3254 *Inorg. Chem.* **1980**, *19*, 3254–3256

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Canoga Park, California 91304

Synthesis and Characterization of $(NF_4)_2MnF_6$

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Received March 28, 1980

The synthesis of novel NF_4^+ salts containing doubly or triply charged 3d transition-metal fluoride anions was studied. The new compound $(NF_4)_2MnF_6$ was prepared and characterized. The combination of good thermal stability and high active fluorine content makes $(NF_4)_2MnF_6$ an outstanding solid oxidizer.

Introduction

Due to the high-energy kinetic stability of the NF_4^+ cation,[1] NF_4^+ salts are important high-energy oxidizers. In order to maximize the oxidizing power of such salts, it is desirable to combine as many NF_4^+ cations as possible with a given anion. Furthermore, the anion should be as light as possible and also be an oxidizer. Of the presently known NF_4^+ salts,[2] $(NF_4)_2NiF_6$[3] has the highest active fluorine content or oxidizing capacity. However, its marginal thermal stability limits its usefulness. Consequently, compounds having comparable fluorine content but possessing better thermal stability are highly desirable. This paper describes the results of a systematic study on the synthesis of NF_4^+ salts derived from 3d transition-metal fluorides and the successful synthesis of the novel $(NF_4)_2MnF_6$ salt.

Experimental Section

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described.[1,2] A literature method[4] was used for the synthesis of NF_4SbF_6. For the synthesis of Cs_2MnF_6, a previously reported method[5] was slightly modified. Anhydrous $MnCl_2$ and dry CsF, in a 1:2 mole ratio, were fluorinated in a Monel cylinder at 400 °C for 36 h by using a $MnCl_2$:F_2 mole ratio of 1:10. On the basis of the observed material balance, elemental analysis, X-ray diffraction powder pattern, and vibrational spectra, the resulting yellow solid consisted of high-purity Cs_2MnF_6.

The Cs_2CuF_6 salt was prepared by high-pressure fluorination of a mixture of CsF and $CuCl_2$ in a 2:1 mole ratio. The conditions (400 °C, 18 h, 130 atm) were similar to those[6] previously reported. However, during unsuccessful attempts to prepare Cs_3CuF_6 in a similar manner, it was noticed that very mild fluorination conditons (flow reactor, 200 °C) sufficed to prepare Cs_2CuF_6. This brick red compound was always formed as the major product, instead of the pale green Cs_3CuF_6. At the lower fluorination temperatures, the fluorination product also contained $CsClF_4$. The infrared spectrum of Cs_2CuF_6 showed major bands at 670, 570, 480, and 430 cm^{-1}. The compatibility of Cs_2CuF_6 with different solvents was studied. In BrF_5, Cs_2CuF_6 is stable but highly insoluble, whereas in anhydrous HF, it is soluble but undergoes a reaction even at −78 °C, resulting in the formation of a brown solid. When the Cs_2CuF_6–HF solutions were warmed to room temperature, fluorine evolution was observed, in agreement with a previous report.[7]

Preparation of $(NF_4)_2MnF_6$. In the N_2 atmosphere of a drybox a mixture of NF_4SbF_6 (37.29 mmol) and Cs_2MnF_6 (18.53 mmol) was placed into the bottom of a prepassivated (with ClF_3) Teflon FEP double U-tube metathesis apparatus. Dry HF[8] (20 mL of liquid) was added at −78 °C on the vacuum line, and the mixture was warmed to 25 °C for 30 min with stirring. The mixture was cooled to −78 °C and pressure filtered at this temperature. The HF solvent was pumped off at 30 °C for 12 h. The white filter cake (14 g; weight calculated for 37.1 mmol of $CsSbF_6$ = 13.7 g) was shown by Raman spectroscopy to consist mainly of $CsSbF_6$. The yellow filtrate residue (6.1 g; weight calculated for 18.5 mmol of $(NF_4)_2MnF_6$ = 6.46 g) was shown by elemental analysis to have the following composition (weight %): $(NF_4)_2MnF_6$, 91.27; NF_4SbF_6, 4.27; $CsSbF_6$, 4.46. For the elemental analysis, a sample of $(NF_4)_2MnF_6$ was hydrolyzed in H_2O, the NF_3 and O_2 evolution was measured by *PVT* and gas chromatography, and Cs, Sb, and Mn in the hydrolysate were determined by atomic absorption spectroscopy. Anal. Calcd for $[(NF_4)_2MnF_6]_{91.27}[NF_4SbF_6]_{4.27}[CsSbF_6]_{4.46}$: NF_3, 38.07; Mn, 14.37; Sb, 3.07; Cs, 1.61. Found: NF_3, 37.8; Mn, 14.5; Sb, 3.10; Cs, 1.62.

Caution! The reaction of $(NF_4)_2MnF_6$ with H_2O is extremely violent, and proper safety precautions must be used.

The CoF_3–NF_4HH_2 System. A suspension of CoF_3 (231 mg = 2 mmol) in a freshly prepared concentrated NF_4HF_2–HF solution[2] (15 mmol of NF_4HF_2) was stirred at −45 °C for 4 h. The tan CoF_3 did not appear to react, and no evidence for the formation of pale blue CoF_6^{3-} was observed. The HF solvent was pumped off while the mixture was allowed to warm slowly toward ambient temperature. At this temperature, the $NF_4HF_2 \cdot nHF$ underwent decomposition and was also pumped off. To ensure complete decomposition of NF_4HF_2, we warmed the mixture to 45 °C for 4 h under a dynamic vacuum. The tan solid residue (230 mg) was shown by vibrational spectroscopy to be unreacted CoF_3.

Results and Discussion

In view of the marginal thermal stability of $(NF_4)_2NiF_6$ it was interesting to investigate the possibility of synthesizing other NF_4^+ salts containing multiply charged anions derived from higher oxidation state transition-metal fluorides. It was hoped to obtain a salt which would be comparable to $(NF_4)_2NiF_6$ in its active fluorine content but possess better thermal stability. The following anions were considered most promising: CuF_6^{3-}, NiF_6^{3-}, CoF_6^{3-}, MnF_6^{3-}, CuF_6^{2-}, CoF_6^{2-}, and MnF_6^{2-}.

Attempted Syntheses of $(NF_4)_3MF_6$ Salts. In a previous study,[7] it was shown that the above listed triply charged anions undergo solvolysis in HF. Furthermore, it was found that CuF_6^{3-} decomposed with F_2 evolution and NiF_6^{3-} disproportionated with NiF_6^{2-} formation but that for CoF_6^{3-} the solvolysis to CoF_4^- + 2 HF_2^- could be suppressed by the addition of a 10–20-fold excess of fluoride ion to the solution. In view of these results, a simple metathetical reaction of an MF_6^{3-} salt in HF solution according to

$$3NF_4SbF_6 + Cs_3MF_6 \xrightarrow{HF} 3CsSbF_6\downarrow + (NF_4)_3MF_6$$

is preempted by the unavoidable solvolysis of MF_6^{3-}. However, the synthesis of a CoF_6^{3-} salt might be possible in the presence of a large excess of fluoride ion, provided the excess of fluoride can be readily removed from the product. Such a method was

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recently discovered[9] and successfully applied to the synthesis of NF_4UF_5O according to

$$NF_4HF_2 + UF_4O \xrightarrow{HF} NF_4UF_5O + HF$$

NF_4HF_2 is thermally unstable[2] and decomposes at 30 °C to NF_3, F_2, and HF, which are all gases. Therefore, the HF solvent can be pumped off first at low temperature, followed by decomposition and removal of the excess NF_4HF_2. Application of this method to the synthesis of $(NF_4)_3CoF_6$ according to

$$3NF_4HF_2 + CoF_3 \xrightarrow[-45\ °C]{HF} (NF_4)_3CoF_6 + 3HF$$

was unsuccessful, and no evidence for the formation of a cobalt-containing NF_4^+ salt was obtained. Only unreacted CoF_3 was recovered.

Syntheses of $(NF_4)_2MF_6$ Salts. Since the MF_6^{2-} anions contain one negative charge less than the MF_6^{3-} ones, they are less basic and, therefore, are less likely to undergo solvolysis in the strongly acidic solvent HF. The compatibility of TiF_6^{2-} and NiF_6^{2-} with HF has previously been demonstrated[3,7,10] and led to the successful syntheses of $(NF_4)_2TiF_6$[10] and $(NF_4)_2NiF_6$.[3] During this study the compatibility of Cs_2CuF_6 with HF was studied. It was found that Cs_2CuF_6 reacts, even at low temperature, with HF to form a dark brown solid. At room temperature, decomposition with fluorine evolution occurs. The compatibility of Cs_2CoF_6 with HF was not examined since Court had previously shown[7] that this salt is unstable in HF solution.

In agreement with a previous report,[7] MnF_6^{2-} was found to be stable in HF solution. Consequently, the metathetical reaction

$$2NF_4SbF_6 + Cs_2MnF_6 \rightarrow 2CsSbF_6\downarrow + (NF_4)_2MnF_6$$

was carried out which resulted in the isolation of the novel $(NF_4)_2MnF_6$ salt. Since the impurities NF_4SbF_6 and $CsSbF_6$ are well characterized, no attempts were undertaken to purify the compound by well-established[4] recrystallization techniques.

Properties of $(NF_4)_2MnF_6$. The $(NF_4)_2MnF_6$ salt is a yellow, crystalline solid which is highly soluble in anhydrous HF. At 24 °C, its solubility exceeds 1.30 g/g of HF. It is stable at room temperature, and, in the absence of fuels, it is not shock sensitive. With water a violent reaction occurs, similar to that previously reported[3] for $(NF_4)_2NiF_6$. By analogy with the other known NF_4^+ salts, the hydrolysis was found to result in quantitative NF_3 evolution and, therefore, is a useful analytical method. The hydrolysis also produced oxygen in a NF_3:O_2 mole ratio of 8:5 in excellent agreement with the equation

$$4(NF_4)_2MnF_6 + 10H_2O \rightarrow 8NF_3 + 5O_2 + 20HF + 4MnF_3$$

Table I. X-ray Powder Data for $(NF_4)_2MF_6$ Salts ($M = Mn$, Ge, Ti, Sn)[a]

$(NF_4)_2MnF_6$			$(NF_4)_2GeF_6$			$(NF_4)_2TiF_6$			$(NF_4)_2SnF_6$					
d obsd	Int	d clcd				d obsd	Int	d clcd	d obsd	Int	d calcd	h	k	l
5.53	vs	5.53	5.55	vs	5.54	5.58	vs	5.58	5.65	vs	5.64	1	0	1
3.45	s	3.45	3.47	s	3.46	3.50	s	3.49	3.52	s	3.52	2	0	0
3.35	s	3.35	3.36	s	3.36	3.38	s	3.38	3.42	s	3.42	1	1	2
2.93	ms	2.93	2.94	ms	2.93	2.97	ms	2.96	2.99	s	2.99	2	1	1
2.81	ms	2.81	2.82	m	2.82	2.82	m	2.83	2.86	ms	2.87	1	0	3
2.44	m	2.44	2.449	mw	2.447	2.475	mw	2.470	2.492	m	2.493	2	2	0
2.307	mw	2.307	2.312	w	2.312	2.324	w	2.319	2.347	w	2.352	0	0	4
2.183	s	2.182 2.179	2.186	s	2.188 2.184	2.204	s	2.209 2.198	2.230	s	2.230 2.223	3 2	1 1	0 3
2.085	mw	2.086	2.089	m	2.090	2.101	w	2.099	2.125	mw	2.127	1	1	4
1.975	vw	1.973	1.981	w	1.978	1.995	vw	1.994	2.016	mw	2.015	3	1	2
			1.923	vw	1.922				1.959	w	1.956	2	0	4
1.875	ms	1.874	1.880	ms	1.879	1.897	m	1.897	1.916	m	1.915	3	2	1
			1.846	w	1.847				1.882	w	1.881	3	0	3
1.784	w	1.783	1.787	w	1.787	1.792	mw	1.793	1.815	mw	1.818	1	0	5
1.726	vw	1.725	1.729	vw	1.730				1.763	vw	1.763	4	0	0
1.677	vw	1.676	1.679	vw	1.680				1.709	w	1.711	2	2	4
1.647	mw	1.647	1.651	w	1.651	1.668	mw	1.667	1.682	mw	1.682	4	1	1
1.627	mw	1.627	1.629	w	1.631	1.644	mw	1.646	1.662	mw	1.662	3	3	0
1.585	w	1.585	1.588	w	1.589	1.598	w	1.599	1.616	w	1.618	3	1	4
1.538	mw	1.538	1.541	w	1.541	1.548	mw	1.546	1.568	w	1.568	0	0	6
1.466	mw	1.467	1.470	w	1.470				1.496	w	1.496	1	1	6

(a) Cu K_α radiation and Ni filter; the crystallographic data are summarized in Table II.

Table II. Crystallographic Data of $(NF_4)_2MF_6$ Salts ($M = Ti$, Mn, Ni, Ge, Sn)[a]

	tetragonal unit cell dimensions				
	a, Å	*c*, Å	*V*, $Å^3$	vol/F, $Å^3$	calcd density, g/cm^3
$(NF_4)_2TiF_6$	6.99	9.28	453	16.2	2.51
$(NF_4)_2MnF_6$	6.90	9.23	440	15.7	2.64
$(NF_4)_2NiF_6$[b]	6.83	9.27	432	15.4	2.71
$(NF_4)_2GeF_6$	6.92	9.25	443	15.8	2.75
$(NF_4)_2SnF_6$	7.05	9.41	468	16.7	2.93

[a] Space group *I*4/*m* (No. 87); $Z = 2$. [b] Data from ref 13.

Thermal Decomposition. At 65 °C, $(NF_4)_2MnF_6$ appears to be stable, but at about 100 °C it starts to slowly decompose. Its decomposition rate in a sapphire reactor was monitored by total pressure measurements over the temperature range 100–130 °C. Except for a slightly faster rate during the first 20 min, the decomposition pressures increased approximately linearly with time at 100 °C. At 130 °C, the rates slightly accelerated with increasing time; however, this rate increase was quite small. At 100 °C, 0.17% of the sample decomposed in 17 h, whereas, at 130 °C, 0.66% of the sample decomposed in the same time. The gaseous decomposition products consisted of NF_3 and F_2 in a mole ratio of about 1:1.2. For identification of the solid residue, a sample of $(NF_4)_2MnF_6$ was completely decomposed under a dynamic vacuum at 240 °C. On the basis of its weight, X-ray powder diffraction pattern,[11] and mauve color, this residue was identified as MnF_3. Consequently, $(NF_4)_2MnF_6$ decomposes according to

$$2(NF_4)_2MnF_6 \rightarrow 4NF_3 + 5F_2 + 2MnF_3$$

A comparison with the decomposition data previously published[3] for $(NF_4)_2NiF_6$ shows that the normal stability of $(NF_4)_2MnF_6$ is significantly higher than that of $(NF_4)_2NiF_6$ which in 6 h at 100 °C exhibited 9% decomposition.

Crystallographic Data. The X-ray powder diffraction pattern of $(NF_4)_2MnF_6$ are listed in Table I. The pattern is very similar to those of other $(NF_4)_2MF_6$ salts ($M = Ge$, Ti, Sn, Ni),[3,5,10,12,13] indicating that these salts are isotypic. Recent studies on both powdered and single-crystal $(NF_4)_2NiF_6$ have shown that this compound crystallizes in a tetragonal form derived from the K_2PtCl_6 structure and belongs to space group *I*4/*m*. Consequently, the indexing, previously proposed for the $(NF_4)_2MF_6$ salts ($M = Ge$, Ti, Sn, Ni),[3,5,10,12] was revised according to ref 13. The revised patterns and the crystallographic data are given in Tables I and II, respectively. Some of the additional lines, previously observed,[3,4,10,12] were found to be due to small amounts of polyanion salts such as $(NF_4)_2Ge_2F_{10}$ or $(NF_4)_2Sn_2F_{10}$. As expected, the size of the unit cell decreass from $(NF_4)_2TiF_6$ to $(NF_4)_2NiF_6$ owing to the transition-metal contraction and then increases again when going from Ni to the main-group elements.

NMR Spectrum. The ionic nature of $(NF_4)_2MnF_6$ in HF solution was established by its ^{19}F NMR spectrum which was recorded over the temperature range +20 to −75 °C. It showed at all temperatures a broad resonance at ϕ −218 (downfield from external $CFCl_3$), characteristic of NF_4^+. The lack of observable NF spin–spin coupling, generally seen for

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Table III. Vibrational Spectra of Solid $(NF_4)_2MnF_6$ and Cs_2MnF_6

obsd freq, cm^{-1}, and rel intens[a]				assign (point group)[b]	
$(NF_4)_2MnF_6$		Cs_2MnF_6			
IR	Raman	IR	Raman	NF_4^+ (T_d)	MnF_6^{2-} (O_h)
2310 vw				$2\nu_3$ (A + E + F_2)	
2000 w				$\nu_1 + \nu_3$ (F_2)	
1759 vw				$\nu_3 + \nu_4$ (A_1 + E + F_2)	
1466 w				$\nu_1 + \nu_4$ (F_2)	
1221 mw				$2\nu_4$ (A_1 + E + F_2)	
		1240 sh			$\nu_1 + \nu_3$ (F_{1u})
		1202 vw			
1160 vs				ν_3 (F_2)	
		1155 vw			$\nu_2 + \nu_3$ (F_{1u} + F_{2u})
1110 sh		1116 w			
1061 vw				$\nu_2 + \nu_4$ (F_1 + F_2)	
915 vw		919 vw			$\nu_1 + \nu_4$ (F_{1u})
856 vvw	855 m			ν_1 (A_1)	
760 sh		745 sh			$\nu_2 + \nu_6$ (F_{1u} + F_{2u})
735 sh		732 w			
620 vs		620 vs		ν_4 (F_2)	ν_3 (F_{1u})
	593 vs		590 vs		ν_1 (A_{1g})
		569 vw			
500 vw	505 m		502 m		ν_2 (E_g)
450 vw	450 w			ν_2 (E)	
		381 vw			
338 s		338 s			ν_4 (F_{1u})
	304 s		304 s		ν_5 (F_{2g})

[a] Uncorrected Raman intensities. [b] By analogy with $(NF_4)_2NiF_6$[13] the actual site symmetries of NF_4^+ and MnF_6^{2-} are probably S_4 and C_4^h, respectively, thus explaining the observed slight deviations from the selection rules for T_d and O_h.

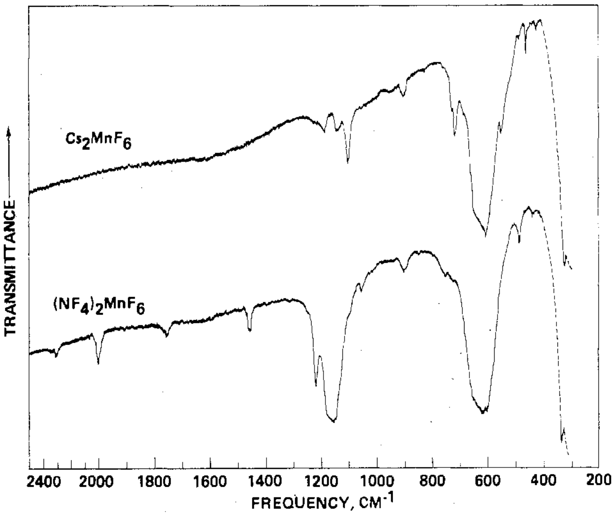

Figure 1. Infrared spectra of solid Cs_2MnF_6 and $(NF_4)_2MnF_6$ recorded at 25 °C as dry powders pressed between AgCl disks. The broken lines indicate absorption due to the window material.

tetrahedral NF_4^+,[14,15] is attributed to the influence of the paramagnetic MnF_6^{2-} anion which can provide rapid relaxation.

Vibrational Spectra. The ionic nature of $(NF_4)_2MnF_6$ in the solid state was established by its vibrational spectra which exhibit the bands characteristic for NF_4^+[12] and MnF_6^{2-}.[16] Figure 1 shows the infrared spectrum of $(NF_4)_2MnF_6$, compared to that of Cs_2MnF_6. Great difficulties were encountered in obtaining good-quality Raman spectra with the blue 4880-Å exciting line of our spectrometer due to strong luminescence[16] (ruby red red light emission). However, the principal Raman lines of NF_4^+[12] and MnF_6^{2-}[16] were observable even under these conditions. The observed vibrational frequencies and their assignments are summarized in Table III. Since the assignments of NF_4^+[12] and MnF_6^{2-}[16] are well established, no further discussion is required.

Summary

The present study shows that, in HF solution, solvolysis preempts the metathetical synthesis of NF_4^+ salts containing triply charged MF_6^{3-} anions derived from 3d transition-metal fluorides. On the other hand, three NF_4^+ salts derived from doubly charged MF_6^{2-} anions are accessible by this method. These salts are $(NF_4)_2TiF_6$,[10] $(NF_4)_2MnF_6$, and $(NF_4)_2NiF_6$.[3] All of them are stable at room temperature, with $(NF_4)_2NiF_6$ possessing the lowest thermal stability. The existence of stable NF_4^+ salts of TiF_6^{2-}, MnF_6^{2-}, and NiF_6^{2-} can be explained by the favorable d^0, d^3 (high-spin) and d^6 (low-spin) electron configurations, respectively, of these anions. The combination of good thermal stability with high active fluorine content (1.58 g/cm^3) renders $(NF_4)_2MnF_6$ a very attractive candidate for solid oxidizer applications.

Acknowledgment. The authors are indebted to Drs. C. J. Schack, L. R. Grant, and M. Lustig for helpful discussion, to Mr. R. Rushworth for the elemental analyses, and to the Army Research Office for financial support.

Registry No. $(NF_4)_2MnF_6$, 74449-37-9; NF_4SbF_6, 16871-76-4; Cs_2MnF_6, 16962-46-2; $CsSbF_6$, 16949-12-5.

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