

Fluorine Compounds of Nickel(III)

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Nickel(III) fluoride is formed by the reaction of $K_2Ni^{IV}F_6$ with AsF_5 in HF. In the absence of AsF_5 , $K_2Ni^{IV}F_6$, and $K_3Ni^{III}F_6$ yield insoluble products, in which the nickel oxidation state varies between 2.00 and 2.50, and the soluble NiF_6^{2-} species. Direct fluorination of nickel salts at 200 °C yields $NiF_{2.1}$. The nature of Ni^{III} in a fluoride environment is discussed.

UNTIL recently the only stoichiometric binary compound of nickel and fluorine was the yellow-green NiF_2 having $\mu_{eff} = 2.85$ B.M. at 298 K and a rutile type structure.^{1,2} Henkel and Klemm² claimed to have prepared a brown compound $NiF_{2.5}$ by direct fluorination of $NiCl_2$; a reinvestigation by Stein and his co-workers³ has shown that under similar conditions fluorochlorates are initially produced which could account for the oxidising behaviour, if not the colour, of the brown solid. We now report on the reaction of fluorine with nickel sulphate and nickel chloride.

Nelson⁴ has suggested that NiF_3 should be just thermodynamically stable and, since high-temperature direct fluorination methods have not proved successful, we have also examined an alternative; the preparation of NiF_3 by low-temperature solvolysis of Ni^{III} and Ni^{IV} in anhydrous HF. This preparative route has been used by Soriano *et al.*⁵ to prepare PrF_4 . Other workers have reported isolating brown solids from the treatment of $K_2Ni^{IV}F_6$ and $K_3Ni^{III}F_6$ with HF,⁶ although they have not reported analytical data. They are less stable than either K_2NiF_6 or K_3NiF_6 and are apparently complex mixtures of NiF_2 , KHF_2 , and a possible nickel(III) species. We have also investigated these solvolyses in anhydrous HF and in HF solutions containing AsF_5 or BF_3 .

A third preparative route to a binary fluoride of Ni^{III} (or of Ni^{IV}) is by electrolysis of HF solutions. Stein *et al.*⁶ observed the formation of a brown solid phase together with hexafluoronickelate(IV) on electrolysis of KF or NH_4F in HF using a nickel anode. Page⁷ has reported obtaining a red impure nickel 'perfluoride' by the electrolysis of a $KF.3HF$ melt using a similar cell to Stein. We suspect that this red species could be impure $K_2Ni^{IV}F_6$ since we find the solubility of this complex in HF to be extremely low in the presence of a large excess of KF.

RESULTS

Fluorination of Nickel(II) Salts with F_2 .—Using either nickel(II) chloride or sulphate, oven-dried at 120 °C as starting materials, we obtained dark brown products free from chloride or sulphate by passing a 1:1 mixture of F_2 and N_2 over the sample for 2 h at 200 °C (fluorination temperatures in excess of 230 °C converted the starting materials into yellow NiF_2). The brown products, from

either starting material, were found to be essentially identical, having the composition $NiF_{2.09 \pm 0.01}$ as determined by weight changes, non-aqueous iodimetry, and elemental analysis (Found: Ni, 59.2, 59.0; F, 40.0; 39.9%; oxidn. state, 2.10. Calc. for $NiF_{2.1}$: Ni, 59.5, F, 40.5%). The brown solids were found to decompose spontaneously in a dry N_2 atmosphere (dew point -60 °C) during *ca.* $\frac{1}{4}$ h. The yellow decomposition product was shown to be $NiF_{2.0}$ by weight change, elemental analysis, and X-ray powder photography; further the NiF_2 so obtained or indeed any other sample of NiF_2 prepared by other routes could not be refluorinated to form the brown phase.

$K_3Ni^{III}F_6$ in Anhydrous HF.—Pure K_3NiF_6 (0.5 mmol) reacted with HF (1 ml) yielding a dark red solution (containing 20% of nickel used) and a brown solid (similar results were observed from $+20$ to -20 °C). This solvolysis could not be reversed in the presence of excess of KF. The brown solid was filtered off, washed with HF without suffering apparent decomposition, and dried briefly *in vacuo*. The oxidation state of nickel in this solid varied from 2.25 to 2.35 whereas μ_{eff} varied from 2.50 to 2.30 B.M. This solid $NiF_{2.30 \pm 0.05}$ was more stable in a dry N_2 atmosphere than the previous $NiF_{2.09 \pm 0.01}$. X-Ray powder patterns of $NiF_{2.30}$ showed only diffuse lines which were similar in position and intensity to those of NiF_2 . The i.r. and u.v. spectra of $NiF_{2.30}$ were featureless. The filtrate from the reaction of K_3NiF_6 with HF was evaporated to dryness and shown to contain KHF_2 and K_2NiF_6 by X-ray powder photography.

$K_2Ni^{IV}F_6$ in HF.—The red complex was found to dissolve well in HF in the range $+20$ to -20 °C but variable amounts of a brown solid were also formed. In plastic tubing pretreated with HF about 20% of the nickel was precipitated. Higher yields of the same solid were obtained by introducing traces of SO_2 with the HF. The brown solid was isolated as before and analysed. The oxidation state of nickel was 2.45–2.51 and μ_{eff} at 298 K was 2.25–2.18 B.M. (Found: Ni, 54.7; F, 45.2. Calc. for $NiF_{2.47}$: Ni, 55.7; F, 44.3%). Samples of this brown compound were the most stable of those so far mentioned, being stable for *ca.* $\frac{3}{4}$ h under dry N_2 before decomposition could be detected.

$K_2Ni^{IV}F_6$ and $Ni^{II}F_2$ in HF.—A solution of K_2NiF_6 in HF reacted instantaneously with a suspension of yellow NiF_2 and an insoluble brown product was isolated. The oxidation state of the nickel was 2.05 and μ_{eff} was 2.83 B.M. (Found: Ni, 59.9; F, 39.3. Calc. for NiF_2 : Ni, 60.7; F, 39.3%). Thus the heterogeneous reaction between K_2NiF_6 and NiF_2 in HF is only superficial.

$K_2Ni^{IV}F_6$ and AsF_5 (or BF_3) in HF.—Solutions of K_2NiF_6

¹ O. Ruff and E. Ascher, *Z. anorg. Chem.*, 1929, **183**, 193.

² P. Henkel and W. Klemm, *Z. anorg. Chem.*, 1935, **222**, 73.

³ L. Stein, J. M. Neil, and G. R. Alms, *Inorg. Chem.*, 1969, **8**, 1779.

⁴ P. G. Nelson, personal communication, 1969.

⁵ J. Soriano, M. Givon, and J. Shamir, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 13.

⁶ L. Stein, J. M. Neil, and G. R. Alms, *Inorg. Chem.*, 1969, **8**, 2472.

⁷ M. Page, *Compt. rend.*, 1967, **264**, C, 2094.

and HF are essentially inert towards the plastic apparatus (after the initial decomposition previously described) and are apparently stable, containing the unsolvolyzed NiF_6^{2-} ion (λ_{max} , 19 000 cm^{-1} and 25 300 cm^{-1}).⁸ However, the addition of either AsF_5 or BF_3 caused the solutions to be decolourised and precipitate black solids. The reaction with BF_3 was slower than with AsF_5 and was more conveniently carried out at 20 °C whereas the AsF_5 reaction took place above -80 °C. Attempts to purify these black solids by successive washing with HF failed in that a brown solid with nickel in the oxidation state 2.20 resulted. Consequently the black solids were isolated by removal of the volatile materials *in vacuo* (Found for the residue from the reaction of AsF_5 with K_2NiF_6 : Ni, 10.4; AsF_6^- , 67.5%; oxidn. state, 2.99, 3.00; μ_{eff} at 298 K, 2.40, 2.41 B.M. Calc. for $\text{NiF}_3 \cdot 2\text{KAsF}_6$: Ni, 10.2; AsF_6^- , 66.5%. Found for residue from reaction of BF_3 with K_2NiF_6 : Ni, 15.9%; oxidn. state, 2.80, 2.82; μ_{eff} at 298 K, 2.41, 2.42 B.M. Calc. for $\text{NiF}_{2.8} \cdot 2\text{KBF}_4$: Ni, 16.3%). E.s.r. measurements showed two strong overlapping signals at 90 K with $g = 1.88$ and 2.01, indicating considerable molecular or lattice distortions. No resonance was detected at room temperature and only weak ones at liquid-helium temperatures. The i.r. spectra of both products contained a broad band at 580 cm^{-1} (half-height-width 100 cm^{-1}) as well as AsF_6^- (and BF_4^-) absorptions.

DISCUSSION

The Reactivity of NiF_6^{2-} .—It has been stated that K_2NiF_6 is inert in 'neutral' HF (*i.e.*, HF to which no acidic or basic solute has been added). The formation of NiF_3 can be viewed as follows: the Lewis acid encourages the loss of a fluoride ion from the octahedral NiF_6^{2-} ion thus reducing the kinetic and also probably the thermodynamic stability of the Ni^{IV} species. This suggests that such high oxidation state complex anions will have an enhanced stability in solutions of high fluoride ion content, *i.e.*, in basic HF solutions. This is analogous to the behaviour of high oxidation state oxy-species in aqueous media.

We are applying such a low-temperature technique for preparing binary fluorides from fluoro-anion complexes to other systems.

The Nature of Ni^{III} in a Fluoride Environment.— K_3NiF_6 . There have been two main opinions about this compound: (a) that it contains nickel(II) and nickel(IV) sites with the possible additional complication of some nickel(III)⁹ also, and (b) that NiF_6^{3-} is the dominant anionic species and exhibits a temperature-dependent equilibrium between high- and low-spin states. The temperature dependence of the magnetic moment has been discussed by several workers.⁹⁻¹¹ Typically, μ_{eff} was 2.12 B.M. at 90 K, 2.26 B.M. at 195 K, and 2.53 B.M. at 294 K. The room-temperature value of the magnetic moment lies between the high and low spin-only values

for a d^7 system. On the basis of magnetic dilution studies, Westland *et al.*¹⁰ concluded that the temperature dependence is satisfactorily explained in terms of an equilibrium between states of differing multiplicity. Nelson and Pearce¹² suggest that K_3NiF_6 is a mixture of $\text{K}_2\text{Ni}^{\text{IV}}\text{F}_6$ and $\text{K}_2\text{Ni}^{\text{III}}\text{F}_4$ on the basis of (i) weight-change experiments during the preparation of K_3NiF_6 , (ii) X-ray powder patterns of the products, and (iii) diffuse reflectance data, which may be assigned equally well to a mixture of either NiF_2 or $\text{KNiF}_3(\text{Ni}^{\text{III}})$ and $\text{K}_2\text{NiF}_6(\text{Ni}^{\text{IV}})$ or to discrete NiF_6^{3-} units. We find that K_3NiF_6 is a unique phase and agree with Henkel and Hoppe¹³ that K_3NiF_6 is not cubic but rather tetragonal or perhaps of a lower symmetry. Although this does not reveal the NiF_6^{3-} site symmetry it strengthens Allen and Warren's interpretation of the electronic spectra (studied by diffuse reflectance at room temperature and 90 K) which they explain in terms of a 2E_g ($t_{2g}^6e_g^1$) low-spin ground state with appreciable tetragonal Jahn-Teller distortion. Their interpretation⁸ also accounts qualitatively for the temperature-dependent magnetic data.

Further evidence for the existence of discrete NiF_6^{3-} ions in M_3NiF_6 lattice comes from the i.r. spectra which show a characteristic absorption at 580 cm^{-1} , which is between the values for NiF_6^{2-} (654 cm^{-1}) and NiF_2 (445 cm^{-1}).¹⁴ Our e.s.r. data at 90 K for K_3NiF_6 ($g = 2.26$) is also compatible with Allen and Warren's interpretation of a 2E_g ground state.

Other e.s.r. studies¹⁵ of Ni^{III} have shown that the ground state varies from high- to low-spin depending on the nature of the host lattice and it appears to us that the argument for Ni^{III} in a fluoride environment being low-spin is more appropriate here. Also the magnitude of the ligand-field splitting in NiF_6^{3-} appears to be extremely close to the crossover value for high to low spin⁸ states.

It is also not easy to understand why the preparation of pure K_3NiF_6 samples is not reproducible. The direct fluorination of a mixture of K^+ and Ni^{2+} salts in a ratio not greater than 4 : 1 gave products containing varying amounts of red K_2NiF_6 : samples free from Ni^{IV} could only be reproducibly obtained when this ratio exceeded 4 : 1.

The solvolysis and disproportionation in HF of K_3NiF_6 is readily explicable if we were to assume that the compound is a lattice aggregate of NiF_6^{2-} , NiF_6^{4-} , and K^+ ions. However we prefer to interpret the disproportionation as follows; NiF_6^{3-} ions are solvolyzed by HF to give solvated F^- and fluorine-bridged units containing Ni^{III} , *e.g.*, $\text{Ni}^{\text{III}}\text{F}_5^{2-}$, which then undergo redox reaction to form the inert, d^6 , $\text{Ni}^{\text{IV}}\text{F}_6^{2-}$ ion and insoluble $\text{NiF}_{2,x}$. The need for excess of K^+ when preparing K_3NiF_6 by direct fluorination can be rationalised similarly: the excess of K^+ should favour the formation of NiF_6^{3-} rather than the less stable fluorine-

⁸ In agreement with the data for solid K_3NiF_6 ; G. C. Allen and K. D. Warren, *Inorg. Chem.*, 1969, **8**, 1895.

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bridged units. Indeed, we find that in the case of K_3CoF_6 and K_3MnF_6 the solvolysis in HF to give CoF_3 and MnF_3 can be reversed by the addition of a 10-fold excess of KF .¹⁶

NiF_3 . These experiments do indicate that NiF_3 has only marginal thermodynamic stability at room temperature. We believe that the nature of Ni^{III} in NiF_3 is similar to that in K_3NiF_6 on the basis of the following observations.

NiF_3 has a broad i.r. absorption at 580 cm^{-1} which is comparable with the i.r. spectrum of K_3NiF_6 . The effective magnetic moment observed for NiF_3 ($2.41 \pm 0.01\text{ B.M.}$) at 298 K differs only by 0.12 B.M. from the value for K_3NiF_6 (2.53 B.M.) at the same temperature. Also the e.s.r. signal from NiF_3 shows the same temperature dependence as that from K_3NiF_6 and is of similar form. It is important to realise that the signals due to NiF_2 and KNiF_3 are more complex and are only observed at liquid-helium temperature.

EXPERIMENTAL

Materials.—Hydrogen fluoride (I.C.I. anhydrous grade) was purified by vacuum transference in a metal-free, fluorocarbon vacuum line.¹⁶ K_3NiF_6 was prepared by direct fluorination of $\text{K}_2\text{Ni}(\text{CN})_4$ in a $1:1\text{ F}_2:\text{N}_2$ stream at 250°C for 3 h. K_3NiF_6 was prepared by direct fluorination of the mixture $3\text{KCl-NiSO}_4\cdot 6\text{H}_2\text{O}$ at $200\text{--}250^\circ\text{C}$ in a $1:1\text{ F}_2:\text{N}_2$ stream for 3 h: after repeated fluorinations the X-ray powder pattern showed no indication of the presence of other phases. NiF_2 was prepared by direct fluorination

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of $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ under similar conditions. BF_3 (Imperial Smelting Corp.) was used without further purification. Arsenic pentafluoride was prepared by direct fluorination of pure arsenic metal at room temperature.

Apparatus.—Most of the work was carried out with a PCTFE manifold constructed at Nottingham. The PCTFE reaction tubes were bought from the Argonne National Laboratories, Illinois. Preparative reactions in HF were carried out on approximately 2 mmol samples of the complex fluorides. In the reactions involving BF_3 and AsF_5 , serious attack of the PCTFE tubes occurred and these were replaced by FEP tubes for this part of the work.

Analysis.—Nickel, hexafluoroarsenate, and fluoride were determined gravimetrically as the dimethylglyoximate, the tetraphenylarsonium salt, and PbClF , respectively. Oxidation states were determined by aqueous iodimetry after reduction with anhydrous HI prepared from dried KI and HF. HI having a higher vapour pressure than HF at room temperature was preferentially distilled from the HF solution on to the sample. X-Ray powder data were obtained by use of a Philips 10 cm camera and $\text{Cu-K}\alpha$ radiation. Magnetic susceptibilities were measured at room temperature by the Gouy method. The u.v.-visible spectra were recorded on a Unicam SP 800 and the i.r. spectra on a Perkin-Elmer 457 grating instrument. E.s.r. data were obtained on a Decca instrument.

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* T. L. Court, Ph.D. Thesis, Nottingham, 1971.