plexes have now been characterized, mainly by chemical analysis, chemical properties, and unit-cell data for a few salts. The three complexes with stoichiometry 1:13, 1:11, and 1:4 appear to be the major species in the system. We plan to carry out magnetochemical investigations of the complexes. X-Ray structure determinations have been initiated on the 1:13 and 3:12 compounds.

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Fluorine-19 Nuclear Magnetic Resonance and Raman Spectral Studies of Tantalum(V)-Fluoride Ion Complexes in Anhydrous Hydrogen Fluoride Solutions

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In the 56.45-MHz ^{19}F nuclear magnetic resonance (nmr) spectra of anhydrous HF solutions of $KTaF_6$ and K_2TaF_7, the only ^{19}F signals that could be distinguished are those of HF and the TaF_6^- ion, the latter occurring 12.8 kHz downfield from the HF resonance. The relative areas and chemical shifts of these signals over a wide range of temperature and solution compositions show that the predominant Ta(V)–F^- ion complex present in these solutions is the TaF_6^- ion. In the Raman spectra of the solutions, the only Ta–F vibrations that could be detected are those of the TaF_6^- ion (ν_1 711 cm^{-1}, ν_2 595 cm^{-1}, and ν_5 282 cm^{-1}). The TaF_7^{2-} ion must be a minor species in these solutions, if it is present at all. The ^{19}F nmr signals of anhydrous HF solutions of $KTaF_6$ and $KF-KTaF_6$ mixtures are broadened by chemical exchange of ^{19}F between HF and the TaF_6^- ion *via* two paths: one is independent of the concentration of added F^- ion (k_1 path); the other depends to the first order upon the F^- ion concentration (k_2 path). The chemical exchange parameters derived from the temperature and solution composition dependence of the line broadening are: $k_1(25°) = 4.9 \times 10^2$ sec^{-1}, $\Delta H_1^{\ddagger} = 1.8 \pm 0.3$ kcal, $\Delta S_1^{\ddagger} = -40 \pm 4$ eu; $k_2(25°) = 2.9 \times 10^4\ m^{-1}$ sec^{-1}, $\Delta H_2^{\ddagger} = 2.4 \pm 0.5$ kcal, $\Delta S_2^{\ddagger} = -31 \pm 4$ eu. The mechanisms for the exchange of ^{19}F are discussed.

Introduction

Tantalum(V) exhibits coordination numbers of 6, 7, and 8 in the simple isolated fluoride ion complexes which have been characterized in the solid compounds $CsTaF_6$,[1] K_2TaF_7,[2] and Na_3TaF_8.[3] One interesting question which arises regarding the solution chemistry of these compounds is whether Ta(V) is present in the form of a single complex or whether there exist in solution several F^- ion complexes in which Ta(V) exhibits different coordination numbers. Viewed from another perspective, the question is concerned with the extent to which the occurrence of the unusual ions TaF_7^{2-} and TaF_8^{3-} in solid compounds can be attributed to favorable crystal forces in K_2TaF_7(s) and Na_3TaF_8(s) or whether the occurrence of these ions reflects an inherently small difference in energy among the isolated TaF_6^-, TaF_7^{2-}, and TaF_8^{3-} coordination polyhedra. If the latter is true, stabilization of each of the ions in solution should be possible through control of the F^- ion activity.

Two studies of Ta(V)–F^- ion complexes in solution have been reported. On the basis of potentiometric studies of the F^- ion activity in Ta(V)–aqueous F^- ion systems, it has been suggested[4,5] that all of the species TaF_{5+n}^{n-} (n = 1–3) do exist in solution. However, since activity measurements are sensitive to relatively weak interactions, it is, in general, not possible to distinguish whether a TaF_8^{3-} "ion" detected in an activity measurement contains eight F^- ions in the first coordination sphere of Ta(V) or contains six F^- ions in the first sphere, the remaining two being weakly associated in the second coordination sphere. Keller and Chetham-Strode[6] used Raman spectroscopy (generally sensitive only to strong first-coordination-sphere interactions) to show the TaF_6^- and TaF_7^{2-} ions are present in aqueous HF solutions and aqueous NH_4F solutions of $CsTaF_6$ and K_2TaF_7.

Although not discussed by Keller and Chetham-Strode, the solvent dependence of the equilibria between TaF_6^- and TaF_7^{2-} observed by them is qualitatively consistent with control of the equilibria by the solvent F^- ion activity. The TaF_7^{2-} ion was found to be the predominant species in aqueous 5.42 *M* NH_4F solutions which should exhibit relatively large F^- ion activities. However in 24 *M* aqueous HF, which is a

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(1) B. Cox, *J. Chem. Soc.*, 876 (1956).

(2) J. L. Hoard, *J. Amer. Chem. Soc.*, **61**, 1252 (1939).

(3) J. L. Hoard, W. J. Martin, M. E. Smith, and J. F. Whitney, *ibid.*, **76**, 3820 (1954).

(4) L. P. Varga and H. Freund, *J. Phys. Chem.*, **66**, 21, 187 (1962).

(5) M. N. Buksh and A. G. Maddock, private communication to F. Fairbrother quoted in F. Fairbrother, "The Chemistry of Niobium and Tantalum," Elsevier, New York, N. Y., 1967, p 83.

(6) O. L. Keller, Jr., and A. Chetham-Strode, Jr., *Inorg. Chem.*, **5**, 367 (1966).

strong F^- ion acceptor (*i.e.*, should exhibit a relatively small F^- ion activity[7,8]), the predominant species was found to be the TaF_6^- ion. In less concentrated aqueous HF solutions, both TaF_6^- and TaF_7^{2-} were found to be present in large amounts.[6]

Because anhydrous HF is a stronger fluoride ion acceptor than aqueous HF,[7–9] it should stabilize the the TaF_6^- ion even more with respect to TaF_7^{2-}. We report here the results of ^{19}F nmr and Raman spectral studies that show that the TaF_6^- ion is the predominant species and indeed is the only one observed in anhydrous HF solutions of $KTaF_6$ and $KF–KTaF_6$. Note, however, the composition dependence of the broadening of the ^{19}F nmr signals of these solutions suggests that the TaF_7^{2-} ion may be an intermediate for the chemical exchange of ^{19}F between TaF_6^- and HF. This suggestion is consistent with the results, also discussed herein, of ^{19}F nmr studies of methylene chloride and aqueous HF solutions of salts of the TaF_6^- ion.

Experimental Section

Solvents.—Hydrogen fluoride (Matheson) was purified in the manner described previously.[10] Methylene chloride (Eastman) was dried over Linde 3A molecular sieves and used without additional purification.

Reagents.—Commercially available TaF_5 (Ozark-Mahoning Co.) was contaminated with paramagnetic impurities as shown by the line broadening of the ^{19}F nmr signal.

To obtain material of satisfactory purity, it was found necessary to include a sublimation step in the process. TaF_5 prepared from Ta metal (99.9%) and F_2 gas in a nickel container, or the commercial TaF_5, was sublimed onto a Pt collector. Material prepared in this manner was suitable for nmr studies.

It was found that $KTaF_6$ prepared from TaF_5 and KHF_2 in anhydrous HF showed significant line broadening due to impurities in the KHF_2 despite the fact that the KHF_2 was prepared from reagent grade KCl. Treatment of AR grade KCl in aqueous solution by $Al(NO_3)_3$ [10 g/l.] was followed by addition of NH_3 gas to the solution at 35° with additional heating for 0.5 hr. The $Al(OH_3)$ precipitate and carried impurities were removed by filtration through a coarse glass filter. The Ta salts prepared from the sublimed TaF_5 and the KHF_2 prepared from the purified KCl was of satisfactory purity for nmr studies. Commercially available K_2TaF_7 (α) was recrystallized from 1 *M* aqueous HF.

All solutions were prepared under anhydrous conditions in a Monel–Kel-F vacuum line so constructed that liquid anhydrous HF contacted only Kel-F or perfluoroethylene (FEP) plastics.[10] The commercial HF (Matheson Co.) was purified by vacuum distillation and dried by 24-hr exposure to F_2 gas.

The salt di-*n*-butylammonium difluoride ($[(C_4H_9)_2NH_2]HF_2$) was prepared by adding di-*n*-butylamine ($(C_4H_9)_2NH$) to a large excess of 42% aqueous HF. The resulting solution was then concentrated to a gel on a hot plate and the $[(C_4H_9)_2NH_2]HF_2$ was extracted from the gel with methylene chloride. The white solid which was obtained after the solvent had been allowed to evaporate was recrystallized twice from methylene chloride. The salt di-*n*-butylammonium fluoride ($(C_4H_9)_2NH_2F$) was prepared by adding a large excess of $(C_4H_9)_2NH$ to $[(C_4H_9)_2NH_2]HF_2$. The white powder which was recovered after the excess $(C_4H_9)_2NH$ had been removed *in vacuo* at 50° was recrystallized from methylene chloride. *Anal.* Calcd for $[(C_4H_9)_2NH_2]F$: F, 12.75. Found: F, 12.59. Calcd for $[(C_4H_9)_2NH_2]HF_2$: F, 22.45. Found: F, 22.21.

Di-*n*-butylammonium hexafluorotantalate(V) ($[(C_4H_9)_2NH_2]TaF_6$) was recovered as a white powder from a methylene chloride solution which resulted from the treatment of 5.52 g (0.02 mol) of TaF_5 powder with 100 ml of methylene chloride containing 3.38 g (0.02 mol) of $[(C_4H_9)_2NH_2]HF_2$. A vigorous reaction occurred in which the TaF_5 dissolved and HF(g) was liberated [$((C_4H_9)_2NH_2)HF_2 + TaF_5 \rightarrow ((C_4H_9)_2NH_2)TaF_6 + HF(g)$]. *HF is extremely toxic and the reaction should be conducted using an efficient fume hood.* The solid, which was recovered from the solution by stripping off the methylene chloride *in vacuo* at 40°, was recrystallized from methylene chloride. It was found that no special precautions to exclude moisture from the system during these operations were necessary.

The $[(C_4H_9)_2NH_2]TaF_6$ appears to be stable with respect to hydrolysis by moisture in the laboratory atmosphere. The HF liberated in the treatment of TaF_5 with $[(C_4H_9)_2NH_2]HF_2$ apparently reverses the partial hydrolysis of TaF_5 which occurs during its weighing and transfer to the reaction vessel. In earlier attempts to prepare $[(C_4H_9)_2NH_2]TaF_6$ from TaF_5 and $[(C_4H_9)_2NH_2]F$, the solids that were recovered exhibited intense Ta–O stretching vibrations in the 800–900-cm^{-1} region of the infrared spectrum. No Ta–O vibrations could be detected in the infrared spectra of the solids prepared using $[(C_4H_9)_2NH_2]HF_2$ as a fluoride ion source. *Anal.* Calcd for $[(C_4H_9)_2NH_2]TaF_6$: Ta, 42.6; F, 26.8. Found: Ta, 43.0; F, 26.6.

Measurements.—Raman spectra were recorded with a Cary 81 laser spectrophotometer using the 6328-Å line of a Spectra Physics 125 He–Ne laser as the source of Raman excitation. The scattered radiation was collected at 180° with respect to the exciting line. Samples were contained in 4-mm o.d. FEP (perfluoroethylene), 0.2-mm wall tubes. The end-window was constructed from the FEP tubing wall using glass-blowing techniques.

Nmr spectra were obtained with a Varian DP-60 spectrometer operated in the high-resolution mode at 56.45 MHz. The measurements were made and the systems were calibrated in the manner described previously.[10] Solutions were prepared by weight using containers and a technique that have also been described in detail previously.[10] The area of the HF and TaF_6^-–^{19}F signals were obtained by planimetry of the recorded signals and by taking the product of the maximum intensity of the signal (H) and the full width at half the maximum intensity ($W_{1/2}$). The values obtained from the formula ($HW_{1/2}$) for the approximate area of a Lorentzian curve were consistently lower ($\leq 20\%$) than those obtained by planimetry. However, the *relative* areas of the signals in a given spectrum obtained by the two techniques differed by less than ±5%. The values reported are the average of those obtained from at least four independent measurements. Because of the disparity in the amplitudes of the TaF_6^- and HF nmr signals, the relative area measurements were made in the manner described previously.[11] Fluorine-19 chemical shifts were measured with respect to the external standard, 5 wt % trifluoroacetic acid in methylene chloride.

Results

1. Fluorine-19 Nmr Spectra of Anhydrous HF Solutions.

—The temperature dependence of the ^{19}F nmr spectra of a representative anhydrous HF solution of $KTaF_6$ is summarized in Figure 1. The high-field ^{19}F signal is readily assigned to HF because its chemical shift with respect to trifluoroacetic acid is identical with that for pure HF. The low-field signal

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(7) Dilute aqueous HF is a weak acid. Concentrated aqueous HF solutions exhibit large Hammett acidity functions and are strong acids.[8] The transition from weakly acidic to strongly acidic behavior has been attributed[8] to the formation of HF_2^- and $HF_2^-(HF)_n$ aggregates in concentrated HF solutions. The formation of these aggregates should be accompanied by a large decrease in the activity of F^- ion in the concentrated solutions.

(8) R. P. Bell, K. N. Bascombe, and I. C. McCowbrey, *J. Chem. Soc.*, 1286 (1956).

(9) H. H. Hyman, M. Kilpatrick, and J. J. Katz, *J. Amer. Chem. Soc.*, **79**, 3668 (1957).

(10) N. A. Matwiyoff, L. B. Asprey, W. E. Wageman, M. J. Reisfeld, and E. Fukushima, *Inorg. Chem.*, **8**, 750 (1969).

(11) N. A. Matwiyoff and S. V. Hooker, *ibid.*, **6**, 1127 (1967).

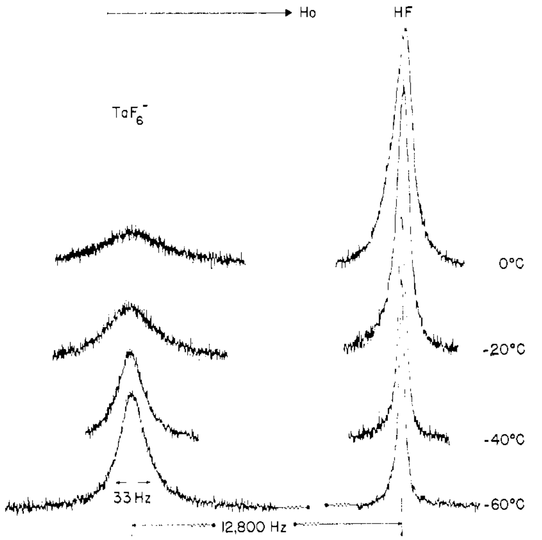

Figure 1—The temperature dependence of the ^{19}F nmr spectra of an anhydrous HF solution of $KTaF_6$ (0.20 *m*). The high-field HF signal was recorded at a lower radiofrequency power level than the TaF_6^- signal.

is assigned to ^{19}F in the TaF_6^- ion on the basis of the dependence of the relative signal areas on the solution composition. The relative areas obtained, together with those expected if ^{19}F resides only at TaF_6^- and HF sites, are listed in Table I for a representative set of solutions.

Table I

Area of the ^{19}F Nmr Signal of the TaF_6^- Ion Relative to That of HF for Representative Anhydrous HF Solutions of $KTaF_6$ and KF–$KTaF_6$

Temp, °C	Rel area, ±6%		Rel area, ±6%	
	0.40 *m* $KTaF_6$	0.72 *m* $KTaF_6$	0.50 *m* KF–0.50 *m* $KTaF_6$	1.22 *m* KF–0.30 *m* $KTaF_6$
−30	0.047 (0.045)[a] [0.0564][a]		0.057 (0.0594)[b] [0.0700][b]	0.031 (0.0351) [0.0412]
−15	0.049	0.085 (0.0864) [0.102]	0.061	
+15	0.050	0.088		

[a] Values in parentheses are the relative areas expected if all the ^{19}F is distributed only between the sites defined as TaF_6^- and HF. Values in brackets are the areas expected if ^{19}F is distributed between TaF_7^{2-} and HF + H^+ sites. [b] Values in parentheses are for the assignments TaF_6^- and HF + F^-; those in brackets are for the assignments TaF_7^{2-} and HF.

The pronounced temperature dependence of the widths of the TaF_6^- and HF signals depicted in Figure 1 can be attributed to chemical exchange of ^{19}F between the two sites.[12,13] Because the chemical shift between the sites is extremely large, the mean lifetime, τ (sec), of ^{19}F at a given site is given to a good approximation by the equation[12,13]

$$1/\tau = k = \pi(\Delta\nu_{1/2} - \Delta\nu_{1/2}{}^0) \qquad (1)$$

where k (sec^{-1}) is the pseudo-first-order rate constant for the exchange of ^{19}F from a given site, $\Delta\nu_{1/2}{}^0$ (Hz) is the full width (at half the maximum intensity) of the ^{19}F signal at that site in the absence of exchange, and $\Delta\nu_{1/2}$ is the width of the exchange-broadened signal.

In Figure 2, the temperature dependence of the widths of the exchange-broadened TaF_6^- signal for a representative set of HF solutions is summarized in a plot of log $\Delta\nu_{1/2}$ *vs.* $10^3/T$. The width of the TaF_6^-

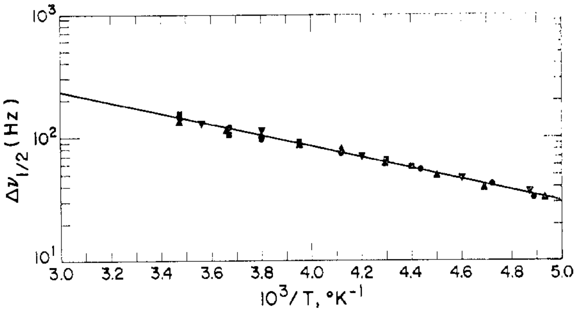

Figure 2.—Arrhenius plot of the exchange-broadened ^{19}F line widths of the TaF_6^- ion in anhydrous HF solutions of $KTaF_6$: ●, 0.05 *m* $KTaF_6$; ▼, 0.28 *m* $KTaF_6$; ■, 0.50 *m* $KTaF_6$.

signal for methylene chloride solutions of $[(C_4H_9)_2NH_2]$-TaF_6 in which chemical exchange of ^{19}F is slow on the nmr time scale is $\Delta\nu_{1/2}{}^0 = 8 \pm 2$ Hz. That value is independent of the temperature (−50 to +35°) and of the solution composition (0.01–0.03 *m* $(C_4H_9)_2NH_2TaF_6$ and 0–0.2 *m* $(C_4H_9)_2NH_2ClO_4$). It is evident from Figure 2 that the TaF_6 line widths of HF solutions of $KTaF_6$ are dominated by chemical exchange throughout the accessible temperature range. The rate constants, k_1, for the exchange of ^{19}F between TaF_6^- and HF were calculated from the data in Figure 2[14] using eq 1 together with the assumption that $\Delta\nu_{1/2}{}^0$ values for TaF_6^- are the same in the solvents HF and methylene chloride. The activation enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) for the exchange were calculated from the temperature dependence of the k values in the conventional manner using the equation

$$1/\tau = k_1 = kT/h \exp(-\Delta H^\ddagger/RT + \Delta S^\ddagger/R) \qquad (2)$$

The exchange parameters obtained are k_1 (sec^{-1} at 25°) = 4.9×10^2, $\Delta H^\ddagger$ (kcal) = 1.8 ± 0.3, and $\Delta S^\ddagger$ (eu) = -40 ± 4.

As illustrated in Figure 3, the addition of KF to the $KTaF_6$ solutions results in an appreciable broadening of both of the ^{19}F nmr signals. Despite a careful search under a variety of conditions, only the TaF_6^- and HF ^{19}F nmr signals could be detected in the spectra of these solutions. The relative areas (see Table I) and chemical shifts of the TaF_6^- signal also show that the predominant Ta(V) complex present (>90%) in HF solutions must be the TaF_6^- ion. Representative ^{19}F

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[12] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

[13] H. M. McConnell, *ibid.*, **28**, 430 (1958).

[14] Because the concentration of ^{19}F at HF sites is much larger than at the TaF_6^- sites, the chemical-exchange broadening of the HF line is small compared to the broadening of the TaF_6^- line. Consequently accurate rate constants could not be derived from the HF line widths.

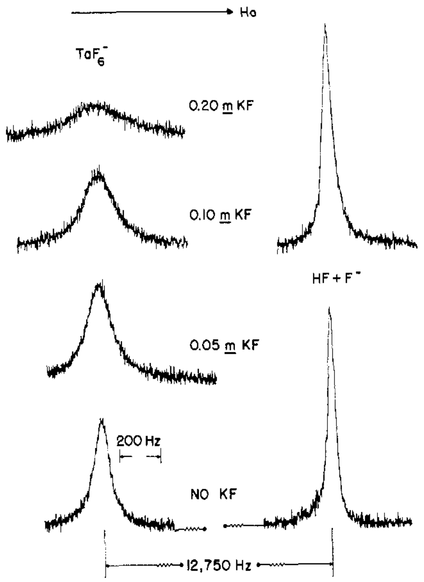

Figure 3.—The ^{19}F nmr spectra of a 0.05 *m* $KTaF_6$ solution in HF containing various amounts of KF. The high-field HF signal was recorded at a lower radiofrequency field than the TaF_6^- signal at 25°.

chemical shifts of the TaF_6^- ion downfield with respect to trifluoroacetic acid at −20° are: 0.05 *m* $KTaF_6$, 6220 ± 30 Hz; 0.25 *m* $KTaF_6$, 6230 Hz ± 20; 0.05 *m* $KTaF_6$–0.1 *m* KF, 6220 ± 30 Hz; 0.05 *m* $KTaF_6$–0.5 *m* KF, 6230 ± 30 Hz. Within the error limits specified, these chemical shifts are independent of the temperature.

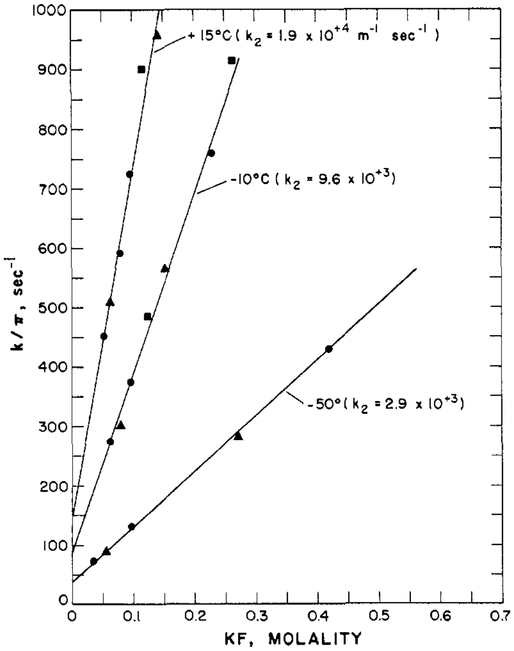

Figure 4.—Plot of the rate constants derived from the TaF_6^- line widths of KF–$KTaF_6$ solutions *vs.* the KF molality: ●, 0.0468 *m* $KTaF_6$; ▼, 0.0643 *m* $KTaF_6$; ■, 0.27 *m* $KTaF_6$.

In Figure 4, the rate constants for the exchange (derived from the TaF_6^- line widths in the manner described above) are plotted *vs.* the concentration (molality) of added KF. It is evident from Figure 4 that the rate constants, *k*, for the exchange of ^{19}F in the KF–$KTaF_6$ solutions can be represented by the equation

$$k = k_1 + k_2[F^-] \qquad (3)$$

where k_1 (sec^{-1}) is the pseudo-first-order rate constant for exchange in the absence of added KF and k_2 (m^{-1} sec^{-1}) is the second-order rate constant for the exchange of ^{19}F *via* a path which is directly dependent upon the concentration of added KF. Values of k_2 derived from the slopes of the lines are also included in Figure 4, and in Figure 5 these values, together with others obtained in this manner, are summarized in a plot of log k_2 *vs.* $10^3/T$. The chemical-exchange parameters calculated from the data in Figure 5 are $k_2(25°) = 2.1 \times 10^4\ m^{-1}$ sec^{-1}, $\Delta H^{\ddagger} = 2.4 \pm 0.5$ kcal, and $\Delta S^{\ddagger}(25°) = -31 \pm 4$ (eu).

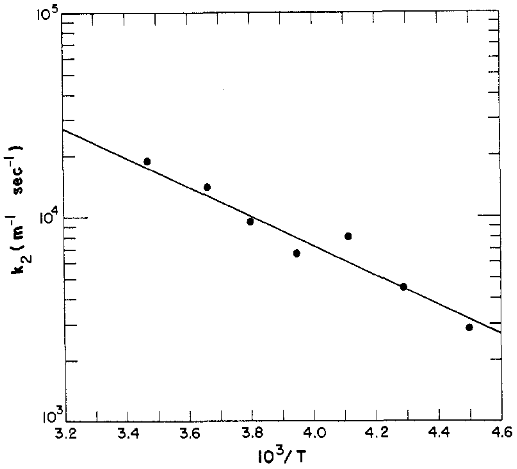

Figure 5.—Plot of log k_2 *vs.* $10^3/T$ for KF–$KTaF_6$ solutions in anhydrous HF.

The k_1 values obtained from the intercepts of plots like those in Figure 4 for the KF–$KTaF_6$ solutions are the same, within the error limits, as those obtained for the $KTaF_6$ solutions containing *no* added KF. Typical values of k_1 (sec^{-1}) obtained from the plots in Figures 2 and 4, respectively, are: +15°, 4.1 × 10^2 and 4.7 × 10^2; −50°, 1.0 × 10^2 and 1.3 × 10^2.

2. Fluorine-19 Nmr Spectra of Aqueous HF and Methylene Chloride Solutions.—In an attempt to elucidate the mechanism of ^{19}F exchange between TaF_6^- and HF (or F^- ion), we have studied the ^{19}F nmr spectra of TaF_6^- in other solvents. For solutions of $KTaF_6$ in 42 wt % aqueous HF, only a single nmr line could be distinguished in the temperature range, −50 to +35°, under a variety of instrument operating conditions. That signal exhibits a chemical shift which is the weighted average of the aqueous HF and TaF_6^- shifts. Consequently rapid exchange of F^- ion between the TaF_6^- and aqueous HF sites occurs throughout the temperature range, −50 to +35°.

Solutions of $[(C_4H_9)_2NH_2]TaF_6$ in methylene chloride exhibit a single, narrow TaF_6^- ^{19}F nmr signal having a chemical shift (−6580 ± 10 Hz) with respect to trifluoroacetic acid and line width ($\Delta\nu_{1/2}{}^0$ = 8 Hz) which are independent of the temperature in the range −50 to

+35°. The addition of small amounts of F^- ion (in the form of $[(C_4H_9)_2NH_2]F$) appreciably broadens the TaF_6^- signal without shifting it detectably. The broadening increases regularly with the amount of $[(C_4H_9)_2NH_2]F$ added to the solution until, at ~0.01 *m* added F^- ion, the signal is too broad to detect. We attribute the broadening to chemical exchange of ^{19}F because the ClO_4^- ion (in the form $[(C_4H_9)_2NH_2]ClO_4$) has no effect on the nmr spectra of the TaF_6^- ion solutions. We do not report any quantitative data here because the low intensity of the signals precludes the measurement of accurate line widths. The ^{19}F signals of the F^-–TaF_6^- solutions were very weak because of their line widths and because of the slight solubility of $[(C_4H_9)_2NH_2]TaF_6$ in the presence of $[(C_4H_9)_2NH_2]F$.

The salt $[(C_4H_9)_2NH_2]TaF_6$ is very soluble ($\geq 0.3\ m$) in methylene chloride solutions containing $[(C_4H_9)_2NH_2]HF_2$. These solutions exhibit two ^{19}F nmr signals the relative areas of which (throughout the concentration range studied, 0.1–0.3 *m* $[(C_4H_9)_2NH_2]TaF_6$ and 0.4–5.3 *m* $[(C_4H_9)_2NH_2]HF_2$) are consistent with their assignments to TaF_6^- and HF_2^-. The TaF_6^- signal is exchange broadened by the HF_2^- ion but to a much smaller extent than by F^- ion. A methylene chloride solution containing 0.3 *m* TaF_6^- and 1.0 *m* HF_2^- exhibits a TaF_6^- ion line width of only 200 Hz at +24°. The TaF_6^- line width increases gradually, but not linearly, with an increase in the HF_2^- ion concentration. A quantitative assessment of the chemical exchange effects must await analysis of the ion-pair equilibria which should be important because CH_2Cl_2 has a low dielectric constant.

3. **Raman Spectra.**—We could detect no Ta–F vibrations in the Raman spectra of methylene chloride solutions of $[(C_4H_9)_2NH_2]TaF_6$ containing $[(C_4H_9)_2NH_2]F$ or $[(C_4H_9)_2NH_2]HF_2$, presumably due to the low solubility of the Ta(V) complex in those solutions. The bands we observed in the Raman spectra of solid Ta–F complexes and of their HF solutions are summarized in Table II. The frequencies of the Ta–F vibrations detected in the spectra of HF solutions of $KTaF_6$ and $KTaF_7$ are the same as those detected in the spectra of solid $KTaF_6$ (which contains the TaF_6^- ion) but different from those of solid K_2TaF_7 (which contains TaF_7^{2-}).

TABLE II

Ta–F VIBRATIONAL FREQUENCIES IN THE RAMAN SPECTRA OF Ta(V)–F^- COMPLEXES

0.83 *m* $KTaF_6$	1.00 *m* K_2TaF_7	$KTaF_6$(s)	K_2TaF_7(s)
711 ($\rho \leq 0.2$)[a]	711 ($\rho \leq 0.2$)	710	645
595[b]	595[b]	590	400
282 (depolarized)	280 (depolarized)	280	290

[a] Depolarization ratio, ρ. [b] The low intensity of this band prevented polarization studies.

Discussion

The ^{19}F nmr and Raman spectral data show that the predominant Ta(V) complex in anhydrous HF solutions of $KTaF_6$ and KF–$KTaF_6$ is the TaF_6^- ion. The TaF_6^- ion thus is a weaker F^- ion acceptor than is anhydrous HF. Indeed, the nmr data show that the TaF_6^- ion cannot even compete effectively for F^- ion with the HF_2^- ion present at large concentrations in methylene chloride solutions.

Although Ta–F complexes having coordination numbers larger than 6 are not present in anhydrous HF solutions at concentrations detectable by nmr and Raman techniques, the TaF_7^{2-} ion may be an intermediate for the chemical exchange of ^{19}F between TaF_6^- and HF. The k_2 path (eq 3) we deduced for that exchange implies a "bimolecular" attack by F^- ion at TaF_6^-, proceeding *via* a direct S_N2 displacement or a TaF_7^{2-} intermediate.[15] The fact that the qualitatively assessed rate of ^{19}F exchange in several solvent systems parallels the expected ranking of the solvent F^- ion donor properties (F^- in methylene chloride and aqueous HF > F^- in anhydrous HF > HF_2^- in methylene chloride) is also consistent with a "bimolecular" mechanism.

Such "bimolecular" displacements are highly unusual for octahedral complexes[15,16] but, of course, the most extensive kinetic data available for the substitution reactions of octahedral complexes have been obtained with compounds of the first transition series elements for which complexes with monodentate ligands are generally restricted to maximum coordination numbers of 6. The TaF_7^{2-} complex, however, exists in the solid K_2TaF_7[2] and in aqueous solutions containing Ta(V) and HF or NH_4F.[6] Accordingly, it is not unreasonable to expect that such a complex could be formed as a low-energy intermediate in anhydrous HF solutions. The unusually small activation enthalpy and abnormally large *negative* activation entropy associated with the k_2 path are consistent with the intervention of a TaF_7^{2-} intermediate in the TaF_6^-–HF chemical exchange.

The k_1 path for the exchange between HF and TaF_6^- also has associated with it a large negative entropy and small enthalpy of activation, the values of which activation parameters are similar to those for the k_2 path. Because the F^- ion certainly is available from the dissociation of HF,[17,18] we cannot definitely exclude a common mechanism for the k_1 and k_2 paths. However, if ^{19}F exchange between TaF_6^- and HF in HF solutions containing only $KTaF_6$ does occur *via* attack at TaF_6^- by the F^- ion arising from the dissociation of HF, then a comparison of the values of k_1 and k_2 requires that the equilibrium constant for the dissociation of HF be $>10^{-4}$. Since the latter is many orders of magnitude larger than the best estimates[18] of the dissociation constant of HF containing no solute, we consider it unlikely that the k_1 path involves attack by the F^- ion. Instead, it may involve an HF-assisted dissociation of the F^- ion from TaF_6^-. In this regard, we have observed[19] that

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[15] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

[16] D. N. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, **90**, 608 (1968).

[17] The F^- ion in ahydrous HF is probably present as an $F^-(HF)_n$ aggregate.[8]

[18] H. H. Hyman and J. J. Katz, in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, New York, N. Y., 1965, p 59.

[19] N. A. Matwiyoff and L. B. Asprey, work in progress.

solute ions such as TiF_6^{2-} and SiF_6^{2-} rapidly exchange ^{19}F with the solvent anhydrous HF (at a rate independent of added F^- ion) *via* a low activation energy path. For the latter complexes, facile nucleophilic displacement of ^{19}F by HF is unlikely, but an HF-assisted dissociation of F^- ion seems reasonable.

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A Calorimetric Study of Prussian Blue and Turnbull's Blue Formation[1a]

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Values of $\Delta H°$ valid at zero ionic strength and 25° have been determined calorimetrically for the formation of "soluble" Prussian blue and Turnbull's blue from their constituent ions in dilute aqueous solution. The calorimetric data are shown to be consistent with literature data for the Fe^{3+}–$Fe(CN)_6^{4-}$ redox reaction. The results are discussed in terms of the energy relationships for two proposed mechanisms of complex formation.

Introduction

The "soluble" forms[2,3] of Prussian blue and Turnbull's blue have been known for many years and present interesting examples of the intense colors exhibited by species containing the same element in different oxidation states. For many years Prussian blue and Turnbull's blue were thought to be different, primarily because of the different method by which they are formed as shown by the reactions

$$Fe^{2+} + Fe(CN)_6^{3-} = \text{Turnbull's blue} \tag{1}$$

$$Fe^{3+} + Fe(CN)_6^{4-} = \text{Prussian blue} \tag{2}$$

Keggin and Miles[4] found the structures of the crystalline forms of Prussian blue and Turnbull's blue to be identical and to consist of one group of iron atoms surrounded by an octahedral arrangement of carbon atoms while another group of iron atoms is surrounded by an octahedral arrangement of nitrogen atoms. A theoretical treatment[5] of the electronic structure of Prussian blue based on ligand field theory considerations is consistent with the compound having the formula $KFe^{III}[Fe^{II}(CN)_6]$. Mössbauer spectra[6] of solid Prussian blue and Turnbull's blue indicate they are identical and these spectral data are in complete agreement with their formulation as a ferric ferrocyanide species. The Mössbauer spectra[6] further indicate that very weak ionic bonding exists between the nitrogen end of the bonded cyanide ion and the ferric ion. A more complete discussion of the evidence for the identity and structure of solid Prussian blue and Turnbull's blue has recently appeared.[7]

A search of the literature reveals that no thermodynamic data have been reported for the formation of soluble Prussian blue and Turnbull's blue. Such data would be useful in understanding the energy relationships involved in such formation. In this paper are presented $\Delta H°$ values for the formation of the soluble forms of Prussian blue and Turnbull's blue from their respective ions.

Experimental Section

Materials.—Reagent grade $FeSO_4 \cdot 7H_2O$ (Baker and Adamson), $K_4Fe(CN)_6$ (Mallinckrodt), $K_3Fe(CN)_6$ (Mallinckrodt), and standard iron wire (Baker and Adamson) were used in the preparation of solutions for this study. An $Fe(ClO_4)_3$ solution was prepared by dissolving a weighed amount of standard iron wire in a known volume of hot concentrated $HClO_4$ and diluting with an appropriate volume of water.

All solution preparations and manipulations were carried out under a nitrogen atmosphere to minimize oxidation of air-sensitive compounds.

Procedure.—The calorimeter and supporting equipment have been described.[8] The calorimetric procedure consisted of adding 10-ml portions of 0.1 *M* potassium ferrocyanide and potassium ferricyanide solutions to 200 ml of 10^{-3} *M* ferric and ferrous solutions, respectively. The time interval from when the solutions were mixed to when the calorimetric measurement was finished was always less than 5 min. The reagents were mixed in stoichiometric amounts in order to avoid formation of any insoluble Prussian or Turnbull's blue.[2] Corrections were made for the dilution of potassium ferricyanide and potassium ferrocyanide

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[2] G. D. Parkes, Ed., "Mellor's Modern Inorganic Chemistry," revised edition, Wiley, New York, N. Y., 1961, p 927.

[3] There appear to be two forms of Prussian blue and Turnbull's blue. One form "dissolves" in water giving a deeply colored blue "solution." This form is referred to as the "soluble" form and results when 1 equiv of Fe^{2+} is added to $Fe(CN)_6^{3-}$ or 1 equiv of Fe^{3+} is added to $Fe(CN)_6^{4-}$. The "insoluble" form results when nonstoichiometric quantities of the above salts are mixed.[2] This paper deals primarily with the "soluble" form of Prussian and Turnbull's blue which is represented as $KFeFe(CN)_6$.

[4] J. F. Keggin and F. D. Miles, *Nature (London)*, **137**, 577 (1936).

[5] M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

[6] E. Fluck, *Advan. Inorg. Chem. Radiochem.*, **6**, 433 (1964).

[7] L. D. Hansen, W. M. Litchman, and G. H. Daub, *J. Chem. Educ.*, **46**, 46 (1969).

[8] J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, **67**, 2605 (1963).