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High yield room temperature syntheses of $KAgF_4$ and AgF_3 and the preparation and unit cell of $LiAgF_4$

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Abstract

AgF_2 dissolves at ~20°C in liquid anhydrous hydrogen fluoride (aHF), containing either LiF or KF, with sunlight or ultraviolet (UV)-irradiated F_2. Concentrated KF–aHF solutions quickly give a nearly quantitative conversion to $KAgF_4$. Preparation of $LiAgF_4$ is less efficient, but it can be prepared in high purity. It is isomorphous with $LiAuF_4$, and has a monoclinic unit cell: $a=4.87(1)$; $b=5.93(1)$; $c=10.08(1)$ Å; $\beta=93.0(1)°$; $V=291(1)$ Å^3; $z=4$. KHF_2 impurity in $KAgF_4$ can be removed as KPF_6 with PF_5 at 0°C. Preparation of AgF_3, with minimum contamination by Ag_3F_8, is achieved at 0°C using GeF_4 as F^- acceptor. The high solubility of the salt K_2GeF_6 makes this possible.

Keywords: $KAgF_4$; $LiAgF_4$; AgF_3; aHF; Sunlight

1. Introduction

Clifford et al. [1] and Clifford and Morris [2] were pioneers in defining the anhydrous hydrogen fluoride (aHF) solvent system on which much of the work in these laboratories, including this paper, is based.

Salts of the AgF_4^- ion were first described by Hoppe [3] and Hoppe and Homann [4]. These were alkali-cation salts and were typically prepared by higher temperature (300–400°C) fluorination of alkali and silver nitrates, mixed halides, or oxides. The products of these syntheses were sufficiently free of silver difluoride and other contaminants to provide X-ray powder diffraction data [4] to establish the unit cell character for the salts of the heavier alkali metals, and to show the diamagnetism (low spin d^8) of AgF_4^- in these salts. The $LiAgF_4$, however, was not structurally defined.

The announcement by Bougon and Lance [5] and Bougon et al. [6] of a synthesis of AgF_3 stimulated a renewal of interest in Ag(III). Žemva et al. [7,8] devised another approach to the AgF_3 synthesis and demonstrated that authentic AgF_3 was thermodynamically unstable. They showed that it lost fluorine in liquid aHF, at ~20°C, to fall to Ag(II){Ag(III)F_4}$_2$. The last compound proved to be identical [8] to the material previously described by Bougon et al. as AgF_3. Indeed, since the effective synthesis of AgF_3 involved [7,8] abstraction of F^- by a good F^- acceptor in aHF, the removal of the salts which were produced incidentally involved prolonged washing of the AgF_3 with aHF. This gave rise to decomposition, resulting in some Ag_3F_8 contaminant in the AgF_3:

$$3AgF_{3(c)}\ (\text{in aHF at } 20°\text{C}) \rightarrow \text{Ag(II)}\,\{\text{Ag(III)}F_4\}_2 + 1/2\,F_2 \qquad (1)$$

It was recently found in these laboratories [9] that the ultraviolet (UV) irradiation of F_2 in aHF, made basic with alkali fluoride, provided a room temperature route to salts of high oxidation state noble-metal fluoro-metallate anions. Included were syntheses of $(AgF_4)^-$ salts. This is particularly effective for the preparation of $KAgF_4$, where nearly quantitative synthesis from AgF_2 is quickly achieved. Such an approach is also useful in making $LiAgF_4$, which has now been structurally defined. In addition, a convenient means of removing excess potassium hydrofluoride from $KAgF_4$ preparations has been devised. A more reliable room temperature route to high purity AgF_3 starts with $KAgF_4$, and exploits the high solubility of K_2GeF_6 in aHF, as this salt is the only other product of the precipitation of AgF_3 by F^- abstraction with GeF_4.

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2. Experimental details

2.1. Materials

AgF_2, PF_5 aHF and F_2 were obtained and used as previously described [8]. GeF_4 was used as supplied by Ozark-Mahoning Pennwalt, Tulsa, OK 74107.

2.2. Apparatus and technique

A metal vacuum line as previously described [10] was used for the distribution of gaseous reactants. However, except during the transfer of gases, all of the preparations were carried out in apparatus constructed entirely of Teflon and FEP, isolated from the metal system by a Teflon valve. (Severe corrosion of the metal vacuum system occurs if aHF and fluoroacids such as GeF_4 are simultaneously present in it.) A typical reactor was constructed in T shape (T reactor) from FEP tubing, Teflon Swagelok T, and Teflon valve as previously described [11]. In the UV- and sunlight-irradiation preparations, one arm of the T reactor was charged with AgF_2 and alkali fluoride in a DRILAB (Vacuum Atmospheres). Then aHF and F_2 were introduced from the vacuum line, and the reactor arm was arranged to be nearly horizontal, in order to maximize the F_2–liquid aHF interface. This nearly horizontal tube was placed adjacent to the water-cooled jacket of a 450-W immersion type Hanovia UV lamp (Ace Glass) and at the approximate line of focus of a cylindrical metal reflector, surrounding and parallel to the lamp. For solar irradiation, the similarly arranged reactor was placed in full sunlight with a suitably curved metal reflector behind it. As the mixture was irradiated, it was mixed by sideward flicking of the tube by a properly placed rotating arm. To fully separate soluble from insoluble products, in all reactions the supernatant solutions in aHF were decanted to the other limb of the T reactor, and the aHF back-distilled to the reaction limb to extract soluble species. Washing of aHF-insoluble residues was repeated as necessary to effect the separation.

X-ray diffraction powder photographs (XRDP) were routinely obtained with Cu Kα (Ni filtered) radiation on each solid, packed as a powder in thin-walled quartz capillaries [8].

2.3. Synthesis of $KAgF_4$

AgF_2 (229.4 mg, 1.57 mmol) and KF (1578.7 mg, 27.2 mmol) in aHF (4.5 g, 220 mmol) with F_2 ($\sim$1500 Torr) was agitated (as a brown slurry) at $\sim$20°C, *without irradiation*, for 12 h. Under these conditions, no visible change occurred, nor was F_2 taken up. With only 5 h of irradiation of the static tube, the bright yellow solution color, characteristic of AgF_4^-, was easily seen. UV irradiation of the agitated tube for 77 h, with periodic replenishing of the F_2 pressure to 1500 Torr, resulted in dissolution of the AgF_2. Additional aHF (2.0 g, 100 mmol) facilitated cleaner decantation from a few particles of brown solid (possibly AgF_2, but $\leq$3 mg). Removal of aHF from the decanted yellow solution gave a free-flowing yellow powder in essentially quantitative yield.

2.4. Preparation of AgF_3 from $KAgF_4$ in aHF with GeF_4

The yellow product ($KAgF_4$ with KHF_2) from Section 2.3 was dissolved in aHF (10 g, 500 mmol) and the resulting mixture was allowed to stand for $\sim$15 h to sediment a small quantity of brown insoluble product. The clear yellow solution was decanted from this residue, cooled to −196°C and GeF_4 (in excess of 1 mmol) condensed in that limb. Slow warming with agitation to 0°C, at which temperature the mixture was kept ($\sim$5 min), resulted in copious amounts of a bright red solid precipitate. The T reactor was back filled with F_2 (1500 Torr), cooled to −78°C and the precipitate allowed to settle at that temperature for $\sim$15 h. To dissolve K_2GeF_6 (some of which had crystallized at −78°C), the mixture was warmed to 0°C, the colorless supernatant decanted, and the red precipitate washed with back-distilled aHF three times at 0°C. The aHF was removed at 0°C under a dynamic vacuum. The bright-red solid was shown by XRDP to be AgF_3, with none of the lines attributable to Ag_3F_8 [8] nor those of K_2GeF_6 [12] being present. Yield of AgF_3: 223.5 mg (1.356 mmol), 86.2%, based on AgF_2 in Section 2.3.

2.5. Synthesis of $LiAgF_4$

(a) A mixture of AgF_2 (153.3 mg, 1.051 mmol) and LiF (28.4 mg, 1.09 mmol) in aHF (2.5 g, 130 mmol) at 20°C was UV-irradiated for 7 h, with the same setup as in Section 2.3. The yellow solution was decanted from the unreacted AgF_2 and the bulk of the aHF removed in a dynamic vacuum. This crystallized most of the $LiAgF_4$. The last drops of aHF, containing lithium hydrofluoride, were decanted to the other arm, then the yellow solid was dried in a dynamic vacuum. XRDP of the yellow solid showed it to be isomorphous with $LiAuF_4$.[1] The diffraction data are in Table 1. Yield of $LiAgF_4$: 15.6 mg, 0.082 mmol; 7.8%, based on AgF_2 used.

(b) In a second synthesis of $LiAgF_4$, the T reactor was exposed to full sunlight (total 26 h) with a curved metal reflector placed behind it. The reaction mixture was AgF_2 (97.0 mg, 0.665 mmol), LiF (86.2 mg, 3.32 mmol), and HF (1.5 g, 75 mmol), of which 0.385 mmol AgF_2 was converted to $LiAgF_4$ (57.9% yield).

2.6. Purification of $KAgF_4$ admixed with KHF_2

A mixture of $KAgF_4$ and KHF_2, in $\sim$1:2 molar ratio (160.4 mg) dissolved in aHF ($\sim$1.6 g) in a T reactor, was vigorously agitated as an overpressure of PF_5 gas from the Teflon FEP line was slowly admitted, with precipitation of colorless KPF_6. At the first appearance of a permanent red precipitate

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[1] $LiAuF_4$ has the space group $C2/c$, not $P2/c$ as reported by Engelmann and Müller [13]. A new structure determination finds Au–F in the anion to be 1.915(3) Å [14].

Table 1
X-ray powder data (Cu Kα, Ni filter) for $LiAgF_4$ with a monoclinic unit cell

I/I_0	$1/d^2 \times 10^4$		hkl
	Observed	Calculated	
7	393	394	002
2	515	502	$10\bar{1}$
9	704	709	110
8	1056	1059	$11\bar{2}$
9	1140	1137	020
10	1534	1530	022
1	1582	1575	004
3	1634	1638	$12\bar{1}$
4	1708	1701	200
2	2005	2007	$20\bar{2}$
3	2070	2088	104
6	2185	2183	202
5	2375	2372	114
3	2520	2514	123
5	2720	2719	203
5	2833	2838	220
5	2917	2892	$22\bar{1}$
3	2983	2983	130
3	3087	3100	$20\bar{4}$
3	3133	3144	$22\bar{2}$
4	3322	3320	222
3	3435	3443	033
2	3553	3544	006
1	3919	3913	$12\bar{5}$
3	4098	4101	106
3	4139	4144	$31\bar{1}$
2	4240	4237	$22\bar{4}$
2	4296	4313	$23\bar{1}$
1	4358	4353	302
3	4419	4401	231
2	4476	4470	$13\bar{4}$
3	4648	4645	041
3	4966	4964	320
2	5399	5403	107
3	5958	5960	027
4	6133	6122	044
2	6246	6248	240
3	9533	9528	$24\bar{6}$
		9530	$33\bar{6}$
2	9864	9868	424
1	10 072	10 071	209
2	10 336	10 334	$11\overline{10}$
		10 336	061
2	10 874	10 877	406
2	11 031	11 046	$25\bar{5}$

$a_0 = 4.859(4)$; $b_0 = 5.932(4)$; $c_0 = 10.096(6)$ Å; $\beta = 93.10(5)°$; $V = 291(1)$ Å^3, $z = 4$, probable space group $C2/c$.

of AgF_3, the system was opened to vacuum (which removed the PF_5 and some aHF). The yellow solution was decanted at 0°C from the colorless KPF_6 precipitate and aHF was removed under a dynamic vacuum, with the solution held at that temperature. An XRDP revealed only the pattern characteristic of $KAgF_4$ [4,15].

3. Results and discussion

Although the original syntheses of AgF_4^- salts [3,4] provide a simple route to these high-oxidation-state materials, it is tedious to derive them in high purity. Fluorination, in these laboratories of, 1:1 molar mixtures of KNO_3 and $AgNO_3$, with repeated treatment with fluorine (but no regrinding) has usually given a less than 50% conversion of the silver to $KAgF_4$ (as measured by extraction with aHF and subsequent precipitation of AgF_3 by acid displacement). The silver that is not converted to AgF_4^- becomes AgF_2; since that fluoride is insoluble in aHF, the $KAgF_4$, which is highly soluble, is readily separated from it. That aHF solution does, however, contain all of the original potassium as hydrofluoride $\{F(HF)_x^-\}$. An early practical problem was to find a method of separating the $KAgF_4$ and $KF(HF)_x$, both of which are highly soluble in aHF.

In the search for a route to high-purity AgF_3, it was observed [8] that with a moderate pressure of PF_5 gas (> 1 atm) above the aHF solution of AgF_4^-, there was precipitation of AgF_3, but that removal of PF_5 resulted in the AgF_3 redissolving (with displacement of PF_5). Clearly, AgF_3 and PF_5 are comparable F^- acceptors in aHF. Moreover, KPF_6 has very low solubility in aHF at 0°C. It is, therefore, possible to precipitate potassium in the aHF solution as KPF_6 by adding PF_5 gas to a solution of $KAgF_4$ and $KF(HF)_x$, the hydrofluoride combining preferentially. The first indication of precipitated AgF_3 (red) signals the end-point in the hydrofluoride–PF_5 titration. By carrying out this precipitation of KPF_6, and the decantation of the aHF solution of $KAgF_4$ with the solution at 0°C, high purity $KAgF_4$ is obtained.

The original synthetic methods, by requiring the use of elemental fluorine at temperatures of 300–400°C, have been an obstacle to widespread interest in these sources of AgF_3 and its extraordinary oxidizing power [11]. This stimulated, in these laboratories, a search for an easier synthetic approach. Gold and each of the platinum metals except rhodium were found [16] to dissolve readily at ~20°C, with F_2 over aHF solutions of alkali fluoride, to yield salts of anions such as AuF_4^- and PtF_6^{2-}. However, no such oxidation of silver or AgF_2 to AgF_4^- was observed.

UV irradiation of the F_2/aHF solution mixture, however, quickly revealed AgF_4^- formation. Even sunlight proved to be an effective photochemical source. Evidently the photoatomization of the F_2 provides a sufficient flux of F atoms in the aHF solvent to convert the insoluble solid AgF_2 {bathed in $F(HF)_x^-$} to AgF_4^-. With persistent irradiation, the conversion approaches completion. Indeed, the high effectiveness of the conversion of AgF_2 to AgF_4^- may signify the presence of species such as $HF_2^{\bullet}$ or $F\text{–}HF_2^{\bullet -}$ in the aHF (i.e., protonated or solvated $F_2^{\bullet -}$)

KF is much more soluble in aHF than is LiF, and it may simply be the higher hydrofluoride ion concentration that can be attained with the former that makes the $KAgF_4$ synthesis easier to achieve in high yield than that of the $LiAgF_4$ relative. Nevertheless, the relatively low solubility of $LiAgF_4$ in aHF and much higher solubility of LiF in that solvent provide for the preparation of $LiAgF_4$ in high purity at ~20°C. The salt proves to be isomorphous with $LiAuF_4$ [13] and the close similarity of the two diffraction patterns indicates that they are probably isostructural.

Decomposition of AgF_3 with F_2 evolution occurs slowly in aHF at ~20°C (Eq. (1)) and leads to contamination of the diamagnetic AgF_3 with paramagnetic $Ag(II)\{Ag(III)F_4\}_2$. It was, therefore, important to have a preparative procedure for AgF_3 that involved minimum exposure of the fluoride to aHF at higher temperatures. In previous preparations [8] using BF_3 or AsF_5 as the fluoride-ion acceptor for precipitation, extensive washing to remove the BF_4^- or AsF_6^- salts was required (except in the case of XeF_5^+ salts, which are highly soluble). The GeF_4 precipitation of AgF_3 from $KAgF_4$ largely avoids this difficulty:

$$2AgF_{4\,(solv)}^{-} + GeF_{4\,(solv)} \rightarrow 2AgF_{3(c)} + GeF_{6\,(solv)}^{2-} \qquad (2)$$

in aHF at 0°C.

4. Conclusions

The new approach to AgF_4^- salt synthesis reported here should be extendible to the other alkali cations. Metathetical reactions of these salts with salts of M^{2+} should further extend the range. However, the major benefit is the convenient source of AgF_3 that this new $KAgF_4$ synthesis now provides.

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