Syntheses and some properties of new nickel fluorides

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Nickel tetrafluoride is obtained as a light brown solid by precipitation from solution of NiF_6^{2-} salts in anhydrous hydrogen fluoride (AHF) by fluoride ion acceptors at $\leqslant -65$ °C. Detectable F_2 release from dry NiF_4 is observed above -55 °C, but the rate of decomposition is slow and even at 18 °C takes nearly 100 h to transform to NiF_3. In liquid AHF, the decomposition of NiF_4 is more rapid at any temperature than when dry. Precipitation of nickel fluoride from K_2NiF_6 in liquid AHF at $\leqslant 0$ °C yields black rhombohedral nickel trifluoride (R–NiF_3, $a_o = 5.16$ Å; $\alpha = 55.7°$; $Z = 2$) but if the precipitation occurs at ca. 18 °C, the dominant phase is the hexagonal tungsten bronze material, H–NiF_3 ($a_o = 7.10$ Å; $c_o = 7.19$ Å; $Z = 6$), which is nearly black, with a deep red reflectance. R–NiF_3 decomposes slowly ($NiF_3 \rightarrow NiF_2 + 1/2F_2$) in liquid AHF at room temperature. H–NiF_3 decomposes similarly, but more slowly. Warmed dry NiF_4 (studied at 18 °C and above) yields a cubic, pyrochloric material (C–NiF_3, with $a_o = 9.96$ Å, $Z = 8$).

An alternative route to the synthesis of NiF_3 (R– or H–) which lends itself to bulk production of the material, is via the interaction of NiF_6^{2-} salts with Ni^{2+} salts, each dissolved separately in AHF. In harmony with the thermodynamic instability of all forms of NiF_3, these fluorides are powerful oxidizing and fluorinating agents. R–NiF_3 is the most reactive and as a solid at room temperature oxidizes xenon (ultimately to XeF_6), perfluoropropene to perfluoropropane, and in a highly exothermic reaction, LiCl liberates Cl_2. Even at -60 °C dry acetonitrile burns in contact with R–NiF_3. H–NiF_3 and C–NiF_3 react less violently as free solids and this may be due to some reduction of the nickel in these open channel fluorides as a consequence of cation incorporation (e.g. K_xNiF_3 with $x \ll 0.2$).

In all three NiF_3 structures, Ni atoms are at the center of an octahedral arrangement of six F ligands. In R–NiF_3, the F ligands are in a nearly ideal hexagonal close-packed array, ABAB..., with one-third of the octahedral holes occupied in an ordered manner by Ni atoms. The formula unit volume ($V/Z = 43.8$ Å³) is the smallest of any trifluoride of the first transition series. This is indicative of the high effective nuclear charge at nickel and is in accord with the high oxidizing power of NiF_3. The magnetic properties of R–NiF_3 indicate a formulation $Ni^{II}Ni^{IV}F_6$ with high spin d^8 Ni^{II} and low spin d^6 Ni^{IV}. Below ca. 220 K, the material exhibits field dependence of the magnetic moment, indicative of ferromagnetic superexchange. The H–NiF_3 structure ($V/Z = 52.3$ Å³) is less close-packed than R–NiF_3. This is a consequence of the formation of open hexagonal channels (parallel to c_o) caused by the tighter clustering of the apex-shared octahedra in the H–NiF_3 form. The apex sharing, via Ni–F–Ni bridges involves six-membered rings in the H–NiF_3 form versus eight-membered rings in the F-ligand close-packed structure of R–NiF_3. In C–NiF_3, the NiF_6 octahedra are in tetrahedral clusters (again involving six-membered $\cdot\cdot$Ni–F–Ni–F$\cdot\cdot$ rings) which results in even more hexagonal channels, now directed along all threefold axes of the cubic unit cell. As a result, the formula unit volume ($V/Z = 61.8$ Å³) is 18 Å³ larger than that for the close-packed R–NiF_3 structure. This difference in volume is approximately that of a F ligand. Thus C–NiF_3 has a formula unit volume akin to that expected for its NiF_4 precursor.

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