ with CH₃CN at ~20 °C. R-NiF₃. CH₃-CN was condensed onto the dry *R*-NiF₃ at -196 °C and as it thawed (~-45 °C) it reacted exothermically to give NiF₂ and fluorination products of the CH₃CN.

H-NiF₃. The solid reacted slowly with CH₃CN at \sim 20 °C over 30 min to give a paler solid (NiF₂).

P-NiF₃. *P*-NiF₃ (59.1 mg) was stirred in contact with CH₃CN for 30 min and the solid rapidly became yellow-green (NiF₂ by XRPP) as the CH₃CN was oxidized. Remaining CH₃CN and volatile oxidation products were removed under dynamic vacuum and the residual solid was washed with aHF to extract KH₂F₃. The yield of KH₂F₃ (by XRPP) 4.0 mg signified 0.041 mmol, 1.59 mg of K⁺ in the *P*-NiF₃ and a composition $K_{0.08}NiF_3$.

2. Interaction of dry R-, H-, and P-NiF₃ with gaseous Xe at \sim 20 °C. Dry R-, H-, and P-NiF₃ do not interact with gaseous Xe at 20

Table 6. Results of the Interaction of R-, H-, and P-NiF₃ with Xe in aHF, at $\sim 20 \text{ °C}^a$

	_		$R-NiF_3$			
reacta	nts		prod	ucts		
R-NiF3 Xe 108 (0.93) (0.2)		Xe product	KH ₂ F ₃ product	N	JiF _x	
		41, XeF ₄ (0.2)	none	95 obs (0.8NiF ₂) + 92.4	$(0.13 \text{NiF}_3) =$	
			H-NiF3			
	reacta	ants		products		
H-Nil	F ₃	Xe	$\overline{\text{XeF}_2 + \text{KH}}$	$_{2}F_{3} + KBF_{4}$	NiFx	
180		excess	93	93.2		
			P-NiF3			
	read	ctants		products		
P-NiF ₃			5, XeF ₂	3, KH ₂ F ₃	NiF ₂ yield	
23.3	mu	ltimolar exce	ss (0.03)	(0.031)	no recorded	

^a Quantities not in parentheses are in milligrams; quantities in parentheses are in millimoles.

°C, but if *R*-NiF₃ is first exposed to HF vapor (100 Torr) it is converted within a few hours to a homogeneous light red-brown solid in an exothermic interaction with a multimolar excess of Xe (~1 atm). (This reaction even proceeds in the dark.) XeF₂ was identified by IR⁴² and XRPP⁴³ as the oxidation product. The XRPP of the light red-brown nickel fluoride showed a broad line pattern like that from the thermal decomposition of NiF₃ at 83 °C (q.v.) given in Table 4.

3. Interaction of R-, H-, and P-NiF₃ with Xe in aHF, at ~20 °C. The trifluoride in suspension in aHF (typically 2.5 mL) in one arm of a T reactor was agitated with a known quantity of gaseous xenon for ~8 h. In each case the trifluoride was converted to a tan solid. Colorless soluble products were obtained by decanting the aHF solution to the other arm, aHF being removed under vacuum at -50 °C. Results are in Table 6.

Assuming the composition from the analysis for H-NiF₃ i.e. $K_{0.12}$ NiF₃·0.0074KBF₄: there are 1.484 mmol of H-NiF₃. There must be 1.484 mmol of NiF_x in the product, which must therefore have a composition NiF_{2.16}. Neglecting loss of F₂ by decomposition of the H-NiF₃ in the aHF, the yield of XeF₂ is expected to be 0.534 mmol = 90.4 mg. Expected KH₂F₃ = 17.5 mg and KBF₄ = 0.9 mg. Total XeF₂ + KH₂F₃ + KBF₄ = 108.8 mg. Results are in Table 6.

Since 23.3 mg of P-NiF₃ contain 1.20 mg of K (based on 0.031 mmol of KH₂F₃), the empirical formula is K_{0.16}NiF₃ (formula weight 122.05). Results are in Table 6.

Excess R-NiF₃. Introduction of Xe to a multimolar excess of *R*-NiF₃ suspended by agitation in aHF at ~20 °C produced a red solution which deepened in color as Xe was introduced [but the Xe added was always much less than required for $2Xe + 14NiF_3 \rightarrow (XeF_5)_2NiF_6 + 13 NiF_2$] and removal of aHF yielded red crystals of $(XeF_5)_2NiF_6$ (by XRPP).¹² When slightly larger xenon quantities were used than required for $(XeF_5)_2NiF_6$ formation, the evaporation of the red aHF solution also gave high purity XeF₄ (XeF₂ and XeF₆ absent).

L. Reaction of R- or H-NiF₃ with XeF₂ in aHF. R-NiF₃. A solution of XeF₂ in aHF at ~20 °C added quickly to an equivalent quantity of R-NiF₃ under aHF at ~20 °C, with agitation, produced a tan solid in less than 6 h. Decantation of the colorless supernatant aHF solution followed by washing left a tan solid (XRPP indicating NiF₂) and evaporation of aHF from the combined decantate and washings at ~-40 °C yielded a nearly colorless sublimable solid identified⁴³ (XRPP) as XeF₄.

H-NiF₃. 1. XeF₂ (67 mg; 0.40 mmol) in aHF (2.5 mL) added to H-NiF₃ (92 mg; 0.80 mmol) with vigorous stirring, resulted in the black H-NiF₃ becoming a red-brown solid in ~50 min. The colorless supernatant and three washings yielded, on removal of aHF at -47 °C a nearly colorless solid identified⁴³ by XRPP as XeF₄ (66 mg; 0.32 mmol). The XRPP of the reddish-brown residue showed it to contain

⁽⁴²⁾ Yeranos, W. A. Mol. Phys. 1967, 12, 529.

⁽⁴³⁾ Siegel, S.; Gebert, E. J. Am. Chem. Soc. 1963, 85, 240.

Table 7. Results of the Interaction of R-, H-, or P-NiF₃ with aHF Solutions of KF^{α} R-NiF₃

react	tants		products		
R-NiF ₃	KF	NiF ₂	K ₂ NiF ₆	+	KH ₂ F ₃
1.109	56	59 observed	104 observed		
(0.94)	(0.96)	(0.61)	(0.33)		(0.30)
			82.8		29.4
			112.2 required		
2.97.2	53.7	47.8 observed	107.4 observed		
(0.84)	(0.92)	(0.497)	(0.343)		(0.234)
` '	· · /		85.96		22.96
			108.9 required		

H-NiF₃

react	tants		pro	duct	:s		
H-NiF3	KF	NiF ₂	K_2NiF_6	+	KH ₂ F ₃	+	KBF ₄
1. 136.3	75.3	99.9 observed	135.4 observed				
(1.123) ^b	(1.296)	(1.033)	(0.090) 22.6 146.2 required		(1.250) 122.6		(0.0083) 1.0
2. 151.9	86.9	110	164.7 observed				
(1.252) ^b	(1.498)	(1.138)	(0.114) 28.6 169.1 required		(1.420) 139.3		(0.0093) 1.2
			P-NiF3				
rea	actants		р	rod	ucts		
P-NiF ₃	K	F NiF ₂	K ₂ N	liF ₆	+		KH ₂ F ₃
92.7 (0.760) [•]	c 70.9 c (1.2	65.2 20) (0.674	149.7 of 4) (0.086) 21.6	oser	ved		(1.170)

^{*a*} Quantities no in parentheses are in milligrams; quantities in parentheses are in millimoles. ^{*b*} $K_{0.12}$ NiF₃·0.0074KBF₄ from analysis. ^{*c*} $K_{0.16}$ NiF₃ composition from reduction with Xe in aHF.

136.3 required

 NiF_2 (82 mg; 0.85 mmol) although the color and gravimetry indicated a higher F content.

2. XeF₂ (48 mg; 0.28 mmol) and *H*-NiF₃ (130 mg; 1.12 mmol) were loaded into opposite arms of a reactor and aHF (2.5 mL) was condensed onto the XeF₂, and the resulting solution poured onto the *H*-NiF₃. After 1 h, the black solid had become reddish-brown. Removal of aHF below -39 °C gave an almost colorless residue (XRPP indicated XeF₄, 46 mg; 0.22 mmol). The XRPP of the reddish-brown residue (121 mg) showed *H*-NiF₃ and NiF₂. Required for 0.56 mmol NiF₂, 54 mg; and (0.56 mmol) *H*-NiF₃, 67.9 mg; total 122.1 mg.

M. Interaction of R-, H-, or P-NiF₃ with aHF Solutions of KF. A known weight of the trifluoride (R, H, or P) was combined with an approximately equimolar quantity of KF, accurately weighed; aHF (\sim 2 mL) was added and the mixture agitated for a period of one to several days at ~20 °C. In all cases K_2NiF_6 formation was signaled by the red coloration of the aHF and this was confirmed subsequently for the solid product by gravimetry which also indicated KH_2F_3 and NiF_2 . The K_2NiF_6 and KH_2F_3 were separated from the NiF_2 by decantation of their aHF solution, with several washings. It was observed that the R-NiF₃ produced K_2NiF_6 the reaction being effectively complete in 1 day. H-NiF₃ and P-NiF₃ produced the K_2NiF_6 much more slowly, the intensity of the solution color growing steadily over two or more days. The results are shown in Table 7.

N. Oxidation of LiCl by *R*- or *H*-NiF₃. *R*-NiF₃. When an equimolar mixture of *R*-NiF₃ and LiCl were ground together in an agate mortar in the Drilab they interacted with incandescense, the yellow green product being (XRPP) a mixture of NiF₂ and LiF. The interaction was much more controlled when an aHF solution, at 0 °C, of LiCl was added slowly to *R*-NiF₃ under aHF (at 0 °C). Fast evolution of Cl₂ was accompanied by simultaneous conversion of the *R*-NiF₃ to a yellow green solid (NiF₂ by XRPP).

H-NiF₃. LiCl (46.2 mg; 1.09 mmol) in the side arm of a T-reactor was transferred in aHF (~ 2 mL) to *H*-NiF₃ (112.7 mg; 0.974 mmol) in the main tube and the mixture stirred at ~ 20 °C. Cl₂ gas was rapidly evolved and the nearly black NiF₃ quickly changed to a yellow green solid. The latter was recovered by decantation of the aHF solution into the other tube and was washed several times by back-distillation of the aHF in the usual manner. Removal of aHF and Cl₂ under dynamic vacuum at ~ 20 °C left the yellow green product (XRPP showed NiF₂, 100.8 mg; 1.04 mmol) in the main tube and in the other a colorless solid, XRPP of which showed LiHF₂ with some LiF (48.3 mg; required for 1.09 mmol of LiHF₂ = 50.1 mg).

O. Oxidation of C_3F_6 by *R*-NiF₃. *R*-NiF₃ exposed to C_3F_6 (less than half the molarity of the trifluoride) at 20 °C rapidly interacted in an exothermal reaction in which the black trifluoride was rapidly reduced to a tan solid (NiF₂ present by XRPP). IR spectra showed the gaseous product to be perfluoropropane, C_3F_8 with only a trace of CF₄ present. A similar quantitative conversion of C_3F_6 to C_3F_8 also occurred with the *R*-NiF₃ suspended in aHF but in this instance CF₄ was not observed.

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