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Thermodynamically Unstable Fluorides of Nickel: NiF_4 and NiF_3 Syntheses and Some Properties[§]

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Abstract: F^- acceptors (BF_3, AsF_5, SbF_5, or BiF_5) added to solutions of NiF_6^{2-} salts in anhydrous hydrogen fluoride (aHF) below -65 °C precipitate the tan solid NiF_4. This solid, preserved at ≤ -65 °C, is quantitatively converted, by 2 equiv of F^- donor (XeF_6 or KF) in aHF, to dissolved NiF_6^{2-}. Dry NiF_4 loses F_2 above -60 °C, the decomposition to nearly black NiF_3 becoming rapid at ~ 0 °C. When the dry NiF_4 is prepared from K_2NiF_6, inclusion of some K^+ leads, on thermolysis at 0 °C, to a pyrochlore form of NiF_3 (P-NiF_3). P-NiF_3 contains K^+ in the open channels, with K_xNiF_3, $x \approx 0.1$. The nearly cubic P-NiF_3 unit cell is rhombohedral: $a_0 = 9.933(3)$ Å, $\alpha = 91.01(3)°$, $V = 980$ Å^3, $z = 16$, with absent reflections coincident with those of the cubic space group O_h^7-$Fd3m$, appropriate for pyrochlore. Decomposition of NiF_4 in aHF begins at -65 °C and is rapid at 0 °C, giving black rhombohedral NiF_3 (R-NiF_3) with $a_0 = 5.168(2)$ Å, $\alpha = 55.46(3)°$, $V = 87.3$ Å^3, $z = 2$. When the NiF_4 is made and decomposed at ~ 20 °C, with K^+ present, a hexagonal tungsten bronze form of NiF_3 is precipitated (H-NiF_3), with $a_0 = 7.074(6)$ Å, $c_0 = 7.193(6)$ Å, $V = 312$Å^3, $z = 6$. R- and H-NiF_3 can also be made by mixing solutions of Ni^{2+} salts [e.g., $Ni(AsF_6)_2$] with NiF_6^{2-} salts (e.g. K_2NiF_6) in aHF. All forms of the trifluoride (R, H, and P) lose F_2 on warming ($R > 39°$, $H > 72°$ and $P > 138$ °C) to yield NiF_2, but an intermediate red-brown phase is observed for R-NiF_3. R-NiF_3 at ~ 20 °C, oxidizes Xe to Xe(VI), perfluoropropene, C_3F_6, to perfluoropropane, C_3F_8, and solid LiCl with incandescence. H-NiF_3 and P-NiF_3 interact similarly but less energetically.

Introduction

At the centennial celebrations for the discovery of fluorine, Christe described[1] the first chemical route to fluorine. This was achieved via the release of thermally unstable MnF_4 from K_2MnF_6 with the strong fluoride ion acceptor SbF_5. 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 AgF_3, NiF_4, and NiF_3 were quickly achieved as a result of that approach.[2,3]

The idea was not new however. Court and Dove in 1971 had described[4] both the precipitation, at 20 °C, of MnF_4 from solutions of K_2MnF_6 in aHF, and a black precipitate, claimed to be NiF_3, from a like solution of K_2NiF_6, using AsF_5 as the F^- acceptor. This black NiF_3 was described as decomposing to NiF_2 when the AsF_6^- salt produced along with it was extracted with aHF at 20 °C. In addition they remarked explicity that NiF_4 was not produced from the K_2NiF_6 with AsF_5 reaction. It is clear from their later detailed descriptions[5] that they had indeed achieved a preparation of NiF_3, but their materials were always heavily contaminated with the coproduced potassium salts (KBF_4 or $KAsF_6$) 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 NiF_4, or isolate the relatively long-lived NiF_3, which is thermally stable at 20 °C, when dry.

The interest in nickel fluorides higher than NiF_2 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 review[9] 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 Page[10] and Stein[11] 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 NH_4F electrolyte) had "appreciable oxidizing power (0.30−0.48 equiv of iodine per mole of nickel)". Stein noted similar brown

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[§] Dedicated to the memory of fluorine chemist Warren E. Falconer (d. Aug 8, 1995).

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precipitates from K_3NiF_6 in aHF. He did not report black solids (appropriate for NiF_3 forms) nor was he able to obtain any X-ray powder diffraction information from any of his brown solids. Although Page claimed[10] 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 NiF_4, which can be kept indefinitely as a dry solid at −55 °C and below. In addition, three forms of NiF_3 have been prepared, their structures identified, these related to other first transition series trifluoride structures, and the oxidizing properties briefly described. NiF_4 and the three known forms of NiF_3 are seen to be thermodynamically unstable with respect to loss of F_2 at 20 °C.

Results and Discussion

Nickel Tetrafluoride Synthesis. The precipitation of a tan solid on introduction of BF_3 to an aHF solution of K_2NiF_6 at −65 °C was the first indication of the possible existence of NiF_4. 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 XeF_5AsF_6, which is highly soluble in aHF even at −65 °C. In this set of experiments, AsF_5 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 AsF_5 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 AsF_5 had been added, this dissolution needed vigorous mixing and the next AsF_5 addition resulted in a permanent tan precipitate. Clearly, the first 2 equiv of AsF_5 merely neutralized the second XeF_6 molecule of the complex cation:

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

An additional AsF_5 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 AsF_5 had been added, the supernatant solution had only a pale-straw color, typical for solutions of XeF_5AsF_6 in aHF:

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

Quenching this system to −196 °C showed that there was no F_2 present. The solution of XeF_5AsF_6 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, XeF_6 was added tensimetrically. Addition of 2 equiv of XeF_6 dissolved all of the tan solid to a red solution, from which $(XeF_5)_2NiF_6$ was recovered:

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

This established that the tan solid is NiF_4 and that it retains its integrity at −60 °C, since NiF_2 does not interact with XeF_6 in aHF, nor dissolve in that solution.[12] This did not prove, however, that the tan precipitate, obtained from interaction of K_2NiF_6 with BF_3 in aHF, was also NiF_4, since earlier studies of the K_2PdF_6/BF_3 in aHF system,[13] had shown the existence of $KPdF_5$ as a precursor to PdF_4.

Precipitation of the tan solid at −65 °C, with BF_3, from a K_2NiF_6 solution in aHF, has established, from gravimetry, that 2 mol of KBF_4 are formed from 1 mol of K_2NiF_6:

$$K_2NiF_6 + 2BF_3 \rightarrow NiF_4\downarrow + 2KBF_4 \quad (4)$$

The tan solid, mixed with colorless KBF_4, 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 NiF_4 has hampered the structural and magnetic investigations of the material, but as its ready liberation of F_2 implies, it is a powerful oxidizer and fluorinator. It has already been shown[14] 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:

$$NiF_3^+ + MF_6^- \rightarrow NiF_3 + MF_6 \quad (5)$$

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

Nickel Trifluoride Syntheses. As a dry solid, NiF_4 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):

$$NiF_4 \text{ solid} \xrightarrow{>-55\ ^\circ C} P\text{-}NiF_3 + {}^1/_2F_2 \quad (6)$$

A pyrochlore form of FeF_3 is known,[15] having been obtained by topotactic oxidation of $NH_4Fe_2F_6$ with Br_2 in CH_3CN, the product being cubic, with $a_0 = 10.325(2)$ Å. In the instance of P-NiF_3, this poorly packed structure probably arises as a consequence of the release of F_2 from its dry NiF_4 precursor, there being no solvent to provide for recrystallization to a more thermodynamically stable form.

The decomposition of NiF_4 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-NiF_3, Table 2) common to the late transition series element trifluorides:

$$NiF_4 \xrightarrow{aHF,\ 0\ ^\circ C} R\text{-}NiF_3 + {}^1/_2F_2 \quad (7)$$

Suspensions of R-NiF_3 at 20 °C slowly evolve F_2 over several days to give yellow-brown NiF_2. This loss of F_2 in aHF at 20 °C may be the cause of the formation of a hexagonal tungsten bronze form[16] of the trifluoride (H-NiF_3) when the tetrafluoride is decomposed, in aHF, at 20 °C rather than at 0 °C:

$$NiF_4 \xrightarrow[K^+]{aHF,\ 20\ ^\circ C} H\text{-}NiF_3 + {}^1/_2F_2 \quad (8)$$

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 $K_{0.12}NiF_3$. 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 Kα radiation, Ni filter) for Pyrochlore NiF_3 (Unit cell: $a_o = 9.933(3)$ Å; $\alpha = 91.01(3)°$; $V = 980(2)$ Å^3; $Z = 16$; $V/Z = 61.25(13)$ Å^3)

	$1/d^2_{hkl} \times 10^4$				
I/I_o	obsd	calcd	h	k	l
100	300	300	1	1	$\bar{1}$
100	317	315	1	1	1
20	408	405	2	0	0
w[a]	803	—[b]	—	—	—
70	1104	1097	$\bar{3}$	1	1
		1111	3	$\bar{1}$	1
30	1141	1140	3	1	1
80	1197	1202	$\bar{2}$	2	2
30	1257	1260	2	2	2
—	—	1893	$\bar{3}$	3	1
—	—	1937	3	3	$\bar{1}$
5	1993	1980	3	3	1
vw[a]	2246	—	—	—	—
20	2403	2389	$\bar{4}$	2	2
		2418	4	$\bar{2}$	2
5	2510	2505	4	2	2
50	2701	2704	$\bar{3}$	3	3
20	2841	2835	3	3	3
60	3181	3185	$\bar{4}$	4	0
60	3307	3302	4	4	0
20	3485	3485	$\bar{5}$	3	1
		3500	5	$\bar{3}$	1
10	3564	3573	5	3	$\bar{1}$
10	3632	3631	5	3	1
5	4020	4010	$\bar{6}$	2	0
5	4112	4098	6	2	0
10	4290	4281	$\bar{5}$	3	3
—	—	4325	5	$\bar{3}$	3
—	—	4386	$\bar{6}$	2	2
20	4446	4445	6	$\bar{2}$	2
10	4562	4501	5	3	3
		4562	6	2	2
10	4812	4806	$\bar{4}$	4	4
20	5069	5040	4	4	4
		5078	$\bar{5}$	5	1
—	—	5121	$\bar{7}$	1	1
5	5212	5165	7	$\bar{1}$	1
		5224	7	1	1
5	5295	5297	5	5	1
20	5896	5888	$\bar{7}$	3	1
5	6030	5918	7	$\bar{3}$	1
		6020	7	3	$\bar{1}$
—	—	6093	7	3	1
10	6481	6486	8	0	0

[a] Line due to a small R-NiF_3 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-NiF_3 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 NiF_3, a Ni^{2+} salt in aHF was added to a solution of K_2NiF_6 in aHF. At 0 °C, with slow mixing, this gives predominantly R-NiF_3, but when the solutions are mixed at 20 °C the dominant phase is H-NiF_3:

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

The relatively high solubility of $KBiF_6$ in aHF eases the purification of the NiF_3 prepared using $Ni(BiF_6)_2$.

Thermal and Solution Stability of *R*-, *H*-, and *P*-NiF₃. All forms of dry solid NiF_3 (R, H, and P) lose F_2 when the solids are warmed (R- > 39 °C, H- > 72 °C, and P-NiF_3, > 138 °C) and there is X-ray powder diffraction evidence for the red-brown solid, derived from the pyrolysis of R-NiF_3 at 83 °C being similar to that remaining from the reduction of solid R-NiF_3 by gaseous xenon at 20 °C. The composition of this phase is not known, but lies between NiF_3 and NiF_2.

Table 2. X-ray Powder Diffraction Data (Cu Kα radiation, Ni Filter) for Rhombohedral NiF_3 (Unit cell: $a_o = 5.168(2)$ Å; $\alpha = 55.46(3)°$; $V = 87.3(2)$ Å^3; $Z = 2$)

	$1/d^2_{hkl} \times 10^4$				
I/I_o	obsd	calcd	h	k	l
vs	810	810	1	1	0
m	1515	1512	2	1	1
vw	1728	1729	1	0	$\bar{1}$
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	$\bar{1}$
w	4314	4320	3	3	2
vw	4987	4971	3	1	0
w	5178	5188	2	$\bar{1}$	$\bar{1}$
vvw	6036	6049	4	2	2
vw	6455	6425	4	3	3
		6467	4	3	2[a]
vvw	6914	6917	2	0	$\bar{2}$
vvw	7412	7444	3	1	$\bar{1}$[a]
vw	7767	7728	3	0	$\bar{1}$
		7778	4	3	1
vvw	8411	8430	3	2	$\bar{1}$
		8422	4	4	4
vvw	9031	9023	4	2	0
vvw	9463	9457	2	2	$\bar{2}$
vvw	9891	9884	5	3	2

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

In suspension in liquid aHF at ~20 °C all forms of NiF_3 are observed to evolve F_2 over several days to finally produce NiF_2:

$$R\text{-}, H\text{-}, \text{and } P\text{-}NiF_3 \xrightarrow{\text{aHF, 20 °C}} NiF_2 + {}^1/_2F_2 \qquad (10)$$

the R-NiF_3 decomposing most rapidly and P-NiF_3 least. When a good F^- donor is also present (e.g. KF or XeF_6)[17] in the aHF, NiF_3 is partially converted in a disproportionation reaction to the appropriate NiF_6^{2-} salt:

$$2NiF_3 + 2F^- \xrightarrow{\text{aHF, 20 °C}} NiF_6^{\ 2-} + NiF_2 \qquad (11)$$

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-NiF_3 (approximately two-thirds of that expected for eq 11) and the least with P-NiF_3.

Some Oxidizing Properties of *R*-, *H*-, and *P*-NiF₃. An instance of both the oxidizing power of R-NiF_3 and the disproportionation reaction indicated by eq 11 is seen in the interaction of a multimolar excess of R-NiF_3 in aHF, at ~20 °C, with xenon. The xenon is oxidized, by the abundant oxidizer, to XeF_6, which, acting as a F^- donor (eq 11), converts the remaining R-NiF_3 to $(XeF_5)_2NiF_6$ and NiF_2:

$$14R\text{-}NiF_3 + 2Xe \xrightarrow{\text{aHF, 20 °C}} (XeF_5)_2NiF_6 + 13NiF_2 \qquad (12)$$

When excess xenon is used, all forms of NiF_3 yield XeF_2, H- and P-NiF_3 reacting relatively slowly and both R-NiF_3 and H-NiF_3 also oxidize XeF_2 to XeF_4:

$$2NiF_3 + Xe \xrightarrow{\text{aHF, 20 °C}} 2NiF_2 + XeF_2 \qquad (13)$$

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$$XeF_2 + 2R\text{- or } H\text{-}NiF_3 \xrightarrow{\text{aHF, 20 °C}} XeF_4 + 2NiF_2 \quad (14)$$

Although R-NiF_3 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 F_2, does proceed in the dark. The R-NiF_3 therefore behaves much more like a fluorine atom source. It is of interest that studies[18-21] in the early 1960s showed that the interaction of xenon with F_2 in nickel vessels occurred via a NiF_x intermediate. The red-brown nickel fluoride remaining from the R-NiF_3 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-NiF_3 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 °C, was more controlled, with no trace of CF_4:

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

A more surprising observation was the violence of the interaction of solid R-NiF_3 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 NiF_3 forms to release chlorine and form NiF_2.. It was expected that this reaction

$$LiCl + R\text{-}, H\text{-}, \text{and } P\text{-}NiF_3 \xrightarrow{\text{aHF, 20 °C}} LiHF_2 + NiF_2 + {}^1/_2Cl_2 \quad (16)$$

might result in some Li^+ incorporation into the H- or P-NiF_3 but no evidence for this was found.

Since dry acetonitrile is an effective solvent for many strongly oxidizing materials (e.g. XeF_2) 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-NiF_3 was violent even at ~−40 °C, but H- and P-NiF_3 interacted very slowly even at 20 °C, but with eventual reduction of the NiF_3 to NiF_2. In the instance of the reaction with P-NiF_3 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-NiF_3 (~$K_{0.12}NiF_3$) and P-NiF_3, (~$K_{0.1}NiF_3$) 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-NiF_3, in which all of the nickel is formally Ni^{III}. These K_xNiF_3 forms may also have lower solubility in the aHF and lower tendency to disproportionate than does R-NiF_3, and these differences could also diminish their oxidizing potency relative to the R-NiF_3.

Structural Features in *R*-, *H*-, and *P*-NiF₃. The three observed forms of NiF_3 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 NiF_3 forms has been 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.

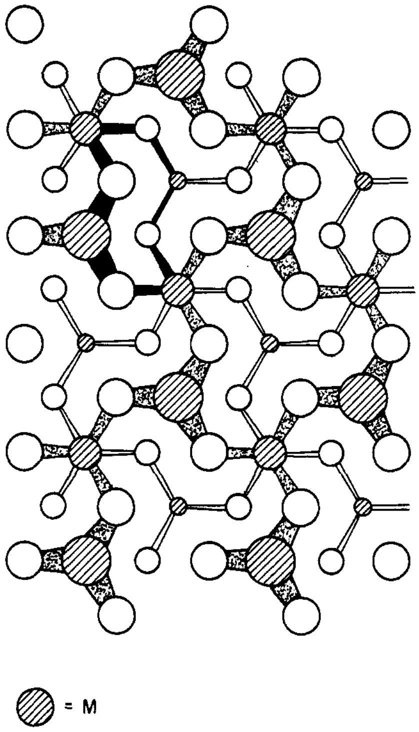

Figure 1. Representation of the hexagonal close-packed F-ligand array in the R-MF_3 typified by NiF_3. M's are located in octahedral hole sites. Heavy shading of interatom connectors shows the puckered eight-membered M_4F_4 rings.

The R-NiF_3 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 array[24] shown in Figure 1. The unit cell parameters of R-NiF_3 are not very different from those of R-CoF_3, but the formula unit volume (FUV) of 43.7 Å is smaller, and the least of any other known trifluoride except[25] AlF_3 (FUV = 43.6 Å^3). This demonstrates that the effective nuclear charge of the metal atom in R-NiF_3 must be high. The plot of FUV for each of the first transition-series 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 ScF_3 to CrF_3 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 FeF_3 to CoF_3 is attributable to the $e_g{}^*$ population, being the same in both, the additional electron of the Co^{III} d^6 configuration being placed in the $t_{2g}{}^*$ orbital set. The absence of Jahn−Teller distortion in R-NiF_3 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 $Ni^{II}Ni^{IV}F_6$.

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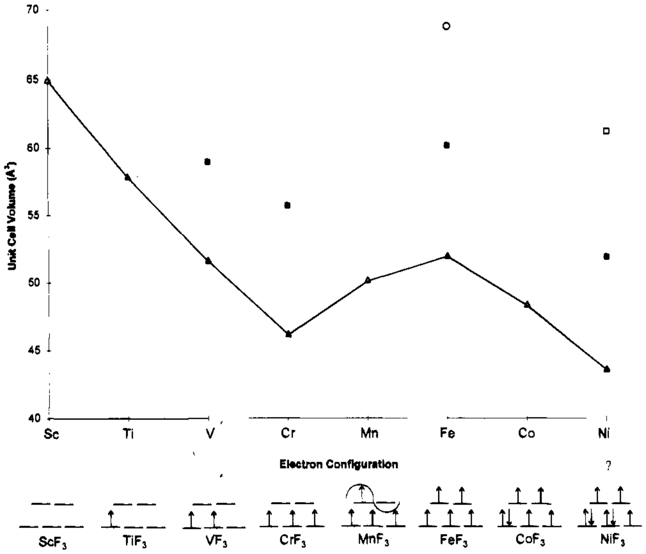

Figure 2. Formula unit volume (Å^3) for each of the known forms of the first-transition series trifluorides, plotted as a function of atomic number. Δ = R-MF$_3$, ● = H-MF$_3$, and □ = P-MF$_3$ **491**, 199 (1982). References: (R-ScF$_3$) Lösch, R.; Hebecker, C.; Ranft, Z. *Z. Anorg. Chem.* **1982**, *491*, 199. (R-TiF$_3$) Ehrlich, P.; Pietzka, G. *Z. Anorg. Chem.* **1954**, *275*, 121. (R-VF$_3$) Gutmaun, V.; Jack, K. H. *Acta Crystallogr.* **1951**, *4*, 244. (R-CrF$_3$) Jack, K. H.; Maitland, R. *Proc. Chem. Soc.* **1957**, 232. (MnF$_3$, monoclinic) Hepworth, M. A.; Jack, K. H. *Acta Crystallogr.* **1957**, *10*, 345. (R-FeF$_3$ and R-CoF$_3$) ref 24. (H-VF$_3$ and H-CrF$_3$) ref 29. (H-FeF$_3$) ref 28. (P-FeF$_3$) ref 15.

Although neutron diffraction data for R-NiF$_3$ have been collected, the sample was not sufficiently crystalline to distinguish unambiguously between $R\bar{3}c$ and $R\bar{3}$. 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 e$_g$* electron population, which is the same for all, would have prime impact on effective size.[26] The low-spin 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}F$_6$ octahedron would be very much smaller than for the high spin relative, since the FUV for R-NiF$_3$ 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-NiF$_3$, 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-NiF$_3$ form has the structure first described[16] by Magneli for the tungsten bronzes, M$_x$WO$_3$ (M a heavier alkali metal). As with Magneli's bronzes, H-NiF$_3$ 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-FeF$_3$ derived from (H$_2$O)$_{0.33}$FeF$_3$ by Leblanc *et al.*[28] In their study of the hexagonal tungsten bronze forms of CrF$_3$ and VF$_3$, 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. Since high-quality neutron or X-ray diffraction data have not been available so far for H-NiF$_3$, because of the relatively poor microcrystallinity of the samples, it has not been possible to establish beyond doubt that the H-NiF$_3$ is not orthrhombic, and therefore merely pseudo-hexagonal.

Table 3. X-ray Powder Diffraction Data (Cu Kα radiation, Ni filter) for the Hexagonal Tungsten Bronze Form of NiF$_3$ (Unit cell: a_o = 7.074(6) Å; c_o = 7.193(6) Å; V = 311.7(8) Å; Z = 6; V/Z = 51.95(13) Å^3)

	$1/d^2_{hkl} \times 10^4$				
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; ± sh = a shoulder on the high (+) or low (−) angle side.

Table 4. X-ray Powder Diffraction Data (Cu Kα radiation, Ni filter) for NiF$_x$ ($2 < x < 3$) (Heavy Background and Broad Lines Indicative of Small Particle Size in Each Sample)[a]

	$1/d^2_{hkl} \times 10^4$						$1/d^2_{hkl} \times 10^4$	
I/I_o	obsd	calcd[b]	h	k	l	I/I_o	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-NiF$_3$ up to 83 °C, and the data on the right are from the residue from the reaction of Xe with dry R-NiF$_3$. [b] Based on a hexagonal cell with a_o = 4.97(2) Å; c_o = 6.57(2) Å, V = 140.4 Å^3; volume fits ~9 F atoms, with 4 Ni. [c] Based on a hexagonal cell with a_0 = 5.05(2) Å; c_o = 6.71(2) Å; V = 148.3 Å^3; volume fits ~10 F atoms with 4 Ni.

The structure of H-NiF$_3$ 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 KH$_2$F$_3$ recovered on reduction of H-NiF$_3$ with Xe, indicate that the K$^+$ content, x in K$_x$NiF$_3$, ≈ 0.12; only abut one third of that allowed by the structure, since

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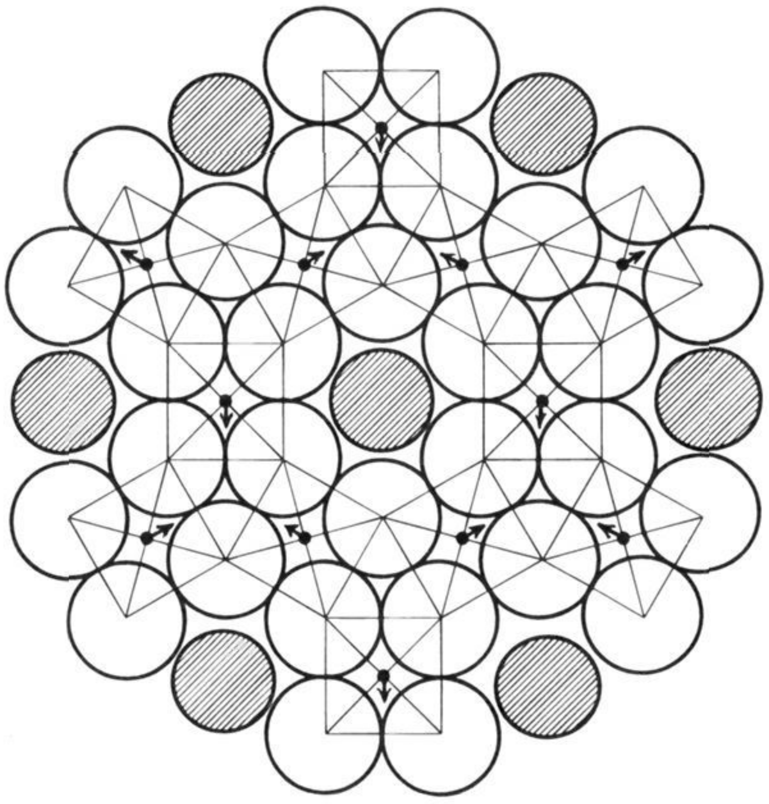

Figure 3. Representation of a single idealized sheet of the hexagonal tungsten bronze *H*-MF_3 structure. Open circles represent the F ligands close to the plane containing the M atoms (small black spots). MF_6 octahedra represented by the squares, crossed diagonally, are tilted in the direction indicated by the short arrows. Shaded circles indicate K^+ sites at $c_o/4$ above or below the plane of the M atoms.

this could accommodate a composition $K_{1/3}NiF_3$. As the *H*-NiF_3 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*-NiF_3, 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*-NiF_3 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 $c_0 = [4 \times \text{Ni−F distance} \times \cos t]$ and $a_0 = [\sqrt{2} \times \text{Ni−F distance} \times (1 + \sqrt{3}\cos t)]$. This requires $t = 17.60°$ (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-workers[24] had found for *R*-FeF_3 and *R*-CoF_3, 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 NiF_3 forms.

The change in structure from *R*-NiF_3 to *H*-NiF_3 results in a FUV increase of 8.3 $Å^3$, (comparison of Figures 1 and 3 reveals the close ligand packing in *R*- and its absence in *H*-NiF_3) this being associated with the open hexagonal channels of *H*-NiF_3, 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 $NiF_3{}^{x-}$ 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 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*-MF_3 FUV, across the period, is the same as for *R*-MF_3. Although the Ni species in *R*- and *H*-NiF_3 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*-NiF_3, the octahedra are linked through bridging F ligands, in 8 membered Ni_4F_4 rings (alternating Ni and F) as seen in Figure 1. As shown in Figure 3 NiF_6 octahedra in *H*-NiF_3 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 Ni_3F_3 rings with alternating Ni and F. It is this closer grouping of the octahedra in *H*-NiF_3 that provides for the "open" hexagonal channels that run parallel to *c*.

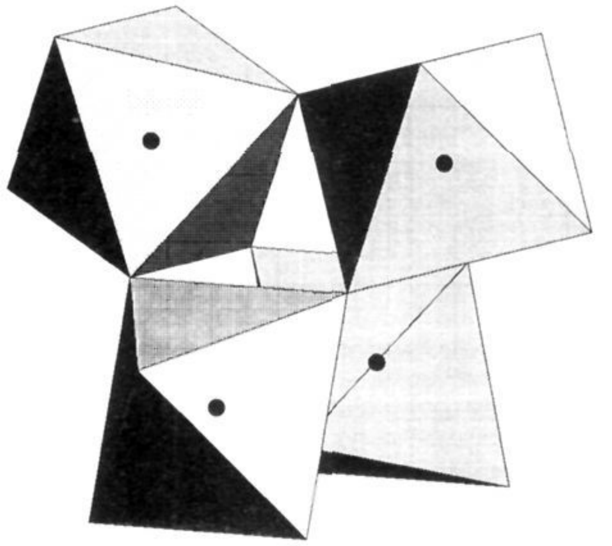

Figure 4. A tetrahedral cluster of MF_6 octahedra, representative of the *P*-NiF_3 structure. All Ni are linked through F bridges to other Ni in Ni_3F_3 rings. Open hexagonal channels (at ~109° 28′ to one another) run through the structure and in *P*-NiF_3 are partially occupied by K^+.

For the *P*-NiF_3, the clustering of octahedra of NiF_6 is in tetrahedral sets, illustrated in Figure 4. The unit cell must be similar to that of the cubic pyrochlore described for *P*-FeF_3 by dePape *et al.*[15] It is also similar in size to the cell described[30] 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*-NiF_3 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*-NiF_3, 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 NiF_3, 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*-NiF_3 but ~120 K in *H*-NiF_3 and only ~50 K in *P*-NiF_3. 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 FeF_3, where the transition temperatures are *R*-FeF_3, 365 K; *H*-FeF_3, 110 K; and *P*-FeF_3, 20 K.

In *R*-NiF_3 like *R*-FeF_3, each metal center is linked by bridging F ligands in eight-membered rings, as illustrated in Figure 1. For the high-spin d^5 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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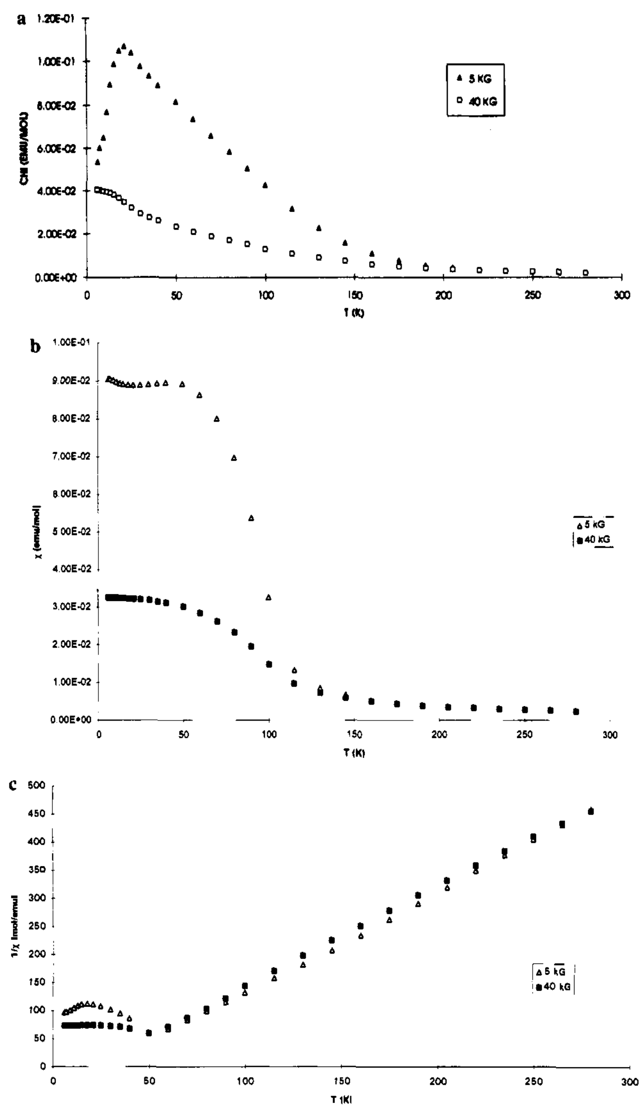

Figure 5. Magnetic susceptibility data at two fields (Δ 5 kg, ■ 40 kg) as a function of temperature (K) for (a) *R*-NiF$_3$, (b) *H*-NiF$_3$, and (c) *P*-NiF$_3$ (a Curie–Weiss plot).

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*-NiF$_3$ to *R*-FeF$_3$ suggests antiferromagnetic coupling of Ni^{III} species of configuration t$_{2g}^5$e$_g$*^{2}, at temperatures below ~250 K, these canted magnets producing the observed field dependence. A mixed-valence formulation Ni^{II} t$_{2g}^6$e$_g$*^{2}, Ni^{IV} t$_{2g}^6$ could also contribute, but by itself would merely provide for weak ferromagnetism akin to that discussed[33] by Tressaud and Dance for Pd^{II}Pd^{IV}F$_6$ and Pt^{II}Pt^{IV}F$_6$ (the second[34,35] and third[36,37] transition series analogues of Ni^{II}Ni^{IV}F$_6$) where the T_c values are 10 and 16 K, respectively. The magnetic behavior of a high-spin mixed-valence formulation, Ni^{II} t$_{2g}^6$e$_g$*^{2}, Ni^{IV} t$_{2g}^4$e$_g$*^{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*-NiF$_3$.

Because, in *H*-NiF$_3$, the Ni species, in the *ab* plane, are linked via F-ligand bridges to four other Ni species, but always in six-membered Ni$_3$F$_3$ 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$_{2g}^5$e$_g$*^{2} species that would be effective, would be that parallel to *c*. Such a coupling situation occurs[31,39] in *H*-FeF$_3$, which exhibits much weaker antiferromagnetic coupling (T_N = 110 K) than *R*-FeF$_3$ (T_N = 365 K). The magnetic behavior of *P*-NiF$_3$ 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*-NiF$_3$ 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*-NiF$_3$, is everywhere present in the *P*-NiF$_3$. 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 Ni$_3$F$_3$ ring.

The magnetic properties of all three forms of NiF$_3$ 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}F$_6$ 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 described[40]) 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 F$_2$ (~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

starting weight of K_2NiF_6, mg (mmol)	required weight for the stated solid products, mg				observed weight for the solid product, mg
	(1) $KNiF_5 + KBF_4$	(2) $KNiF_4 + KBF_4$	(3) $NiF_4 + 2KBF_4$	(4) $NiF_3 + 2KBF_4$	
(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 F_2 for 12 h.

B. Materials. K_2NiF_6 (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 K_2NiF_6, enough aHF (~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 K_2NiF_6. This was repeated twice, and then the K_2NiF_6 was dried under a dynamic vacuum. To remove any insoluble phase from the K_2NiF_6, the tube containing the KF-free K_2NiF_6 was placed on a second Teflon T-reactor with a 5−10 μ porous Teflon filter (Berghof-America) inserted in the neck of the "T". The K_2NiF_6 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). BiF_5 (Ozark-Mahoning Pennwalt) was fluorinated under the same conditions as the K_2NiF_6, and then recrystallized from aHF following decantation of the solution from any insoluble material. BF_3 (Matheson) was used as supplied.

C. Preparation of NiF_4 and Evidence for its Composition. NiF_4 from K_2NiF_6 with BF_3. Solutions of K_2NiF_6 in aHF at −78 °C were exposed to BF_3 until the solutions no longer took up the gas. The aHF and remaining BF_3 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 KBF_4 and either an amorphous or poorly crystalline *P*-NiF_3 (q.v.) phase. Two reactions were followed gravimetrically as shown in Table 5. Washing with aHF at ~20 °C extracted the KBF_4 to leave poorly crystalline *P*-NiF_3. **NiF_4 from $(Xe_2F_{11})_2NiF_6$ with AsF_5.** $(Xe_2F_{11})_2NiF_6$ prepared as previously described[12] was dissolved in aHF. AsF_5, 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*-NiF_3. K_2NiF_6 with BF_3. K_2NiF_6 (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 BF_3 (measured out tensimetrically) was added to the solution over a span of 2 h. A tan precipitate of NiF_4 settled to the bottom of the reactor, below a clear, slightly yellow-tinted solution. The tan color changed to black as F_2 evolved. Decomposition was considered to be complete when F_2 evolution had ceased (~2 h). The byproduct, KBF_4, 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 and decantation (seven times). The black residue was dried at 0 °C under dynamic vacuum. This yielded black *R*-NiF_3 (346 mg, 2.99 mmol, 95% yield), represented by the XRPP given in Table 2.

K_2NiF_6 with BiF_5. K_2NiF_6 (309 mg; 1.23 mmol) was loaded into one arm of an FEP T-reactor and BiF_5 (754 mg; 2.48 mmol) into the other. Each reactant was dissolved in aHF (~3 mL each). Both solutions were cooled to 0 °C. The solution of BiF_5 was decanted dropwise into the solution of K_2NiF_6 to precipitate tan NiF_4. 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 F_2. Cessation of F_2 evolution signaled completion of the reaction. The byproduct, $KBiF_6$ 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*-NiF_3 (142 mg; 1.23 mmol, 99% yield).

E. Synthesis of *H*-NiF_3. The preparation of the hexagonal tungsten bronze form of NiF_3 (designated *H*-NiF_3) involved essentially the same experimental conditions as for the *R*-NiF_3 except that for *H*-NiF_3, the preparation temperature was ~20 °C, with slow addition of the acid.

K_2NiF_6 with BF_3. K_2NiF_6 (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*-NiF_3 (82% yield).

K_2NiF_6 with BiF_5. K_2NiF_6 (351 mg; 1.40 mmol) and BiF_5 (860 mg; 2.83 mmol), each reactant in aHF (~3 mL) gave 160 mg *H*-NiF_3 (from XRPP in Table 3), a yield of 98%.

F. Synthesis of *P*-NiF_3. Purified K_2NiF_6 (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 BF_3 added to the solution, at that temperature, over 2 h, tan NiF_4 precipitated, the supernatent solution having a pale-yellow tint. The BF_3 was removed at −65 °C and the aHF solution became turbid brown as the BF_3 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 NiF_4) was removed and aHF (8 mL) was added. KBF_4 was extracted at −30 °C with seven washings with the aHF (back-distilled). The brown (nearly black) trifluoride, KBF_4 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*-NiF_3 = 294.9 mg, i.e. 2.47 mmol $K_{0.1}NiF_3$, 72% yield.

G. Preparation of *R*- and *H*-NiF_3 from $Ni(MF_6)_2$ (M = As, Sb, Bi) + K_2NiF_6 in aHF. $Ni(MF_6)_2$, prepared by dissolving NiF_2 in aHF containing 2 equiv of MF_5 (M = As, Sb, Bi) at 20 °C, was in each case highly soluble in aHF and gave a yellow solution. The $Ni(MF_6)_2$ salt was loaded in one arm of a T-reactor and an equimolar quantity of purified K_2NiF_6 in the other. The solution of $Ni(MF_6)_2$ in aHF was poured slowly into a solution of the K_2NiF_6, 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*-NiF_3 and when done at 20 °C *H*-NiF_3 was the major product. The NiF_3 product was in each case washed with back-distilled aHF at 0 °C to minimize NiF_2 production. Example: $Ni(AsF_6)_2$ (1330.3 mg; 3.048 mmol) + K_2NiF_6 (764.6 mg; 3.048 mmol) → 2*H*-NiF_3 (found: 700.8 mg; 6.058 mmol) + $2KAsF_6$ (slightly contaminated by *H*-NiF_3 transferred in the multiple decantations).

H. Thermal Decomposition of *R*-, *H*-, and *P*-NiF_3. *R*-NiF_3. The release of F_2 from *R*-NiF_3 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*-NiF_3 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*-NiF_3 with a molar excess of Xe gas (q.v.).

***H*-NiF_3.** The pyrolysis of *H*-NiF_3 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*-NiF_3.** F_2 release from *P*-NiF_3 was not seen until ~138 °C at which temperature the dark brown solid became lighter in color.

I. Decomposition in aHF at ~20 °C. R-NiF$_3$. When prepared from K$_2$NiF$_6$ with BF$_3$ at 0 °C, the decomposition of R-NiF$_3$ in aHF, at 20 °C, was usually complete within 24 h, but in the instance of the R-NiF$_3$ precipitated by a stoichiometric quantity of BiF$_5$ the decomposition was much slower as follows: aHF (1.5 mL) agitated with R-NiF$_3$ (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 NiF$_2$, identified by XRPP (71.5 mg; 0.74 mmol) was recovered.

H-NiF$_3$. H-NiF$_3$ (68.7 mg; 0.59 mmol if NiF$_3$) 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 NiF$_2$ (57.3 mg; 0.59 mmol).

P-NiF$_3$. P-NiF$_3$ (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 NiF$_2$ (XRPP) on removal of aHF gave KH$_2$F$_3$ (1.7 mg) from which the K content of the P-NiF$_3$ is 0.68 mg, indicating composition K$_{0.13}$NiF$_3$. The P-NiF$_3$ (0.131 mmol of K$_{0.13}$NiF$_3$) should yield 0.131 mmol of NiF$_2$, 12.6 mg. Found "NiF$_2$", 13.6 mg.

J. Analysis of NiF$_3$. Analysis of R-NiF$_3$. The major difficulty associated with the analysis of samples of R-NiF$_3$ (most of which were prepared from K$_2$NiF$_6$) lay in the removal of the K$^+$ salts generated simultaneously with the R-NiF$_3$. Washing with aHF at ~ 20 °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 F$_2$ and lower fluoride was also greater at the higher temperature. The R-NiF$_3$ 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 NiF$_2$ production (as revealed by XRPP). Removal of salts was greatly aided by bringing the entire reaction product (R-NiF$_3$ and KX) to dryness before washing with aHF. (This probably crystallized K$^+$ and X$^-$ adsorbed on the R-NiF$_3$.) For samples for analysis, care was taken to minimize the NiF$_2$ formation, but KX salt removal was in such instances rarely complete. R-NiF$_3$ (prepared from K$_2$NiF$_6$ and BF$_3$, 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%. NiF$_3$, plus 0.04KBF$_4$ impurity, requires: F, 49.7; Ni, 48.6, K, 1.3; B, 0.4%. NiF$_3$ requires: F, 49.3; Ni 50.7%. The low K and high B content could signify some NiF BF$_4$ 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-NiF$_3$ 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 (KBF$_4$, KAsF$_6$, etc.) produced on addition of the F$^-$ acceptor (BF$_3$, AsF$_5$, etc.) to the aHF solution of K$_2$NiF$_6$. It was found that a more reliable indicator of the K$^+$ present in the hexagonal channels of the H- or P-NiF$_3$ was given by the formation of KH$_2$F$_3$ (highly soluble in aHF) as the trifluoride was reduced. Three sets of observations were employed for this: (1) the decomposition of the trifluoride in aHF at 20 °C (a slow process); (2) the reduction of the trifluoride with xenon (faster); and (3) the reduction of the P-NiF$_3$ with CH$_3$CN (moderately fast).

Analysis of H-NiF$_3$. This material decomposed less quickly in 20 °C aHF and was therefore more easily washed than R-NiF$_3$. Found: F, 47.1; 47.0; Ni, 48.3; 48.3; K 4.07; B, 0.62%. H-NiF$_3$ (contaminated with 0.0074 mmol KBF$_4$ impurity) having a composition K$_{0.12}$NiF$_3$·0.0074KBF$_4$, requires: F, 47.4; Ni, 48.4; K, 4.09; B, 0.07%.

K. Some Chemical Reactions of R-, H-, or P-NiF$_3$. 1. Interaction of R-, H- and P-NiF$_3$ with CH$_3$CN at ~20 °C. R-NiF$_3$. CH$_3$CN was condensed onto the dry R-NiF$_3$ at −196 °C and as it thawed (~−45 °C) it reacted exothermically to give NiF$_2$ and fluorination products of the CH$_3$CN.

H-NiF$_3$. The solid reacted slowly with CH$_3$CN at ~20 °C over 30 min to give a paler solid (NiF$_2$).

P-NiF$_3$. P-NiF$_3$ (59.1 mg) was stirred in contact with CH$_3$CN for 30 min and the solid rapidly became yellow-green (NiF$_2$ by XRPP) as the CH$_3$CN was oxidized. Remaining CH$_3$CN and volatile oxidation products were removed under dynamic vacuum and the residual solid was washed with aHF to extract KH$_2$F$_3$. The yield of KH$_2$F$_3$ (by XRPP) 4.0 mg signified 0.041 mmol, 1.59 mg of K$^+$ in the P-NiF$_3$ and a composition K$_{0.08}$NiF$_3$.

2. Interaction of dry R-, H-, and P-NiF$_3$ with gaseous Xe at ~ 20 °C. Dry R-, H-, and P-NiF$_3$ do not interact with gaseous Xe at 20 °C, but if R-NiF$_3$ 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.) XeF$_2$ was identified by IR[42] and XRPP[43] 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 NiF$_3$ at 83 °C (q.v.) given in Table 4.

Table 6. Results of the Interaction of R-, H-, and P-NiF$_3$ with Xe in aHF, at ~20 °C[a]

R-NiF$_3$

reactants		products		
R-NiF$_3$	Xe	Xe product	KH$_2$F$_3$ product	NiF$_x$
108 (0.93)	(0.2)	41, XeF$_4$ (0.2)	none	95 obs (0.8NiF$_2$) + (0.13NiF$_3$) = 92.4

H-NiF$_3$

reactants		products	
H-NiF$_3$	Xe	XeF$_2$ + KH$_2$F$_3$ + KBF$_4$	NiF$_x$
180	excess	93.2	148

P-NiF$_3$

reactants		products		
P-NiF$_3$		5, XeF$_2$	3, KH$_2$F$_3$	NiF$_2$ yield
23.3	multimolar excess	(0.03)	(0.031)	no recorded

[a] Quantities not in parentheses are in milligrams; quantities in parentheses are in millimoles.

3. Interaction of R-, H-, and P-NiF$_3$ 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-NiF$_3$ i.e. K$_{0.12}$NiF$_3$·0.0074KBF$_4$: there are 1.484 mmol of H-NiF$_3$. There must be 1.484 mmol of NiF$_x$ in the product, which must therefore have a composition NiF$_{2.16}$. Neglecting loss of F$_2$ by decomposition of the H-NiF$_3$ in the aHF, the yield of XeF$_2$ is expected to be 0.534 mmol = 90.4 mg. Expected KH$_2$F$_3$ = 17.5 mg and KBF$_4$ = 0.9 mg. Total XeF$_2$ + KH$_2$F$_3$ + KBF$_4$ = 108.8 mg. Results are in Table 6.

Since 23.3 mg of P-NiF$_3$ contain 1.20 mg of K (based on 0.031 mmol of KH$_2$F$_3$), the empirical formula is K$_{0.16}$NiF$_3$ (formula weight 122.05). Results are in Table 6.

Excess R-NiF$_3$. Introduction of Xe to a multimolar excess of R-NiF$_3$ 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$_3$ → (XeF$_5$)$_2$NiF$_6$ + 13 NiF$_2$] and removal of aHF yielded red crystals of (XeF$_5$)$_2$NiF$_6$ (by XRPP).[12] When slightly larger xenon quantities were used than required for (XeF$_5$)$_2$NiF$_6$ formation, the evaporation of the red aHF solution also gave high purity XeF$_4$ (XeF$_2$ and XeF$_6$ absent).

L. Reaction of R- or H-NiF$_3$ with XeF$_2$ in aHF. R-NiF$_3$. A solution of XeF$_2$ in aHF at ~20 °C added quickly to an equivalent quantity of R-NiF$_3$ 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 NiF$_2$) and evaporation of aHF from the combined decantate and washings at ~−40 °C yielded a nearly colorless sublimable solid identified[43] (XRPP) as XeF$_4$.

H-NiF$_3$. 1. XeF$_2$ (67 mg; 0.40 mmol) in aHF (2.5 mL) added to H-NiF$_3$ (92 mg; 0.80 mmol) with vigorous stirring, resulted in the black H-NiF$_3$ 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 identified[43] by XRPP as XeF$_4$ (66 mg; 0.32 mmol). The XRPP of the reddish-brown residue showed it to contain

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(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*-NiF_3 with aHF Solutions of KF[a]

R-NiF_3

reactants		products			
R-NiF_3	KF	NiF_2	K_2NiF_6	+	KH_2F_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-NiF_3

reactants		products					
H-NiF_3	KF	NiF_2	K_2NiF_6	+	KH_2F_3	+	KBF_4
1. 136.3	75.3	99.9 observed	135.4 observed				
(1.123)[b]	(1.296)	(1.033)	(0.090)		(1.250)		(0.0083)
			22.6		122.6		1.0
			146.2 required				
2. 151.9	86.9	110	164.7 observed				
(1.252)[b]	(1.498)	(1.138)	(0.114)		(1.420)		(0.0093)
			28.6		139.3		1.2
			169.1 required				

P-NiF_3

reactants		products			
P-NiF_3	KF	NiF_2	K_2NiF_6	+	KH_2F_3
92.7	70.9	65.2	149.7 observed		
(0.760)[c]	(1.220)	(0.674)	(0.086)		(1.170)
			21.6		114.7
			136.3 required		

[a] Quantities no in parentheses are in milligrams; quantities in parentheses are in millimoles. [b] $K_{0.12}NiF_3{\cdot}0.0074KBF_4$ from analysis. [c] $K_{0.16}NiF_3$ composition from reduction with Xe in aHF.

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

2. XeF_2 (48 mg; 0.28 mmol) and *H*-NiF_3 (130 mg; 1.12 mmol) were loaded into opposite arms of a reactor and aHF (2.5 mL) was condensed onto the XeF_2, and the resulting solution poured onto the *H*-NiF_3. After 1 h, the black solid had become reddish-brown. Removal of aHF below −39 °C gave an almost colorless residue (XRPP indicated XeF_4, 46 mg; 0.22 mmol). The XRPP of the reddish-brown residue (121 mg) showed *H*-NiF_3 and NiF_2. Required for 0.56 mmol NiF_2, 54 mg; and (0.56 mmol) *H*-NiF_3, 67.9 mg; total 122.1 mg.

M. Interaction of *R*-, *H*-, or *P*-NiF_3 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 (~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*-NiF_3 produced K_2NiF_6 the reaction being effectively complete in 1 day. *H*-NiF_3 and *P*-NiF_3 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*-NiF_3. *R*-NiF_3. When an equimolar mixture of *R*-NiF_3 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 NiF_2 and LiF. The interaction was much more controlled when an aHF solution, at 0 °C, of LiCl was added slowly to *R*-NiF_3 under aHF (at 0 °C). Fast evolution of Cl_2 was accompanied by simultaneous conversion of the *R*-NiF_3 to a yellow green solid (NiF_2 by XRPP).

***H*-NiF_3.** LiCl (46.2 mg; 1.09 mmol) in the side arm of a T-reactor was transferred in aHF (~2 mL) to *H*-NiF_3 (112.7 mg; 0.974 mmol) in the main tube and the mixture stirred at ~20 °C. Cl_2 gas was rapidly evolved and the nearly black NiF_3 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 Cl_2 under dynamic vacuum at ~20 °C left the yellow green product (XRPP showed NiF_2, 100.8 mg; 1.04 mmol) in the main tube and in the other a colorless solid, XRPP of which showed $LiHF_2$ with some LiF (48.3 mg; required for 1.09 mmol of $LiHF_2$ = 50.1 mg).

O. Oxidation of C_3F_6 by *R*-NiF_3. *R*-NiF_3 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 (NiF_2 present by XRPP). IR spectra showed the gaseous product to be perfluoropropane, C_3F_8 with only a trace of CF_4 present. A similar quantitative conversion of C_3F_6 to C_3F_8 also occurred with the *R*-NiF_3 suspended in aHF but in this instance CF_4 was not observed.

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