complexes thus seem to show increased covalency, it is not obvious that there is a sufficiently large difference to cause the marked difference in behavior between the two elements. Instead, the difference in the nature of the tetrahalo complexes in aqueous solution may lie in the fact that the smaller gallium ion does not exhibit a coordination number greater than 4 as would be called for by a mixed halide–water complex.

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO 87544

Fluorine-19 Nuclear Magnetic Resonance Studies of Diamagnetic Fluoride Complexes of Nickel(IV), Palladium(IV), and Platinum(IV) in Anhydrous Hydrogen Fluoride Solutions[1]

BY N. A. MATWIYOFF,[2] L. B. ASPREY, W. E. WAGEMAN, M. J. REISFELD, AND E. FUKUSHIMA

Received July 9, 1968

The ^{19}F nuclear magnetic resonance spectra of the complexes MF_6^{2-} [M represents Ni(IV), Pd(IV), and Pt(IV)], prepared by dissolving the K^+ or Rb^+ salts in anhydrous HF, have been studied over the temperature range −60 to +15°. These diamagnetic complexes, having M(IV) in the low-spin d^6 electronic configuration, exhibit extremely large diamagnetic ^{19}F shifts which are independent of the temperature: NiF_6^{2-}, +253 ppm; PdF_6^{2-}, +284 ppm; and PtF_6^{2-}, +297 ppm, with respect to the doublet signal of the external standard, $CFCl_2CF_2Cl$. The ^{19}F line widths of the PtF_6^{2-} and PdF_6^{2-} ions are narrow at all temperatures indicating that the ions are nonlabile. The line widths obtained for the solutions of K_2NiF_6 and Rb_2NiF_6 are large, but evidence is presented that these are due, not to the lability of NiF_6^{2-}, but to the presence of small amounts of a paramagnetic Ni(III) complex in the salts. The ^{195}Pt–^{19}F spin–spin coupling constant, 2082 Hz, was obtained from the spectra of PtF_6^{2-}.

Introduction

Nickel(IV),[3,4] palladium(IV),[5] and platinum(IV)[5] form diamagnetic fluoride complexes A_2MF_6 containing the octahedral MF_6^{2-} unit in which the central metal ion has the low-spin d^6 electronic configuration. Spectroscopic and magnetic data[3-5] have been obtained for the solids but little is known about the chemistry of these unusual species in solution. As part of a general program of study of the solution chemistry of fluoride complexes, particularly those of metal ions in unusual oxidation states, we have obtained the ^{19}F nmr spectra of solutions of the salts KMF_6. Because these tetravalent ions are reduced by water, we found it was necessary to employ another solvent. Anhydrous HF, which is an excellent solvent for electrolytes and which is extremely resistant to oxidation, proved to be satisfactory.

Experimental Section

1. Preparation of K_2MF_6.—The salts K_2MF_6 were prepared by fluorinating the appropriate divalent cyanide $K_2M(CN)_4$ or chloride K_2MCl_4 complexes. Both starting materials gave the same solid product after the treatment with fluorine. In several experiments, the salt Rb_2NiF_6 was employed. It was prepared by fluorinating $Rb_2Ni(CN)_4$.

In a representative preparation of the K_2MF_6 salt, several grams of $K_2M(CN)_4$ was charged to a sapphire boat which was then placed in a nickel reactor. An equimolar ratio of F_2 and He gases at 1 atm was then streamed through the reactor for several hours at 425°. Following this treatment, pure F_2 gas at 3 atm was admitted to the reactor which was held at 425° for 24 hr. After cooling the reactor to $\sim$25°, the residual F_2 gas was displaced by helium.

The reactor was opened to an inert-atmosphere (helium) box, the sapphire boat was removed, and the product was ground in a mortar. The product was then recharged to the sapphire boat in the reactor and was refluorinated to ensure complete conversion to K_2MF_6.

The ^{19}F nmr spectra of concentrated HF solutions of the K_2MF_6 salts prepared from $K_2M(CN)_4$ are identical with those of K_2MF_6 prepared from K_2MCl_4. In each case, only the signals attributable to HF and the MF_6^{2-} ion could be distinguished. X-Ray powder patterns of the preparations were in excellent agreement with the data reported by Klemm and Huss for K_2NiF_6.[3]

2. Preparation of Solutions.—All solutions for the nmr measurements were prepared by weight under inert-atmosphere conditions. Cylindrical Kel-F tubes (inner diameter $\sim$3 mm and outer diameter $\sim$3.5 mm) were sealed at one end. These were fitted with nickel valves at the open end and attached to a fluorine-transfer line and treated with F_2 gas to remove adsorbed water and oxygen. After F_2 had been displaced from the tube with He gas, the tube was evacuated, detached, weighed, charged with 100–200 mg of K_2MF_6 in an inert-atmosphere box, again evacuated, and reweighed. The tube was then attached to an HF-transfer line and 0.5–0.8 ml of prepurified HF was distilled into the tube.[6] After the appropriate amount of HF had been

---

(1) This work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Visiting Staff Member from The Pennsylvania State University.

(3) W. Klemm and E. Huss, *Z. Anorg. Chem.*, **258,** 221 (1949).

(4) M. J. Reisfeld, L. B. Asprey, and R. A. Penneman, *J. Mol. Spectry.*, **29,** 109 (1969).

(5) D. H. Brown, D. R. Russell, and D. W. A. Sharp, *J. Chem. Soc., A,* 18 (1966), and references therein.

(6) HF (Matheson) was purified by treatment with F_2 gas on a fluorine-transfer line. It was then distilled into a Kel-F storage bulb containing K_2NiF_6, an excellent scavenger for oxygen. In the preparation of the solutions it was distilled from the storage bulb.

transferred, the tube was heat-sealed at its upper end just below the nickel valve and pulled off the line. The weight of HF transferred to the tube was obtained by difference. The Kel-F tube was then inserted into standard 5-mm glass nmr tubes and stored in a liquid nitrogen bath until the nmr measurements were made. No decomposition of the samples stored in the bath was detectable within a 3-month period.

3. Fluorine-19 Nmr Measurements.—Fluorine-19 nmr spectra were recorded by the use of a Varian DP-60 spectrometer operated at 56.45 MHz and equipped with a Varian variable-temperature probe insert. The temperature was controlled and the systems were calibrated in a conventional manner.[7]

Results

The ^{19}F nmr spectrum of a solution of K_2NiF_6 in HF is reproduced in Figure 1. The intense low-field signal is assigned to HF and the high-field signal to the ion NiF_6^{2-}. The assignment is based upon the changes in the relative signal intensities as a function of solution composition. In addition, the chemical shift of the signal assigned to HF is nearly the same as that for pure HF. The temperature dependences of the ^{19}F chemical shifts of anhydrous HF and two representative HF solutions of K_2NiF_6 are summarized in Table I. Also included in the table are the relative areas of the HF and NiF_6^{2-} signals, which show that the composition of the anion in the HF solutions is NiF_6^{2-}. The chemical shifts obtained for solutions of Rb_2NiF_6 are the same as those obtained for the K_2NiF_6 system.

The spectra of the K_2PdF_6 and K_2PtF_6 solutions are similar to those of K_2NiF_6 and consist of a low-field HF resonance and a high-field MF_6^{2-} signal. For the ion PtF_6^{2-} two satellite lines (relative intensity 16.8%) symmetrically disposed about the central resonance (intensity 66.3%) could be distinguished. The satellites arise from the coupling of ^{19}F with the ^{195}Pt isotope having the natural abundance 33.7% and nuclear spin $^1/_2$. For the PdF_6^{2-} complex, the spin–spin coupling of ^{19}F with the ^{105}Pd isotope (natural abundance 22.23% and nuclear spin $^5/_2$) should have produced a weak sextuplet pattern about an intense central line. No such pattern could be detected even for the most concentrated solutions (1.2 m K_2PdF_6), with the use of a variety of magnetic field sweep rates, radiofrequency power levels, etc. Table II contains a summary of the chemical shift and line width data obtained for a representative solution of K_2PtF_6 and of K_2PdF_6 in HF. The ^{19}F chemical shifts obtained for these systems are independent of the solution concentration. However, as might be expected for a dipolar relaxation process,[8] the line widths of these solutions increase gradually as the solute concentration increases. Their temperature dependences, however, remain the same.

Unlike the Pt(IV) and Pd(IV) systems, the HF solutions containing the NiF_6^{2-} ion exhibit line widths which vary widely among solutions of the same nominal NiF_6^{2-} concentration and which decrease markedly as the temperature is lowered. For example, the line widths (in hertz) of a 0.57 m Rb_2NiF_6 solution at +15 and −30° are respectively: $\Delta\nu_{1/2}(\mathrm{HF}) = 102$ and $\Delta\nu_{1/2}(\mathrm{NiF_6^{2-}}) = 47$; $\Delta\nu_{1/2}(\mathrm{HF}) = 15$ and $\Delta\nu_{1/2}(\mathrm{NiF_6^{2-}}) = 7$. The decrease in the line width as the temperature is lowered is accompanied by the accumulation of a small amount (~2 mg in the most concentrated solution, 1.00 m Rb_2NiF_6, at −30°) of a brown precipitate at the bottom of the nmr tube. The precipitate is probably the paramagnetic M_3NiF_6 which is only slightly soluble in HF.[9] For several solutions, the Kel-F nmr tube was inverted and placed in a −78° trichloroethylene–liquid nitrogen slush. After the tube had been allowed to stand in the slush for ~2 hr, it was tilted carefully to its normal position. During the tilting only a small amount of the precipitate which had collected at the top of the tube was carried along with the solution. The line widths obtained for the resulting solution at +15° were comparable to those obtained for the PdF_6^{2-} and PtF_6^{2-} solutions.

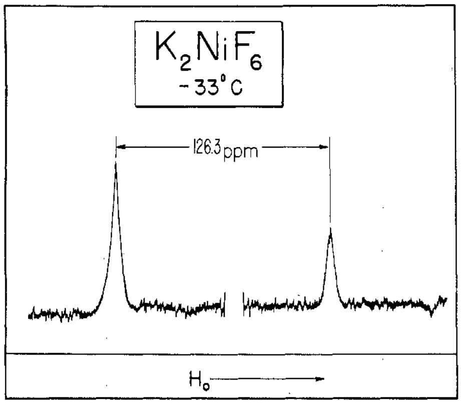

Figure 1.—The ^{19}F nmr spectrum of a 0.63 m solution of K_2NiF_6 in anhydrous HF. The magnetic field increases from left to right. The low-field signal was recorded at a lower radiofrequency field than the high-field one.

In each case, when the precipitate was redissolved, the line widths returned to their former large value. Consequently, we ascribe the temperature dependence of the line widths to an electron–nuclear dipolar relaxation of ^{19}F by the slightly soluble paramagnetic impurity and not to a chemical-exchange process.[10]

Discussion

The ^{19}F nuclei of the MF_6^{2-} complexes studied here are very highly shielded and indeed the ^{19}F resonance for the set occurs at a higher magnetic field than that reported for any diamagnetic complex in solution.[11]

---

(7) N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

(8) N. Bloembergen, "Nuclear Magnetic Relaxation," W. A. Benjamin, Inc., New York, N. Y., 1961.

(9) L. B. Asprey, unpublished observations. The Ni(III) salt could be formed in the reduction of the very reactive Ni(IV) salt by traces of oxygen and water in the inert-atmosphere box or possibly could result from incomplete fluorination of the Ni(II) salt.

(10) Consistent with this proposal is the fact that the HF line widths are larger than those of NiF_6^{2-}. A simple two-site chemical exchange between NiF_6^{2-} and HF would result in HF line widths which are smaller than those of NiF_6^{2-} by a factor of $6[\mathrm{NiF_6^{2-}}]/\{[\mathrm{HF}] + 6[\mathrm{NiF_6^{2-}}]\}$. A significant concentration of a diamagnetic species such as NiF_5^-, which might exchange ^{19}F with HF, can be ruled out because the relative areas and chemical shifts are consistent only with the presence of Ni(IV) in the predominant form NiF_6^{2-}.

(11) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press Ltd., London, 1966, Chapter 11.

Table I

Temperature Dependence of the ^{19}F Chemical Shifts in Anhydrous HF and HF Solutions of K_2NiF_6

Temp, °C	0.63 m K_2NiF_6 soln			1.22 m K_2NiF_6 soln			Anhydrous HF
	Chem shift[a]		Rel area[b]	Chem shift[a]		Rel area[b]	Chem shift[a]
	$\delta(NiF_6^{2-})$	δ(HF)		$\delta(NiF_6^{2-})$	δ(HF)		δ(HF)
−60	. . .	. . .		(128.7)[c]			
−30	253.6	127.3	0.076 (0.076)	. . .	. . .	0.150 (0.146)	+128.8
−15	253.5	128.6	0.075	252.9	128.0		+129.5
0	252.7	128.9	0.074	251.8	128.0	0.148	+130.4
+15	252.4	128.8	0.077	251.3	128.1	0.147	+131.1

[a] Chemical shift in ppm (±0.4) upfield from the doublet of the external standard, $CFCl_2CF_2Cl$; $\delta(NiF_6^{2-})$ refers to NiF_6^{2-} and δ(HF) refers to HF. [b] Area of the NiF_6^{2-} signal relative to that of the solvent HF obtained by manual integration. The relative area expected from the composition of the solution is listed in parentheses. [c] Chemical shift in ppm with respect to the internal standard HF.

Table II

Temperature Dependence of the ^{19}F Chemical Shifts, Line Widths, and Coupling Constants for HF Solutions of K_2PtF_6 and K_2PdF_6

Temp, °C	0.85 m K_2PdF_6 soln				1.67 m K_2PtF_6 soln				
	Chem shift[a]		Line width[b]		Chem shift[a]		Line width[b]		
	PdF_6^{2-}	HF	PdF_6^{2-}	HF	PtF_6^{2-}	HF	PtF_6^{2-}	HF	Coupling constant[c]
−60	(159.3)[d]	. . .	4.7	8.0	. . .	. . .	. .	. .	. . . .
−50	. . . .	. . .	.	. .	297.7	126.7	14.1	17.8	2085
−45	(158.8)[d]	. . .	3.5	. .	. . .	. . .	. .	. .	. . . .
−30	284.2	126.1	2.5	13.1	297.3	126.7	13.2	17.6	2078
−15	(157.5)[d]	. . .	3.8	. .	297.2	126.6	13.8	17.0	2084
0	284.2	127.1	2.0	9.8	297.1	126.5	14.0	16.8	2084
+15	283.9	127.8	5.6	10.8	296.4	126.8	13.2	16.5	2080

[a] See footnote *a*, Table I. [b] Full width of the line at half the maximum height in Hz. The line widths of pure HF as a function of temperature are: −60°, 6.5 Hz; −30°, 5.3 Hz; +15°, 2.2 Hz; 0°, 2.1 Hz. [c] Coupling constant, J_{Pt-F} in Hz (±0.8%), obtained from the separation of the ^{195}Pt–^{19}F satellites in the spectrum of PtF_6^{2-}. [d] Chemical shift in ppm with respect to the internal standard HF.

The large shift is not due to a "solvent effect." Powder samples of K_2PtF_6 and K_2PdF_6 show high-field shifts of the same magnitude as the solutions studied here,[12] while the shifts obtained[12] for the MF_6^{2-} ions in anhydrous HF solutions of K_2SiF_6 and K_2SnF_6 are similar to the values previously reported for the corresponding ions in aqueous solutions.[13] For the purpose of comparison, the chemical shifts of some other representative F^- ion complexes are listed in Table III.

High-field shifts of nuclei adjacent to a transition metal ion with a spin-paired d^6 electronic configuration have been noted by other workers. The ^{17}O resonance of $Co(acac)_3$ (acac represents the acetylacetonate ion) occurs 100 ppm higher in field than the ^{17}O resonance of $Al(acac)_3$.[14] Similarly the ^{14}N shifts of aqueous solutions of hexaammine complexes of Co(III), Rh(III), and Ir(III) with respect to the ^{14}N resonance of aqueous NH_3 are +127, +136, and +157 ppm, respectively.[15]

Table III

^{19}F Chemical Shifts for Representative MF_6^{2-} Complex Ions

Ion	Chem Shift[a]	Ion	Chem shift[a]
TiF_6^{2-}	−152.2	SnF_6^{2-}	+79.3
ZrF_6^{2-}	−73.9	NiF_6^{2-}	+243
HfF_6^{2-}	−33.0	PdF_6^{2-}	+274
SiF_6^{2-}	+51.0	PtF_6^{2-}	+287
GeF_6^{2-}	+46.4		

[a] Shift in ppm with respect to the external standard CF_3CO_2H. A positive sign denotes an upfield shift. Values for the complexes Ti to Sn were taken from ref 13.

The high-field ^{19}F shifts we observed cannot be rationalized using the unmodified theory of Saika and Slichter in which the shift is ascribed largely to paramagnetic contributions from the p electrons localized on the F atom.[16] For that theory to apply, Ni(IV), Pd(IV), and Pt(IV) should have exceptionally small electronegativities. However, the optical electronegativities of these ions (3.25,[4] 2.7,[17]) and 2.7[17] are *larger* than those for Ti(IV) (1.8[17]) and Sn(IV) (1.5[17]). The influence upon the ^{19}F shifts of d–d transitions centered on M(IV) or F→M charge-transfer transitions induced by the magnetic field is difficult to assess. We feel that they must be important but detailed calculations would be premature at this time in view of the complexity of the systems and our uncertainty about their wave functions and electronic energy levels. In this connection Cornwell[18] has shown that the "anomalous" high-field ^{19}F shift of ClF is due to the mixing of a

---

(12) Work in progress in this laboratory.

(13) P. A. W. Dean and D. F. Evans, *J. Chem. Soc., A*, 698 (1967).

(14) Z. Luz, B. L. Silver, and D. Fiat, *J. Chem. Phys.*, **46**, 469 (1967).

(15) R. Bramley, B. N. Figgis, and R. S. Nyholm, *J. Chem. Soc., A*, 861 (1967).

(16) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954); M. Karplus and T. P. Das, *ibid.*, **34**, 1683 (1962).

(17) C. K. Jørgensen, *Mol. Phys.*, **6**, 43 (1963).

(18) C. D. Cornwell, *J. Chem. Phys.*, **44**, 874 (1966).

Cl→F charge-transfer state with ground electronic state in the magnetic field.[19]

It is somewhat surprising that no Pd–F coupling was detected in the nmr spectra. Using the parallelogram rules of Reeves[20] and the coupling constant for the PtF_6^{2-} ion, we would predict a J_{Pd-F} value of ~100 Hz in PdF_6^{2-}. It is unlikely that chemical exchange of the F^- ion would cause collapse of the spin–spin multiplets because the line width and chemical shift data show that all of the MF_6^{2-} ions studied here are nonlabile.

It is possible that the spin–spin interaction is "washed out" *via* the quadrupolar relaxation of the Pd nucleus by electric field gradients (due, for example, to ion-pair formation). The effectiveness of such relaxation depends not only on the field gradient but also on the size of the electric quadrupole moment. For example, M–F spin–spin multiplets can be distinguished in the ^{19}F nmr spectra of the NbF_6^- ion in HF where the ^{93}Nb resonance is also observable, but not in the spectra of the TaF_6^- ion where the ^{181}Ta resonance is too broad to be detected.[12] Both ^{93}Nb and ^{181}Ta are 100% abundant, but the electric quadrupole moment of ^{181}Ta (~3 barns[21]) is more than an order of magnitude larger than that of ^{93}Nb (~−0.2 barns[22]). The magnitude of the ^{105}Pd quadrupole moment apparently has not been measured. Roughly speaking, it must be at least as large as the ^{93}Nb quadrupole moment, if the quadrupolar interaction is responsible for the collapse of the multiplets. An experiment on Pd metal at low temperatures yielded an anomalously large spin–lattice relaxation rate.[23] This could be due to a large quadrupole moment of ^{105}Pd. An upper limit to the moment of ~4 barns was estimated in the latter experiments and it is not inconsistent with our provisional lower limit.

---

(19) It seems clear that a number of electronic states contribute to the chemical shifts of these systems. As noted by Dean and Evans,[13] the ordering of the ^{19}F shifts for the d^0 and d^{10} M(IV) ions in Table IV is not that expected from simple electronegativity considerations. They suggest that the *low-field shift* for the d^0 ions is due to the mixing of the fluorine p and the metal ion d orbitals in the magnetic field.

(20) L. W. Reeves, *J. Chem. Phys.*, **40**, 2423 (1964); P. T. Inglefield and L. W. Reeves, *ibid.*, **40**, 2425 (1964).

(21) K. Murakawa and T. Kamei, *Phys. Rev.*, **105**, 671 (1957).

(22) K. Murakawa, *ibid.*, **98**, 1285 (1955).

(23) A. Narath, A. T. Fromhold, and E. D. Jones, *ibid.*, **144**, 428 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE, CARDIFF, WALES, UNITED KINGDOM

The Electronic Spectrum of the Hexafluoronickelate(IV) Anion

BY G. C. ALLEN AND KEITH D. WARREN

Received October 4, 1968

The electronic spectrum of the hexafluoronickelate(IV) anion has been studied by diffuse reflection in Na_2NiF_6 and K_2NiF_6 between 4 and 45 kK. The weak absorptions at 12.9 and 16.0 kK and the stronger bands at 19.0 and 25.3 kK are assigned, respectively, to d–d transitions from a ${}^1A_{1g}(t_{2g}^6)$ ground state to ${}^3T_{1g}$, ${}^3T_{2g}$, ${}^1T_{1g}$, and ${}^1T_{2g}(t_{2g}^5e_g)$ states, and the intense bands at 30.8 and 38.9 kK, to $\pi \rightarrow e_g$ excitations. The broad band at 19.0 kK shows marked vibrational fine structure which is attributed to the superposition of a symmetric α_{1g} progression on the vibronically (τ_{1u}) allowed transition. Least-squares fitting of the d–d bands using the full Tanabe and Sugano strong-field matrices yields $Dq = 2010\ cm^{-1}$, $B = 515\ cm^{-1}$, and $\beta = 0.43$. The degree of covalency indicated, although exceptionally high for a fluoride complex, is not unexpected in view of the large formal charge on the metal.

Introduction

The fluoride complexes of transition metals exhibit several features of interest in their spectra. They are usually less nephelauxetic even than aquo ions (indicating a smaller tendency toward covalent bonding), and the Laporte-forbidden d–d transitions are not so often masked by allowed charge-transfer bands as in many other complexes. Furthermore, they frequently represent high and unusual oxidation states of the metals involved.

This latter feature is exemplified in potassium hexafluoronickelate(IV), K_2NiF_6, which was first obtained by Klemm and Huss[1] by the action of fluorine on a 2:1 mixture of KCl and $NiCl_2$ at 275°. The rubidium salt was shown by Bodo and Voss[2] to have a regular cubic structure, and the potassium salt by Hoppe[3a] (who also reported, without discussion, a rough spectrum[3b]) to be diamagnetic and therefore to have a low-spin t_{2g}^6 ground state. The measurement of the detailed electronic spectrum has hitherto been hindered by the extreme reactivity of the materials, but Professor R. Hoppe has kindly supplied us with samples of both Na_2NiF_6 and K_2NiF_6 sealed under vacuum in our silica cells, and their diffuse reflectance spectra are now reported.

---

(1) W. Klemm and E. Huss, *Z. Anorg. Chem.*, **258**, 221 (1949).

(2) H. Bodo and E. Voss, *Z. Anorg. Allgem. Chem.*, **286**, 136 (1956).

(3) (a) R. Hoppe, *Angew. Chem.*, **62**, 339 (1950); (b) A. D. Westland, R. Hoppe, and S. S. J. Kaseno, *Z. Anorg. Allgem. Chem.*, **338**, 319 (1965).