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Perfluoroammonium and Cesium Fluorotungstates

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The syntheses of NF_4^+ salts containing fluorotungstate anions were studied. The new NF_4WOF_5 salt was prepared by the reaction of WOF_4 with a concentrated solution of NF_4HF_2 in anhydrous HF. It is a white solid, stable up to 60 °C. At higher temperatures it decomposes to $NF_4W_2O_2F_9$, NF_3, OF_2, and WF_6. The ionic nature of NF_4WOF_5 in the solid state was established by vibrational spectroscopy, but in dilute HF solutions the WOF_5^- anion solvolyzes according to $2WOF_5^- + HF \rightleftarrows W_2O_2F_9^- + HF_2^-$. In HF solution WF_6^- is readily oxidized by NF_4^+ to yield WF_6 and NF_3. The syntheses and some reaction chemistry and properties of $CsWOF_5$, $CsW_2O_2F_9$, $Cs_2WO_2F_4$, and $CsWF_6$ are discussed.

Introduction

The synthesis of a stable NF_4^+ salt containing a fluorotungstate anion is of significant interest for solid-propellant WF_6 gas generators. In this paper the synthesis and characterization of the first known example of a stable NF_4^+ fluorotungstate salt are reported, and some reaction chemistry of various cesium fluorotungstates in anhydrous HF is discussed.

Experimental Section

Apparatus. Volatile materials used in this work were handled in a stainless steel–Teflon FEP vacuum line. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution with use of an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.[1] Thermal decomposition measurements were carried out in a previously described[2] sapphire reactor.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and a Claassen filter[3] for the elimination of plasma lines. Sealed glass, Teflon FEP, or Kel-F tubes were used as sample containers in the transverse-viewing transverse-excitation mode. Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external $CFCl_3$ with positive shifts being downfield from the standard.[4]

Elemental analyses were carried out as previously described.[5]

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[6] NF_4HF_2 solutions in HF,[7] and WOF_4.[8] Hydrogen fluoride (Matheson) was dried by storage over BiF_5 to remove the H_2O.[9] Tungsten hexafluoride (Alfa) and CsI (Alfa, 99.9%) were used as received. Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox. Sulfur dioxide (Matheson) was dried over P_2O_5 and purified by fractional condensation prior to use.

Preparation of $CsWOF_5$. Cesium fluoride (9.93 mmol) was loaded inside the drybox into a prepassivated Teflon FEP ampule. Anhydrous HF (15 mL, liquid) was added to the ampule on the vacuum line, and 9.9 mmol of distilled H_2O was added with a syringe. The mixture was allowed to homogenize, and WF_6 (9.96 mmol) was added in vacuo at −196 °C. After the ampule was kept at ambient temperature for several hours, all material volatile at 55 °C was pumped off. On the basis of its weight and vibrational spectra, the solid residue was mainly $CsWOF_5$[10,11] containing only small amounts of $CsW_2O_2F_9$[12] and $CsHF_2$.

Preparation of $CsW_2O_2F_9$ by Solvolysis of $CsWOF_5$ in HF. A sample of $CsWOF_5$ (2.35 mmol) in a Teflon ampule was stirred in anhydrous HF (10 mL, liquid) for 12 h at 24 °C. The undissolved material was separated from the solution by filtration at 24 °C, and all volatile material was pumped off at 55 °C. On the basis of the observed mass balance and vibrational spectra, the filter cake consisted of $CsW_2O_2F_9$[12] (~1.1 mmol) and the filtrate residue consisted of $CsHF_2$ (~1.2 mmol) containing as an impurity $Cs_2WO_2F_4$,[13] which was formed by hydrolysis of some $CsWOF_5$.

Preparation of $Cs_2WO_2F_4$. Cesium fluoride (37 mmol) and 20 mL of 48% aqueous HF were combined in a Teflon FEP ampule to which WF_6 (18.47 mmol) was added at −196 °C on the vacuum line. When the mixture warmed to room temperature, initially a white precipitate formed, which subsequently dissolved, resulting in a clear solution. The solution was poured into a 250-mL Teflon beaker, and the aqueous HF solvent was evaporated on a hot plate at 60 °C. The resulting white residue (10.24 g, weight calculated for 18.47 mmol of $Cs_2WO_2F_4$ = 10.40 g) was shown by vibrational spectroscopy to be essentially pure *cis*-$Cs_2WO_2F_4$.[13] Treatment of $Cs_2WO_2F_4$ with anhydrous HF resulted in the partial conversion of $Cs_2WO_2F_4$ to $CsWOF_5$, $CsW_2O_2F_9$, and $CsHF_2$.

Preparation of $CsWF_6$. Cesium iodide (21.2 mmol) was loaded in the drybox into a prepassivated Teflon U-tube, equipped with a Teflon filter, and anhydrous HF (26 mL, liquid) was added at −196 °C on the vacuum line. On warming toward ambient temperature, the HF reacted with the CsI to form HI, which accumulated in the bottom of the U-tube as a separate liquid phase. Tungsten hexafluoride (32.46 mmol) was added to the U-tube at −196 °C, and the mixture was allowed to warm to ambient temperature. A copious precipitate of black iodine crystals formed. The mixture was kept at 25 °C for 12 h, and the clear solution was filtered into a second prepassivated Teflon U-tube attached through Teflon tubing and valves to the first U-tube. The HF solvent and small amounts of I_2 were pumped off from the contents of the second U-tube at 55 °C for 2 h, resulting in a slightly off-white solid (4.856 g, weight calculated for 21.2 mmol of $CsWF_6$ = 9.144 g), which was identified by vibrational spectroscopy[14–18] as $CsWF_6$. A second extraction of the precipitate with 16 mL of liquid HF resulted in an additional 3.011 g of $CsWF_6$, indicating that $CsWF_6$ is only moderately soluble in HF.

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Reaction of CsI with SO_2. Dry CsI (6.30 mmol) was loaded in the drybox into a Teflon ampule, and SO_2 (51.4 mmol), which had been stored over P_2O_5, was added at −196 °C on the vacuum line. On warming, all the CsI reacted with SO_2 to form a red solution. Removal of the excess of unreacted SO_2 at −10 °C resulted in a red-orange solid of the approximate composition $CsI\cdot 4SO_2$, which at 25.5 °C exhibited a dissociation pressure of 450 torr. Exhaustive dissociation of the adduct at 25.5 °C produced pure SO_2 and CsI (6.3 mmol).

Preparation of NF_4WOF_5. A mixture of CsF (21.99 mmol) and NF_4SbF_6 (22.14 mmol) was loaded in the drybox into one half and WOF_4 (14.59 mmol) into the other half of a prepassivated Teflon double-U metathesis apparatus. Dry HF (16 mL, liquid) was added on the vacuum line to the half containing the NF_4SbF_6–CsF mixture and was warmed to 25 °C for 30 min with stirring. After this mixture was cooled to −78 °C, the metathesis apparatus was inverted and the NF_4HF_2 solution was filtered into the other half of the apparatus containing the WOF_4. The NF_4HF_2–WOF_4 mixture in HF was stirred for 30 min at 25 °C, and then the volatile material was pumped off for 12 h at 25 °C and 0.8 h at 50 °C. The volatile material, trapped at −196 °C, was shown by infrared spectroscopy to consist of HF and NF_3 and did not contain any tungsten species. The filter cake (8.06 g; weight calculated for 21.99 mmol of $CsSbF_6$ = 8.11 g) and the filtrate residue (4.99 g; weight calculated for 14.59 mmol of NF_4WOF_5 = 5.61 g) were shown by vibrational spectroscopy to consist of $CsSbF_6$ and mainly NF_4WOF_5, respectively. On the basis of its elemental analysis, the filtrate residue had the composition (wt %): NF_4WOF_5, 96.1; $CsSbF_6$, 2.0; NF_4SbF_6, 1.9. Anal. Calcd: NF_3, 18.14; Cs, 0.72; W, 45.91; Sb, 1.37. Found: NF_3, 18.05; Cs, 0.7; W, 46.0; Sb, 1.32.

Preparation of $NF_4W_2O_2F_9$. A sample of NF_4WOF_5 was placed into a sapphire tube equipped with a stainless steel valve. The contents of the tube were heated in a dynamic vacuum to 155 °C for 6.5 h and to 180 °C for 4 h. On the basis of the observed weight change and the vibrational spectra, the conversion of NF_4WOF_5 to $NF_4W_2O_2F_9$ was essentially complete.

In an alternate method, NF_4WOF_5 was dissolved in anhydrous HF and formed a precipitate. This precipitate was separated from the solution by filtration and, on the basis of its vibrational spectra, consisted of $NF_4W_2O_2F_9$.

Results and Discussion

Syntheses and Reaction Chemistry of $CsWOF_5$, $CsW_2O_2F_9$, $Cs_2WO_2F_4$, $CsWF_6$, WOF_4, and H_3OWOF_5. The synthesis of $CsWOF_5$ was first reported[19] in 1958 by Hargreaves and Peacock and involved the reaction of moist CsF with WF_6 in IF_5 solution. In subsequent reports,[10,20] either the original or slightly modified methods were used replacing the IF_5 solvent by CH_3CN and using WOF_4 as a starting material. Since in Hargreave and Peacock's method an excess of water can result in $WO_2F_4^{2-}$ formation, a better control of the amount of water used in the reaction was desirable. Furthermore, the intended reactions with NF_4^+ salts required the use of anhydrous HF as a solvent. Consequently, our $CsWOF_5$ preparation was carried out in such a manner that dry CsF, WF_6, and a stoichiometric amount of water were used in anhydrous HF solution. On the basis of its vibrational spectra, the resulting solid product consisted of $CsWOF_5$[10,11] containing small amounts of $CsW_2O_2F_9$[12] and $CsHF_2$. During an attempt to determine the solubility of $CsWOF_5$ in anhydrous HF, it was found that the salt did not completely dissolve in anhydrous HF. The insoluble material was filtered off and identified by vibrational spectroscopy as $CsW_2O_2F_9$.[12] The residue isolated from the filtrate after solvent removal consisted mainly of $CsHF_2$ contaminated by a small amount of *cis*-$Cs_2WO_2F_4$.[13] The latter was most likely produced by hydrolysis of some $CsWOF_5$ by a trace of water present in the large amount of HF used as a solvent. These results demonstrate the existence of the equilibrium reaction in anhydrous HF shown by eq 1.

$$2CsWOF_5 + HF \rightleftarrows CsW_2O_2F_9\downarrow + CsHF_2 \qquad (1)$$

A large excess of HF and the low solubility of $CsW_2O_2F_9$ can shift this equilibrium all the way to the right. Separation of the $CsW_2O_2F_9$ precipitate from the $CsHF_2$ solution, followed by washing with anhydrous HF, affords essentially pure $CsW_2O_2F_9$ and thus offers a convenient synthetic method for the preparation of this compound. Equilibrium 1 is in excellent agreement with that observed by Bougon and co-workers[12] for the HF–WOF_4 system (eq 2). If the $CsHF_2$ and $CsW_2O_2F_9$

$$2WOF_4 + 2HF \rightleftarrows W_2O_2F_9^- + H_2F^+ \qquad (2)$$

are not separated prior to HF removal, equilibrium 1 is shifted back to the left on HF removal and in our experiments resulted in a mixture containing about 95 mol % $CsWOF_5$ and 5 mol % $CsW_2O_2F_9$.

The above described synthesis of $CsWOF_5$ by controlled hydrolysis of WF_6 in a CsF-containing HF solution is similar to the previously reported[8] hydrolysis of WF_6 in HF according to eq 3. However, on the basis of the results of this study,

$$\begin{aligned} SiO_2 + 4HF &\rightarrow SiF_4 + 2H_2O \\ H_2O + WF_6 &\xrightarrow{HF} WOF_4 + 2HF \end{aligned} \qquad (3)$$

care must be taken to use an excess of WF_6 in this reaction. In the presence of an excess of water, $H_3O^+WOF_5^-$ and $H_3O^+W_2O_2F_9^-$ are formed according to eq 4 and 5. Since

$$2H_2O + WF_6 \xrightarrow{HF} H_3O^+WOF_5^- + HF \qquad (4)$$

$$3H_2O + 2WF_6 \xrightarrow{HF} H_3O^+W_2O_2F_9^- + 3HF \qquad (5)$$

these oxonium salts are also volatile, they are difficult to separate from WOF_4 by sublimation. It should be noted that in the previous report[21] on the synthesis of $H_3O^+WOF_5^-$ the observed anion spectra were incorrectly ascribed to a distorted WOF_5^- anion. The reported spectra[21] are identical with those published[12] for $W_2O_2F_9^-$, which were also confirmed by the results of this study (see below).

For the synthesis of $Cs_2WO_2F_4$, the use of an HF-soluble tungsten species[22] and of an aqueous HF solution are important. In agreement with a previous report,[22] WO_3 or H_2WO_4[23] was found difficult to dissolve completely in aqueous HF, but WF_6 and CsF in a 1:2 mole ratio were found to be a convenient alternate to Cs_2WO_4[22] as a starting material for the preparation of pure *cis*-$Cs_2WO_2F_4$. If anhydrous HF is used in place of aqueous HF as a solvent, equilibria 6 and 1

$$Cs_2WO_2F_4 + 3HF \rightleftarrows CsWOF_5 + CsHF_2 + H_2O \qquad (6)$$

were found to become important. Equilibrium 1 results in a precipitation of $CsW_2O_2F_9$, which can be isolated by filtration, while the residue obtained from the filtrate consists of $Cs_2WO_2F_4$ and $CsHF_2$. The vibrational spectra observed for $Cs_2WO_2F_4$ agree well with those[13,23,24] previously reported and confirm that $WO_2F_4^{2-}$ is present as the cis isomer.

For the synthesis of $CsWF_6$, the original method[25] based on the reaction given by eq 7 did not lead to a pure product,

$$2CsI + 2WF_6 \xrightarrow{SO_2} 2CsWF_6 + I_2 \qquad (7)$$

in agreement with previous reports.[16,26] Even when the reaction was carried out in a well-passivated sapphire reactor with carefully dried reagents, the product always contained

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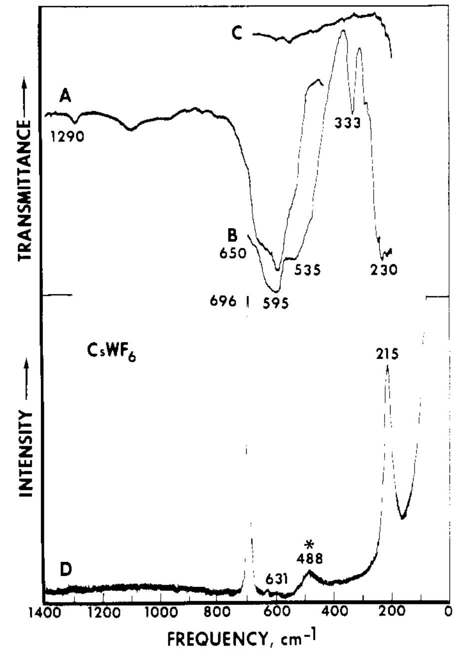

Figure 1. Vibrational spectra of solid $CsWF_6$: trace A, infrared spectrum of the dry powder pressed between AgCl disks; trace B, Nujol mull between CsI windows; trace C, Nujol alone between CsI windows; trace D, Raman spectrum of the solid. The Raman band at 488 cm^{-1}, marked by an asterisk, is probably due to the Pyrex capillary.

significant amounts of $CsWOF_5$, and sometimes $CsW_2O_2F_9$, as byproducts. The replacement of SO_2 as a solvent by HF eliminated this problem and offered the additional advantage of easy separation of the HF-insoluble I_2 from HF-soluble $CsWF_6$. This preparation of the $CsWF_6$ is similar to that[26] previously published for $NaWF_6$ with HF as a solvent, NaF, and cadmium in place of iodide as a reducing agent. Other solvents that have successfully been used for the syntheses of WF_6^- salts include CH_3CN,[16,17] CH_3NO_2,[17] and SF_4.[27]

Since only incomplete spectroscopic data had previously been reported for $CsWF_6$, its vibrational and ^{19}F NMR spectra were recorded. The vibrational spectra and observed frequencies are given in Figure 1. The observed spectra, particularly the infrared spectra, are too complicated for an ideal octahedral anion. It must be kept in mind, however, that $CsWF_6$ samples usually are poor Raman scatterers and also hydrolyze very easily to $CsWOF_5$. The ^{19}F NMR spectrum of $CsWF_6$ in HF solution at −80 °C consisted of a singlet at ϕ 159 with $J_{^{183}WF}$ of about 53 Hz.

The compatibility of SO_2 with CsI and WF_6 was briefly studied in an effort to explain the above described side reaction resulting in $CsWOF_5$ formation. In agreement with a previous report,[28] CsI was found to form with SO_2 an orange-red 1:4 adduct according to eq 8. This adduct was unstable at room

$$CsI + 4SO_2 \xrightarrow{SO_2} CsI(SO_2)_4 \qquad (8)$$

temperature, possessing a dissociation pressure of about 450 torr at 25.5 °C. Its decomposition resulted in SO_2 and CsI as the only products. For the WF_6–SO_2 system, little interaction was noted. Even after an equimolar mixture of WF_6 and SO_2 was kept at 25 °C for 5 days, less than 0.2% of the starting material had reacted to form WOF_4 and SOF_2 according to eq 9. It therefore appears that the interaction of

$$WF_6 + SO_2 \rightarrow SOF_2 + WOF_4 \qquad (9)$$

WF_6 with SO_2 is either catalyzed by CsI or one of its reaction products or that the desired $CsWF_6$ product is more reactive than WF_6 toward SO_2. Such behavior is in accord with a previous report[29] on the enhanced reactivity of SO_2 toward WF_6 in the presence of bases capable of forming adducts with WF_6.

Syntheses of NF_4^+ Fluorotungstate Salts. The possibility was explored to synthesize stable NF_4^+ salts derived from one of the following complex fluorotungstate anions: WF_6^-, $WO_2F_4^{2-}$, WOF_5^-, and $W_2O_2F_9^-$.

For the synthesis of NF_4WF_6 the metathetical reaction eq 10 proved unsatisfactory because of product separation

$$NF_4SbF_6 + CsWF_6 \xrightarrow[-78\ °C]{HF} CsSbF_6\downarrow + NF_4WF_6 \qquad (10)$$

problems due to the limited solubility of the WF_6^- salts in HF especially at low temperature and because of the competing redox reaction (eq 11) during removal. Although the solubility

$$NF_4^+ + 2WF_6^- + HF \xrightarrow[25\ °C]{HF} NF_3 + 2WF_6 + HF_2^- \qquad (11)$$

problem was successfully circumvented by separately generating HF solutions of NF_4HF_2 and WF_5 (eq 12 and 13) and

$$NF_4BiF_6 + CsHF_2 \xrightarrow{HF} CsBiF_6\downarrow + NF_4HF_2 \qquad (12)$$

$$CsWF_6 + BiF_5 \xrightarrow{HF} CsBiF_6\downarrow + WF_5 \qquad (13)$$

combining them, the redox reaction (12) remained a major obstacle, particularly when an excess of NF_4HF_2 was employed in the reaction.

The synthesis of $(NF_4)_2WO_2F_4$ was attempted with use of the metathetical reaction given by eq 14. Although $WO_2F_4^{2-}$

$$2NF_4SbF_6 + Cs_2WO_2F_4 \xrightarrow{HF} (NF_4)_2WO_2F_4 + 2CsSbF_6\downarrow \qquad (14)$$

appeared to be compatible with NF_4^+, the desired $(NF_4)_2WO_2F_4$ could not be isolated due to $WO_2F_4^{2-}$ interacting with anhydrous HF according to reactions 6 and 1. Consequently, the filter cake contained a significant amount of $W_2O_2F_9^-$ salts, whereas the filtrate residue contained a significant amount of WOF_5^- salts. The volatile reaction products contained some NF_3 and OF_2. Nitrogen trifluoride is the product expected for either thermal decomposition of NF_4HF_2[7] or redox reactions involving NF_4^+. Oxygen difluoride could have been formed by fluorination of H_2O generated from $WO_2F_4^{2-}$ and HF according to reaction 6.

Since the products from the $NF_4SbF_6 + Cs_2WO_2F_4$ metathetical reactions had indicated that NF_4WOF_5 and $NF_4W_2O_2F_9$ might be stable but are difficult to separate from the $CsSbF_6$ precipitate, this separation problem was overcome by first preparing an NF_4HF_2 solution according to eq 15, then

$$NF_4SbF_6 + CsHF_2 \xrightarrow{HF} CsSbF_6\downarrow + NF_4HF_2 \qquad (15)$$

separating the $CsSbF_6$ precipitate from the highly soluble NF_4HF_2 by filtration, and reacting a twofold excess of this NF_4HF_2 solution with WOF_4 according to eq 16. The excess

$$NF_4HF_2 + WOF_4 \xrightarrow{HF} NF_4WOF_5 + HF \qquad (16)$$

of unreacted NF_4HF_2 was decomposed at room temperature to NF_3, F_2, and HF, leaving behind the thermally more stable NF_4WOF_5 salt.

The $NF_4W_2O_2F_9$ salt was obtained by controlled vacuum pyrolysis of NF_4WOF_5 at 180 °C in a sapphire reactor. The vibrational spectra of the solid residue showed only the bands characteristic for NF_4^+[1,7,9] and $W_2O_2F_9^-$.[12] The volatile

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Table I. Vibrational Spectra of Solid $NF_4W_2O_2F_9$, $CsW_2O_2F_9$, and NF_4WOF_5

obsd freq, cm^{-1}, and rel intens[a]						assignment (point group)[b]		
$NF_4W_2O_2F_9$		$CsW_2O_2F_9$		NF_4WOF_5		NF_4^+		WOF_5^-[c]
IR	Raman	IR	Raman	IR	Raman	(T_d)	$W_2O_2F_9^-$	(C_{4v})
2320 vw				2315 vw		$2\nu_3$ ($A_1 + E + F_2$)		
2060 vw		2060 vw					(2 × 1035)	
2015 w				1996 w		$\nu_1 + \nu_3$ (F_2)		
1768 vw				1760 wv		$\nu_3 + \nu_4$ ($A_1 + E + F_2$)		
1461 w				1453 w		$\nu_1 + \nu_4$ (F_2)		
1343 w		1338 w					(709 + 640)	
1240 sh		1240 w					(640 + 610)	
1224 mw				1221 mw		$2\nu_4$ ($A_1 + E + F_2$)		
1165 vs	1165 (0.2)			1160 vs	1165 (0.7)	ν_3 (F_2)		
1035 vs	1034 (10)	1048 vs 1035 vs	1036 (10)	991 vs	996 (10)		ν W=O out of phase ν W=O in phase	ν_1 (A_1)
900 vw	850 (1.5)				852 (8.4)	ν_1 (A_1)		
		822 vw						
		790 vw						
709 s	698 (5.4)	704 s	700 (6.3)	688 vs	690 (5.4)		ν_s WF_4 in phase	ν_2 (A_1)
640 vs, br		628 vs, br		620 vs, br			ν_{as} WF_4	ν_8 (E)
610 s	610 (0.9)		610 (0.6)		613 (4.9)	ν_4 (F_2)	ν_s WF_4 out of phase	ν_5 (B_1)
				515 vs				ν_3 (A_1)
462 s 440 s	440 (0.4)	440 vs			446 (1.6)	ν_2 (E)	ν_{as} WFW	
400 vw		400 vw						
	335 sh		340 (0.6)					
	316 (6.2)		320 (5.3)		329 (6.8)			ν_9 (E)
	305 sh		309 sh					
	283 (0.5)		284 (0.2)		285 (0.5)		def vibrations	ν_4 (A_1)
	211 (0.6)		217 (0.5)					
	194 (0.2)		200 (0.2)					
	120 sh		122 (0.3)		140 sh			

[a] Uncorrected Raman intensities. [b] The actual site symmetry of NF_4^+ and WOF_5^- might be lower than T_d and C_{4v}, respectively. [c] Assignments from ref 10 and 12.

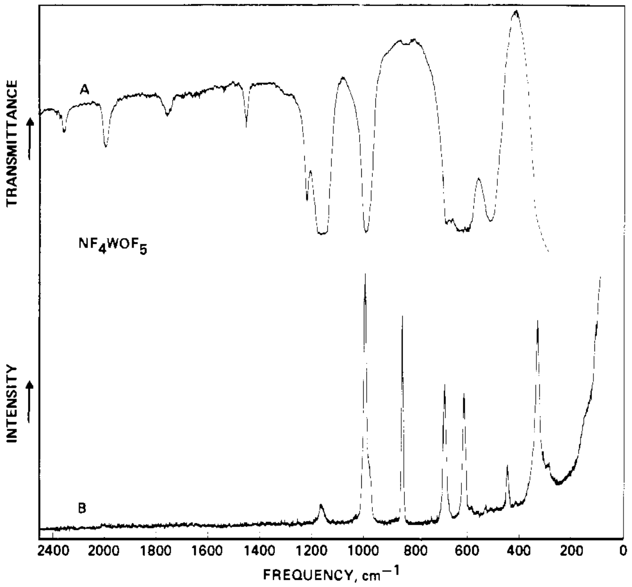

Figure 2. Infrared and Raman spectra of solid NF_4WOF_5. The broken line indicates absorption due to the AgCl window material.

products consisted of NF_3, OF_2, and WF_6 in a mole ratio of about 2:1:1, indicating the reaction shown in eq 17.

$$3NF_4WOF_5 \rightarrow 2NF_3 + OF_2 + WF_6 + NF_4W_2O_2F_9 \quad (17)$$

Properties of NF_4WOF_5 and $NF_4W_2O_2F_9$. Both salts are white crystallinic solids stable at room temperature. The thermal stability of the salts was studied in a static vacuum with a sapphire reactor equipped with a pressure transducer. The NF_4WOF_5 salt was found to be stable at 55 °C but at 85 °C started to undergo slow decomposition according to reaction 17 at an approximate rate of 0.03% h^{-1}. At 155 °C the pyrolysis proceeded at a much faster rate, and after 6.5

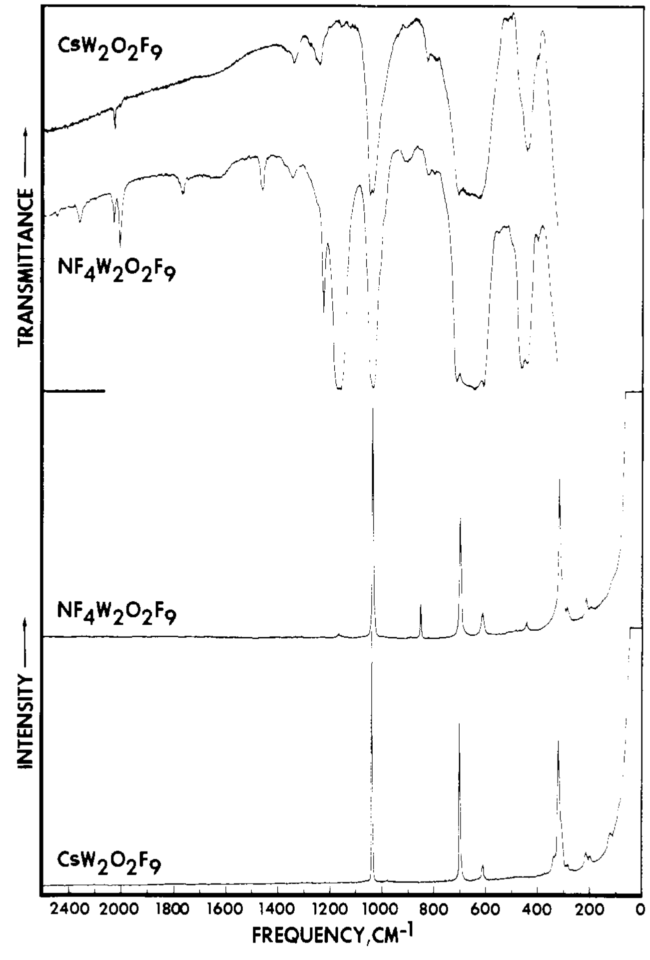

Figure 3. Infrared and Raman spectra of solid $NF_4W_2O_2F_9$ compared to those of solid $CsW_2O_2F_9$.

h about 90% of the starting material was converted to $NF_4W_2O_2F_9$ and to the other products shown in reaction 17. Complete conversion to $NF_4W_2O_2F_9$ was achieved by heating to 180 °C for an additional 4 h.

The ionic structure of NF_4WOF_5 and $NF_4W_2O_2F_9$ in both the solid state and HF solution was demonstrated by vibrational and ^{19}F NMR spectroscopy. The infrared and Raman spectra of solid NF_4WOF_5 and $NF_4W_2O_2F_9$ are shown in Figures 2 and 3, respectively. For comparison, the vibrational spectra of $CsW_2O_2F_9$ are also shown in Figure 3. The observed frequencies, together with their assignments to the NF_4^+,[1,7,9] WOF_5^-,[10,11] and $W_2O_2F_9^-$ [12] ions, are summarized in Table I and clearly establish the nature of these salts in the solid state. In HF solution, however, a significant change was observed. First of all, both NF_4WOF_5 and $NF_4W_2O_2F_9$ were only partially soluble in anhydrous HF. In both cases the insoluble phases were shown by Raman spectroscopy to consist of $NF_4W_2O_2F_9$, and the HF solution showed only NF_4^+ and $W_2O_2F_9^-$ ions. In the HF solution obtained from dissolving NF_4WOF_5, the ratio of NF_4^+:$W_2O_2F_9^-$ was, as expected from eq 18, considerably higher than that found for the $NF_4W_2O_2F_9$ solution. The presence of these ions and the lack of WOF_5^- in these solutions were confirmed by ^{19}F NMR spectroscopy. These spectra showed a triplet of equal intensity at ϕ 215.5 with $J_{NF} = 239.5$ Hz, characteristic for NF_4^+,[1,7] and a singlet at ϕ 54 with two ^{183}W satellites with $J_{^{183}WF} = 84$ Hz, characteristic for $W_2O_2F_9^-$ in HF solution.[12] The latter signal has been attributed to the eight equivalent fluorines of $W_2O_2F_9^-$ with the bridging ninth fluorine undergoing rapid exchange with the HF solvent.[12] This exchange was still rapid at −60 °C, and no evidence for F–F coupling was observed. These Raman and NMR data suggest that NF_4WOF_5 undergoes the solvolysis in anhydrous HF given by eq 18. This solvolysis is analogous to that observed for $CsWOF_5$ in reaction 1 and explains why NF_4WOF_5 could not be prepared by a direct metathesis. Due to their limited solubility in anhydrous HF, some of the $W_2O_2F_9^-$ salt is precipitated out. This was confirmed by ^{19}F NMR peak area measurements on the HF solution of the original NF_4WOF_5 sample; it was shown that the ratio of the fluorines on nitrogen to the equivalent fluorines on tungsten was 1.5:1, indicating that on the basis of (18) about half of the $NF_4W_2O_2F_9$ had precipitated out under the given conditions.

$$2NF_4WO_5 + HF \xrightleftharpoons{HF} NF_4HF_2 + NF_4W_2O_2F_9 \quad (18)$$

Conclusion. The perfluoroammonium cation is capable of forming stable salts derived from the WOF_5^- and the $W_2O_2F_9^-$ anion but rapidly oxidizes the WF_6^- anion to WF_6. The new NF_4WOF_5 and $NF_4W_2O_2F_9$ salts were characterized, and the syntheses and reaction chemistry of tungsten fluoride and oxyfluoride anions were studied in more detail.

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Registry No. NF_4WOF_5, 79028-46-9; $NF_4W_2O_2F_9$, 79056-35-2; $CsWOF_5$, 58341-09-6; $CsW_2O_2F_9$, 79056-36-3; *cis*-$Cs_2WO_2F_4$, 79005-35-9; $CsWF_6$, 19175-38-3; WF_6, 7783-82-6; WOF_4, 52049-91-9.

Contribution from the Department of Chemistry, College of Liberal Arts and Sciences, and the Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Formation Constant of the Tetracyanocuprate(II) Ion and the Mechanism of Its Decomposition

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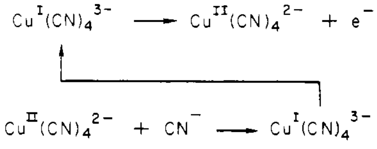
The overall formation constant (β) of tetracyanocuprate(II) ion ($Cu^{II}(CN)_4^{2-}$), which is formed as a reaction intermediate in the anodic oxidation of cyanide ion in the presence of copper ion, has been obtained by measuring the standard electrode potential ($E°$) of the redox couple $Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}$. The results are $E°(Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}) = 0.66$ V vs. NHE and $\beta(Cu^{II}(CN)_4^{2-}) = 10^{22.0}$ M^{-4} at 25 °C. The mechanism of the decomposition of the $Cu^{II}(CN)_4^{2-}$ is discussed by using the $\beta(Cu^{II}(CN)_4^{2-})$ value and the previously obtained kinetic data. It is concluded that a binuclear complex, $Cu^{II}_2(CN)_6^{2-}$, is formed from $Cu^{II}(CN)_4^{2-}$. This complex subsequently decomposes to form $Cu^{I}(CN)_2^-$ and $(CN)_2$, this step being rate determining. The kinetic studies of the chemical reaction between Cu^{2+} and CN^-, which have been reported by several groups of workers, are also interpreted by the same mechanism.

Introduction

In previous studies of the anodic oxidation of cyanide ion in the presence of copper ion, we have found that copper ion has a marked catalytic effect on this reaction[2a] and that the primary reaction product is cyanogen, which gives various secondary products according to the pH of the solution.[3]

We have proposed the reaction mechanism given by eq 1 and 2 from some electrochemical studies.[2] We have further studied the kinetics of reaction 2 by means of ESR spectroscopy[4,5] and have obtained the rate equation given by eq 3. On the basis of this result, we have proposed two possible



$$Cu^{I}(CN)_4^{3-} \longrightarrow Cu^{II}(CN)_4^{2-} + e^- \quad (1)$$

$$Cu^{II}(CN)_4^{2-} + CN^- \longrightarrow Cu^{I}(CN)_4^{3-} + \tfrac{1}{2}(CN)_2 \quad (2)$$

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