

## 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.<sup>1,2</sup> Henkel and Klemm<sup>2</sup> claimed to have prepared a brown compound  $NiF_{2.5}$  by direct fluorination of  $NiCl_2$ ; a reinvestigation by Stein and his co-workers<sup>3</sup> 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.

Nelson<sup>4</sup> 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.*<sup>5</sup> 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,<sup>6</sup> 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.*<sup>6</sup> 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. Page<sup>7</sup> 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  $\mu_{eff}$  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  $\mu_{eff}$  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  $\mu_{eff}$  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  $K_2NiF_6$

<sup>1</sup> O. Ruff and E. Ascher, *Z. anorg. Chem.*, 1929, **183**, 193.

<sup>2</sup> P. Henkel and W. Klemm, *Z. anorg. Chem.*, 1935, **222**, 73.

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

<sup>4</sup> P. G. Nelson, personal communication, 1969.

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

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

<sup>7</sup> 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  $\text{NiF}_6^{2-}$  ion ( $\lambda_{\text{max}}$ , 19 000  $\text{cm}^{-1}$  and 25 300  $\text{cm}^{-1}$ ).<sup>8</sup> However, the addition of either  $\text{AsF}_5$  or  $\text{BF}_3$  caused the solutions to be decolourised and precipitate black solids. The reaction with  $\text{BF}_3$  was slower than with  $\text{AsF}_5$  and was more conveniently carried out at 20 °C whereas the  $\text{AsF}_5$  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  $\text{AsF}_5$  with  $\text{K}_2\text{NiF}_6$ : Ni, 10.4;  $\text{AsF}_6^-$ , 67.5%; oxidn. state, 2.99, 3.00;  $\mu_{\text{eff}}$  at 298 K, 2.40, 2.41 B.M. Calc. for  $\text{NiF}_3 \cdot 2\text{KAsF}_6$ : Ni, 10.2;  $\text{AsF}_6^-$ , 66.5%. Found for residue from reaction of  $\text{BF}_3$  with  $\text{K}_2\text{NiF}_6$ : Ni, 15.9%; oxidn. state, 2.80, 2.82;  $\mu_{\text{eff}}$  at 298 K, 2.41, 2.42 B.M. Calc. for  $\text{NiF}_2 \cdot 2\text{KBF}_4$ : 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  $\text{cm}^{-1}$  (half-height-width 100  $\text{cm}^{-1}$ ) as well as  $\text{AsF}_6^-$  (and  $\text{BF}_4^-$ ) absorptions.

#### DISCUSSION

*The Reactivity of  $\text{NiF}_6^{2-}$ .*—It has been stated that  $\text{K}_2\text{NiF}_6$  is inert in 'neutral' HF (*i.e.*, HF to which no acidic or basic solute has been added). The formation of  $\text{NiF}_3$  can be viewed as follows: the Lewis acid encourages the loss of a fluoride ion from the octahedral  $\text{NiF}_6^{2-}$  ion thus reducing the kinetic and also probably the thermodynamic stability of the  $\text{Ni}^{\text{IV}}$  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  $\text{Ni}^{\text{III}}$  in a Fluoride Environment.*— $\text{K}_3\text{NiF}_6$ . 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)<sup>9</sup> also, and (b) that  $\text{NiF}_6^{3-}$  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.<sup>9-11</sup> Typically,  $\mu_{\text{eff}}$  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.*<sup>10</sup> concluded that the temperature dependence is satisfactorily explained in terms of an equilibrium between states of differing multiplicity. Nelson and Pearce<sup>12</sup> suggest that  $\text{K}_3\text{NiF}_6$  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  $\text{K}_3\text{NiF}_6$ , (ii) X-ray powder patterns of the products, and (iii) diffuse reflectance data, which may be assigned equally well to a mixture of either  $\text{NiF}_2$  or  $\text{KNiF}_3(\text{Ni}^{\text{III}})$  and  $\text{K}_2\text{NiF}_6(\text{Ni}^{\text{IV}})$  or to discrete  $\text{NiF}_6^{3-}$  units. We find that  $\text{K}_3\text{NiF}_6$  is a unique phase and agree with Henkel and Hoppe<sup>13</sup> that  $\text{K}_3\text{NiF}_6$  is not cubic but rather tetragonal or perhaps of a lower symmetry. Although this does not reveal the  $\text{NiF}_6^{3-}$  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 interpretation<sup>8</sup> also accounts qualitatively for the temperature-dependent magnetic data.

Further evidence for the existence of discrete  $\text{NiF}_6^{3-}$  ions in  $\text{M}_3\text{NiF}_6$  lattice comes from the i.r. spectra which show a characteristic absorption at 580  $\text{cm}^{-1}$ , which is between the values for  $\text{NiF}_6^{2-}$  (654  $\text{cm}^{-1}$ ) and  $\text{NiF}_2$  (445  $\text{cm}^{-1}$ ).<sup>14</sup> Our e.s.r. data at 90 K for  $\text{K}_3\text{NiF}_6$  ( $g = 2.26$ ) is also compatible with Allen and Warren's interpretation of a  ${}^2E_g$  ground state.

Other e.s.r. studies<sup>15</sup> of  $\text{Ni}^{\text{III}}$  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  $\text{Ni}^{\text{III}}$  in a fluoride environment being low-spin is more appropriate here. Also the magnitude of the ligand-field splitting in  $\text{NiF}_6^{3-}$  appears to be extremely close to the crossover value for high to low spin<sup>8</sup> states.

It is also not easy to understand why the preparation of pure  $\text{K}_3\text{NiF}_6$  samples is not reproducible. The direct fluorination of a mixture of  $\text{K}^+$  and  $\text{Ni}^{2+}$  salts in a ratio not greater than 4 : 1 gave products containing varying amounts of red  $\text{K}_2\text{NiF}_6$ : samples free from  $\text{Ni}^{\text{IV}}$  could only be reproducibly obtained when this ratio exceeded 4 : 1.

The solvolysis and disproportionation in HF of  $\text{K}_3\text{NiF}_6$  is readily explicable if we were to assume that the compound is a lattice aggregate of  $\text{NiF}_6^{2-}$ ,  $\text{NiF}_6^{4-}$ , and  $\text{K}^+$  ions. However we prefer to interpret the disproportionation as follows;  $\text{NiF}_6^{3-}$  ions are solvolyzed by HF to give solvated  $\text{F}^-$  and fluorine-bridged units containing  $\text{Ni}^{\text{III}}$ , *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  $\text{NiF}_2 \cdot x$ . The need for excess of  $\text{K}^+$  when preparing  $\text{K}_3\text{NiF}_6$  by direct fluorination can be rationalised similarly: the excess of  $\text{K}^+$  should favour the formation of  $\text{NiF}_6^{3-}$  rather than the less stable fluorine-

<sup>8</sup> In agreement with the data for solid  $\text{K}_3\text{NiF}_6$ ; G. C. Allen and K. D. Warren, *Inorg. Chem.*, 1969, **8**, 1895.

<sup>9</sup> W. Klemm, *Angew. Chem.*, 1954, **66**, 468.

<sup>10</sup> A. D. Westland, R. Hoppe, and S. S. I. Kaseno, *Z. anorg. Chem.*, 1965, **338**, 319.

<sup>11</sup> W. Klemm, W. Brandt, and R. Hoppe, *Z. anorg. Chem.*, 1961, **308**, 179.

<sup>12</sup> R. V. Pearce, Ph.D. Thesis, Hull, 1966.

<sup>13</sup> H. Henkel and R. Hoppe, *Z. anorg. Chem.*, 1969, **364**, 253.

<sup>14</sup> R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 1959, 2762.

<sup>15</sup> P. B. Ayscough, 'Electron Spin Resonance in Chemistry,' Methuen, London, 1967.

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.<sup>16</sup>

$NiF_3$ . 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  $580\text{ cm}^{-1}$  which is comparable with the i.r. spectrum of  $K_3NiF_6$ . The effective magnetic moment observed for  $NiF_3$  ( $2.41 \pm 0.01$  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.<sup>16</sup>  $K_2NiF_6$  was prepared by direct fluorination of  $K_2Ni(CN)_4$  in a 1 : 1  $F_2$  :  $N_2$  stream at  $250^\circ\text{C}$  for 3 h.  $K_3NiF_6$  was prepared by direct fluorination of the mixture  $3KCl-NiSO_4 \cdot 6H_2O$  at  $200-250^\circ\text{C}$  in a 1 : 1  $F_2$  :  $N_2$  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

of  $NiSO_4 \cdot 6H_2O$  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  $Cu-K_\alpha$  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.

We thank the S.R.C. for a research studentship (to T. L. C.) and Dr. P. G. Nelson for discussions.

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<sup>6</sup> T. L. Court, Ph.D. Thesis, Nottingham, 1971.