meso or *d*,l isomers can be selectively formed. Further studies are in progress and will be reported later.

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Supplementary Material Available: Listings of crystal structure data and details of the determination, positional parameters, anisotropic thermal parameters, hydrogen atom parameters, bond distances, bond angles, and least-squares equations and planes (20 pages); listings of calculated and observed structure factors (49 pages). Ordering information is given on any current masthead page.

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Crystal Structures of $XeF_5^+MF_4^-$ (M = Ag, Au) and Their Relevance to the Basicity and Oxidizability of MF_4^-

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$XeF_5^+AuF_4^-$ has been prepared from $BrF_3 \cdot AuF_3$ by displacement of BrF_3 with XeF_6. The salt interacts quantitatively with KrF_2 in anhydrous HF, below 0 °C, to yield $XeF_5^+AuF_6^-$. XeF_5AuF_4 (I) is isostructural with XeF_5AgF_4 (II), and these compounds crystallize in space group *I*4/*m* with the following unit cell dimensions: I, a_0 = 5.735 (5) Å, c_0 = 20.007 (17) Å, V = 658 (2) Å^3, Z = 4; II, a_0 = 5.593 (2) Å, c_0 = 20.379 (5) Å, V = 637.5 (8) Å^3, Z = 4. The structure of II was solved by the Patterson method and refined to conventional R and R_w values of 0.077 and 0.090, respectively. The structure contains double layers of XeF_5^+ and layers of AgF_4^- ions, all layers being parallel to the *ab* plane. The XeF_5^+ ion had C_{4v} symmetry with Xe-F(axial) = 1.853 (19) Å, Xe-F(equatorial) = 1.826 (9) Å, and F(axial)-Xe-F(equatorial) = 77.7 (3)°. The anion (site symmetry D_{2h}), which is not significantly different from D_{4h} symmetry, has Ag-F = 1.902 (11) Å. Differences between the XeF_5AgF_4 and XeF_5AuF_4 structures are attributed to lower ligand charges in the anion of the former, relative to those in the latter, and these in turn are related to observed differences in the basicity and oxidizability of the anions.

Introduction

Krypton difluoride has the lowest mean thermochemical bond energy[1] of any known fluoride and is an oxidizer of extraordinary power.[2] The demonstration by Bougon and his co-workers[3] of the effectiveness of KrF_2 as an oxidative fluorinator in the production of a binary fluoride of silver, of composition close to that of AgF_3, suggested that it might also be valuable in the generation of even higher oxidation states of silver in anionic species.

Since Ag(V) had been claimed by Hagenmuller and his co-workers,[4] in the diamagnetic antifluorite-structure materials Cs_2AgF_6 and $Cs_2Ga_{0.5}Ag_{0.5}F_6$, it was anticipated that KrF_2 would be capable of generating AgF_6^- under suitably basic conditions. In an attempt to produce the silver relative of the first Au(V) salt,[5] $Xe_2F_{11}^+AuF_6^-$, AgF_2 was treated with KrF_2 in anhydrous HF (AHF) in the presence of the fluoro base XeF_6. The product was[6] $XeF_5^+AgF_4^-$.

Although many AuF_4^- salts are known,[7-9] the gold relative of $XeF_5^+AgF_4^-$ was not. On the other hand, the Au(V) salt $XeF_5^+AuF_6^-$ was known.[10]

It appeared that if $XeF_5^+AuF_4^-$ could be prepared, it would be a structural relative of $XeF_5^+AgF_4^-$. The high thermal stability[10] of $XeF_5^+AuF_6^-$ also suggested that its preparation from $XeF_5^+AuF_4^-$ would be readily achieved by using KrF_2. These expectations have been realized. In addition the structural relationship of $XeF_5^+AgF_4^-$ to $XeF_5^+AuF_4^-$ has shed light on the factors that cause AgF_4^- both to be a poor base and to be difficult to oxidize.

Experimental Section

1. Apparatus and Reagents. A nickel vacuum line was used. It had a mercury diffusion pump, a mechanical pump, and soda-lime scrubbers (for removal of fluorine, HF, and oxidizing fluorides) and was equipped with a Monel Acco Helicoid pressure gauge (0-1400 Torr, ±0.3%) and nickel valves with Teflon packing. Teflon FEP reaction vessels (18 mm o.d.) equipped with Teflon valves were used for all preparations. AgF_2 (99.5% purity; Fluka, Buchs, Switzerland) was used as supplied. KrF_2 was prepared[11] by irradiation of a liquefied mixture of fluorine and krypton with near-UV light at −196 °C. XeF_6 was prepared by the interaction of xenon with fluorine, in the presence of NiF_2 as a catalyst,[12] at 120 °C. F_2 was prepared and purified as described elsewhere.[13] Additional purification was performed by photolysis (to make O_2F_2 from O_2 impurity).[14] Xenon and krypton (each 99.99%) were used as supplied (Messer Griesheim, Linz, Austria). Anhydrous hydrogen fluoride (Kalie Chemie, Hannover, Germany) was purified as described previously[15] and then treated with KrF_2. Bromine trifluoride was prepared by the fluorination of bromine at ambient temperatures in a nickel vessel.

2. Instrumentation. Raman spectra were obtained with use of a Spex 1401 double monochromator, and a detection system that utilized photon-counting techniques was used in conjunction with a variety of laser lines (Coherent Radiation; principally 488.0, 514.5, and 647.1 nm). Powdered samples were loaded into 1 mm i.d. quartz capillaries in the drybox, and the capillaries were sealed temporarily with a plug of Kel-F grease and then drawn and sealed in a small flame outside the drybox.

X-ray Powder Photography. X-ray powder diffraction patterns of solid samples were obtained with an Enraf apparatus (Delft, Holland), using graphite-monochromatized Cu Kα radiation. A finely powdered sample was sealed into 0.5-mm quartz capillaries as described for Raman spectroscopy.

3. Preparation of $XeF_5^+AgF_4^-$ Single Crystals. The compound $XeF_5^+AgF_4^-$, as previously described,[6] was weighed into a FEP apparatus,

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[†] University of Ljubljana.

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Table I. Crystal Data and Details of the Structure Determination and Refinement for $XeF_5^+AgF_4^-$

formula	XeF_5AgF_4	Z	4
mol wt	410.16	d_{calcd}, g cm^{-3}	4.273
space group[a]	$I4/m$	shape of cryst	thin plate
cryst syst	tetragonal	color	yellow
a,[b] Å	5.593 (2)	prominent axis	{100}
c, Å	20.379 (5)	$F(000)$	728
V, Å^3	637.5 (8)		

diffractometer	CAD-4 Enraf Nonius
data collected	$\pm h,\pm k,+l$
radiation (λ, Å)	Mo Kα (0.71069)
monochromator (angle, deg)	graphite (12.1)
temp, K	293–295
scan technique	ω–2θ
2θ scan width, deg	$1.0 + 0.3 \tan \theta$
scan rate, deg min^{-1}	4.12–16.48
bkgd	0.25 of scan time at each of scan limits
$2\theta_{max}$, deg	54
max scan time, s	20
no. of ref rflns	3 after each 4 h
no. of orient rflns	3 after 600 rflns
intens decrease, %	2
no. of measd rflns	2851
no. of averaged rflns	363
mean discrepancy on I, %	11.2
no. of obsd rflns	331
criterion	$I > 3\sigma(I)$
μ, cm^{-1}	84.84
abs cor	Gaussian, 8 × 8 × 8
transmissn factor	0.054–0.425
program used	XRAY76,[c] SHELX76[d]
scattering factors	neutral atoms[e]
R, R_w[f]	0.077, 0.090
weight	$10.06(\sigma^2(F_o) + 0.0005F_o^2)^{-1}$
no. of params	30
ratio of observns to params	10.96
max shift/error	0.23
residual electron density, e Å^{-3}	−3.67 to +3.38

[a] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1965; Vol. I. [b] Cell dimensions were determined by a least-squares fit of the setting angles of 25 reflections within the range 8–13°. [c] Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H. L.; Flack, H. "The XRAY76 System"; Tech. Rep. TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976. [d] Sheldrick, G. "SHELX76 System of Computing Programs"; University of Cambridge: Cambridge, England, 1976. [e] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. [f] The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for XeF_5AgF_4

	x	y	z	U[a]
Xe	0	0	1539 (1)	21 (1)
F_{ax}	0	0	2448 (9)	40 (9)
F_{eq}	−2903 (16)	−1322 (18)	1730 (5)	34 (5)
Ag	0	5000	0	22 (1)
F	−1504 (18)	6925 (17)	−649 (6)	39 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths and Angles for $XeF_5^+AgF_4^-$

	Bond Lengths (Å)		
Xe–F_{ax}	1.852 (19)	(4×) Ag–F	1.902 (11)
(4×) Xe–F_{eq}	1.826 (9)	(4×) Ag···F	2.921 (10)
(4×) Xe···F_{br}	2.637 (11)		
	Bond Angles (deg)		
F_{ax}–Xe–F_{eq}	77.7 (3)	F–Ag–F	91.9 (5)
F_{eq}–Xe–F_{eq}	87.4 (4)	F–Ag–F	88.1 (5)
F_{ax}–Xe–F_{br}	133.5 (2)		

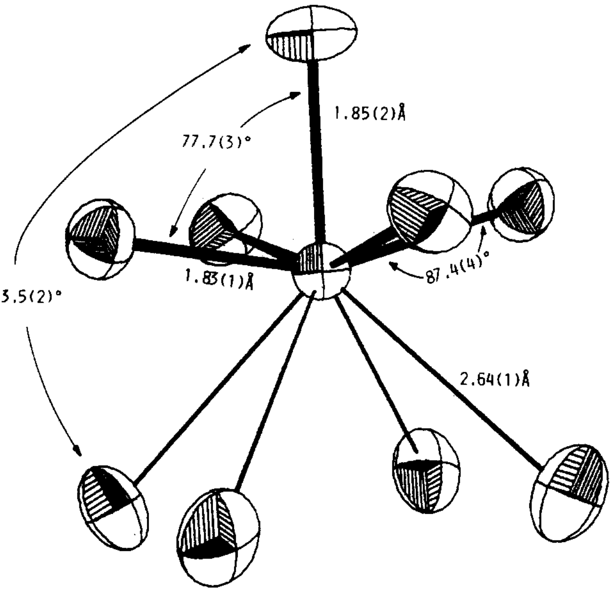

Figure 1. ORTEP diagram of the XeF_5^+ ion in $XeF_5^+AgF_4^-$.

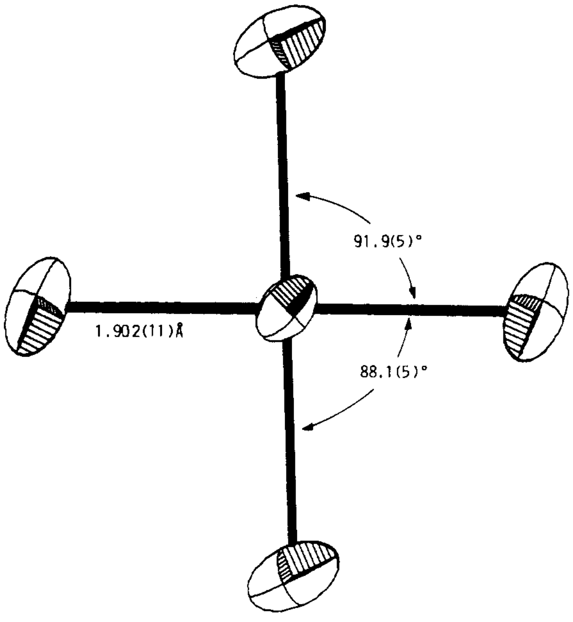

Figure 2. ORTEP diagram of the AgF_4^- ion in $XeF_5^+AgF_4^-$.

and anhydrous HF (AHF) was added by sublimation to −196 °C. After the AHF was saturated with the salt by dissolving it at room temperature, the solution was decanted. Crystallization of $XeF_5^+AgF_4^-$ occurred as the solvent evaporated. This was achieved by a small thermal gradient to a colder trap (20 to 14 °C) over a period of 3 weeks. Crystals, which were thin yellow plates, were loaded in 0.5-mm quartz capillaries in a drybox, and the capillaries were sealed temporarily with a plug of Kel-F grease and then drawn down in a small flame outside the drybox.

4. Structural Determination of $XeF_5^+AgF_4^-$. The crystals of $XeF_5^+AgF_4^-$, which were very sensitive to light and moisture, were mounted in quartz capillaries and tested on a CAD-4 automated diffractometer. Preliminary precession photographs suggested tetragonal symmetry, space group $I4/m$. This was borne out by the successful structure analysis. Details of procedures used for data collection and structure determination are given in Table I. Atomic coordinates and temperature factors are given in Table II, and selected bond lengths and angles are in Table III. Anisotropic temperature factors and structure factor tables are included in the supplementary material.

5. Description of the $XeF_5^+AgF_4^-$ Structure. The crystal structure of $XeF_5^+AgF_4^-$ is the result of the interaction of square-based-pyramidal (C_{4v}) XeF_5^+ and essentially square-planar AgF_4^-. Each cation (centered on a 4-fold axis) interacts (bridges) with one F ligand of each of four anions, as illustrated in Figure 1. The approximately square-planar AgF_4^- groups, one of which is illustrated in Figure 2, have their pseudo-4-fold axes perpendicular to c_0 (and are centered on point symmetry $2m$). These anions lie in distinct layers in which the Ag atoms have a common z parameter (0 or $^1/_2$). The AgF_4 plane of each anion is per-

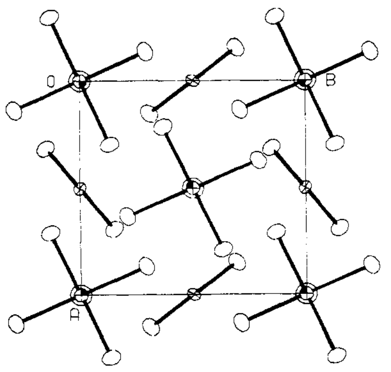

Figure 3. Coordination of near-neighbor anions and cations in $XeF_5^+AgF_4^-$.

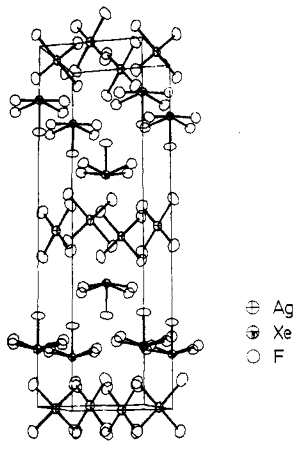

Figure 4. Unit cell of $XeF_5^+AgF_4^-$.

pendicular to the AgF_4 plane of its four nearest neighbors (see the projection of half the unit cell in Figure 3), and the mutual tilting is such that each Ag atom, in addition to its four F ligands at 1.902 (11) Å, has four other F ligands, of the two diagonally related AgF_4 groups, at 2.921 (10) Å. Thus, the F ligand arrangement about each Ag atom can be described as that of a cubic assembly grossly distorted by moving diagonally opposite parallel edges away from the Ag atom along that diagonal. This is an anion arrangement reminiscent of that in the alkaline AuF_4^- salts.[16]

Each AgF_4^- interacts with two XeF_5^+ groups above and two below the layer of anions. Thus, each layer of n anions has a layer of $n/2$ cations above and a layer of $n/2$ cations below it. This set of three strongly attracting layers (Xe···F(Ag) = 2.637 (11) Å) is fully charge compensated. Because of the cation–anion interaction and resultant arrangements just described, the cation arrangement in a given layer is a rather open one. This allows for the cation arrangement in one layer to pack closely with those of an adjacent layer as illustrated in the unit cell representation in Figure 4. Thus, the axial ligands of XeF_5^+ project into the adjacent cation layer and close-pack with the equatorial F ligands of that layer. Clearly there can be no strong cohesion of these interpenetrating cation layers, and it is probably the ready separation of these layers that explains the mica-like crystal habit of this material and its ready cleavage perpendicular to the (001) axis.

6. Preparation of $XeF_5^+AuF_4^-$. $BrF_3{\cdot}AuF_3$ was prepared after the method of Sharpe.[7] Finely divided gold (precipitated by reduction with oxalic acid from chloroaurate solution), contained in a FEP tube, was first covered with dry bromine, and then BrF_3 was vacuum-distilled onto the mixture, which was then brought slowly to room temperature. The interaction appeared to be largely complete at or below ~20 °C, but to ensure complete dissolution of the gold, the reaction mixture was slowly brought to the distillation temperature of the bromine. Removal of bromine under a dynamic vacuum left a clear golden solution of $BrF_3{\cdot}AuF_3$ in BrF_3. Removal of the latter at ~20 °C gave a yellow crystalline sample of the adduct. A large molar excess of XeF_6 was transferred by vacuum distillation to the FEP reaction vessel and was melted in contact with the $BrF_3{\cdot}AuF_3$, a lemon yellow suspension being formed in the melt. BrF_3 and excess XeF_6 were removed under vacuum to leave a lemon yellow solid. A Raman spectrum (see Figure 5) showed this solid to be $XeF_5^+AuF_4^-$, and the X-ray powder diffraction pattern (see Table IV) showed a close similarity (with significantly different unit cell parameters, however—see Results and Discussion) to that of $XeF_5^+AgF_4^-$.

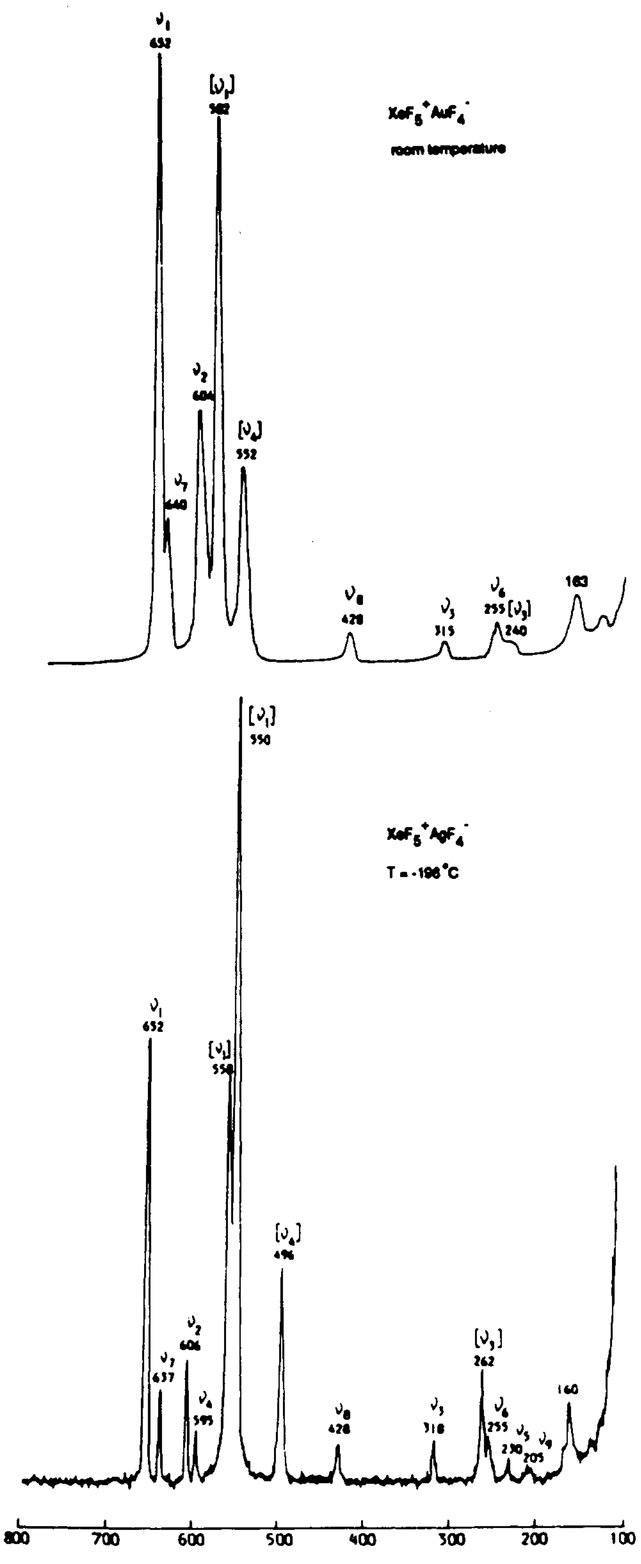

Figure 5. Raman spectra of $XeF_5^+AuF_4^-$ and $XeF_5^+AgF_4^-$ ([ν] for anions).

7. Interaction of $XeF_5^+AuF_4^-$ with Liquid HF. Anhydrous HF (AHF) was melted onto a sample of $XeF_5^+AuF_4^-$ contained in a FEP tube. The lemon yellow salt quickly interacted with the liquid AHF to produce an orange-yellow solid. Removal of volatiles provided the latter solid. Raman spectroscopy[10] and an X-ray powder photograph[17,18] showed it

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Table IV. X-Ray Powder Diffraction Data for $XeF_5^+AuF_4^-$ [a]

	$10^4/d^2$, Å		
I/I_0	obsd	calcd	*hkl*
10	105	100	002
2	401	400	004
3	720	710	112
10	906	900	106
		930	105
2	1022	1010	114
≪1	1333	1320	202
1	1528	1510	116
		1530	107
		1620	204
1	1763	1750	213
2	2118	2120	206
2	2206	2210	118
2	2339	2330	109
2	2446	2440	220
1	2553	2540	222
2	2831	2820	208
		2840	224
5	3114	3110	1,1,10
		3150	312
2	3329	3330	1,0,11
		3340	226
2	3467	3450	314
4	3606	3600	0,0,12
≪1	4189	4190	323
≪1	4435		
1	4640	4650	318
1	4783	4770	309
1	4890	4880	400
		4900	0,0,14
1	5534	5510	1,1,14
		5550	3,1,10
		5750	2,1,13
1	5775	5780	406
		5770	3,0,11
		6040	2,2,12
1	6095	6100	420
3	6980	6970	3,0,13
		6905	3,2,11
1	7262	7210	419
		7340	2,2,14
1	8322	8250	505
		8370	3,0,15

[a] Cu Kα radiation from Ni filter. Unit cell: body-centered tetragonal with $a_0 = 5.735$ (5) Å, $c_0 = 20.007$ (17) Å, $V = 658$ (2) Å^3, and $Z = 4$.

to be AuF_3. Addition of a large molar excess of AsF_5 to the distillate afforded a colorless solid, formed from the AHF solution as the last drops of AHF were removed. Raman spectroscopy showed it to be[19] $XeF_5^+AsF_6^-$.

8. Interaction of $XeF_5^+AuF_4^-$ with KrF_2 in AHF. A several-fold molar excess of KrF_2 (~5 g) was vacuum-sublimed onto a sample of $XeF_5^+AuF_4^-$ (1.2 g) contained in an FEP tube. AHF (~5 mL) was condensed onto this mixture, which was then brought slowly toward 0 °C. As the KrF_2 dissolved in the liquid HF, it interacted with XeF_5AuF_4 with gas evolution. As the interaction continued, the solid phase disappeared and a transparent pale yellow solution was obtained at or below 0 °C. Removal of AHF and excess KrF_2 produced a highly concentrated solution, which yielded a crystalline pale yellow solid only as the last drops of AHF were removed. Raman spectroscopy (see Figure 6) and an X-ray powder photograph showed[10] the pale yellow solid to be $XeF_5^+AuF_6^-$.

Results and Discussion

The crystal structure of $XeF_5^+AgF_4^-$ confirms the earlier conclusion,[6] based on Raman spectroscopy, that the material is an essentially ionic assembly. The interatomic distance in the anion is not significantly different from that given by Hoppe and Homann[9] for $AAgF_4$ (A = Na, K). Also, the observed Ag^{III}–F interatomic distance of 1.902 (11) Å is not significantly different from that of 1.95 (2) Å given[16] for Au^{III}–F in $KAuF_4$.

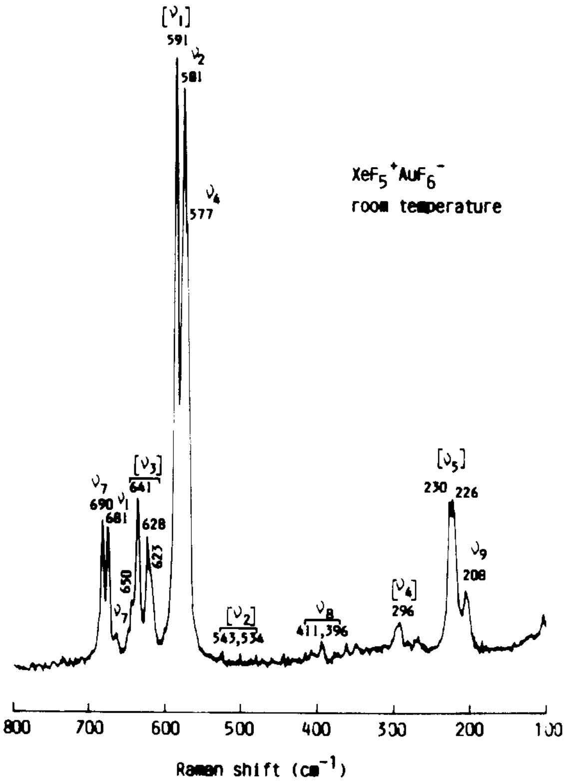

Figure 6. Raman spectrum of $XeF_5^+AuF_6^-$ ([ν] for anion).

Although the coordination of the cation to four anionic F ligands, to generate a capped-Archimedian-antiprism geometry, is like that observed in the $XeF_5^+MF_6^-$ salts,[20] where M = Pt,[21] Ru,[22] and Nb,[23] the cation shape is slightly different from that observed in those salts. In the $XeF_5^+MF_6^-$ salts the axial Xe–F interatomic distance in the cation is in all cases shorter than the equatorial, the difference ranging from 0.03 to 0.06 Å, and the axial Xe–F distance is close to 1.80 Å. In $XeF_5^+AgF_4^-$ the axial bond is longer (1.85 (1) Å). Additionally, the F(axial)–Xe–F(equatorial) angle in the MF_6^- salts is in each case close to 80°, whereas in the AgF_4^- salt the angle is smaller (77.7 (8)°). Although this angle reduction is barely significant, when it is taken together with the stretching of the Xe–F axial distance, the impression is gained that the anion F ligand interaction with the cation in $XeF_5^+AgF_4^-$ is greater than in the case of the $XeF_5^+MF_6^-$ salts. The general shortness of the cation–anion Xe–F distances in the former (four at 2.64 (1) Å) also hints at this, since in the MF_6^- salts, although there are two short Xe···F distances (in XeF_5RuF_6, one at 2.55 (1) Å and another at 2.60 (1) Å) the other two are long (two at 2.92 (1) Å for M = Ru). It appears that on the average the charge on the F ligand in AgF_4^- is larger than the average charge for the MF_6^- salt ligands (M = Ru, Pt, Nb). Of course the lower ligand number in the AgF_4^- anion is a major contributor to this.

Although $Xe_2F_{11}^+$ salts exist for a wide range of MF_6^- and MF_6^{2-} salts,[5,20] they appear not to exist for either AgF_4^- or AuF_4^-. The syntheses of $Xe_2F_{11}^+MF_4^-$ (M = Ag, Au) were attempted (using a large excess of XeF_6), but no hint of their existence was detected. It appears that the ligand charge in AgF_4^- and AuF_4^- is high enough that XeF_6 is an insufficiently strong base to displace the anion ligands from their interaction with XeF_5^+. Clearly this cannot be the case for those anions that stabilize $Xe_2F_{11}^+$. These include[5] AuF_6^-.

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The indications of high ligand charge in AgF_4^- suggest that AgF_3 is not a strong acid. Yet the salt $XeF_5^+AgF_4^-$ is not solvolyzed by HF and is indeed effectively recrystallized from that solvent. On the other hand, $XeF_5^+AuF_4^-$ interacts quantitatively with liquid AHF below 20 °C to yield AuF_3:

$$XeF_5AuF_4 + xHF \rightarrow XeF_5^+ + F(HF)_x^- + AuF_3$$

The moderate fluoroacidity of HF is crucial to this solvolysis. Evidently AgF_4^- is a poorer fluorobase than AuF_4^-, with the hydrofluoride ion $F(HF)_x^-$ ($1 < x \leq 4$), of intermediate basicity. The greater basicity of AuF_4^- relative to that of AgF_4^- indicates that the ligand charge in the gold anion should be higher than that in the silver salt. This appears to be so from a comparison of the unit cells of $XeF_5^+AgF_4^-$ and $XeF_5^+AuF_4^-$.

As the X-ray powder data in Table IV show, the gold salt $XeF_5^+AuF_4^-$ is isomorphous with its silver relative and the structures must be similar. Significant differences are readily apparent, however, the most striking being the shorter c_0 axis and the larger a_0 axis of the gold salt. This contraction of c_0 must mean a stronger interaction of the cationic and anionic layers in $XeF_5^+AuF_4^-$ than obtains in $XeF_5^+AgF_4^-$. Since the ionic volumes in the two structures must be approximately the same, the contraction of c_0 requires an expansion in a_0. Unfortunately, the solvolysis of $XeF_5^+AuF_4^-$ has made it difficult to obtain single crystals and precise details of the structure are therefore not available. However, the simplicity of the structural arrangement and the close similarity of the cationic contributions in the Raman spectra of the two salts (compare the spectra in Figure 5) suggest that the nature of the cation–anion interaction is the cause of the unit-cell dimension differences.

The intense (totally symmetric) Raman band for AgF_4^- (centered on $\sim$554 cm^{-1}) indicates (since the heavy central atom does not move in ν_1) that the bond-stretching force constant for this ion must be akin to that in its gold relative ($\nu_1 \approx 582$ cm^{-1}). Indeed, the small reduction in stretching frequency for AgF_4^- relative to the frequency for AuF_4^- could signify (since the anions are almost isodimensional and ligand–ligand repulsions must therefore be similar) that the bonding in AgF_4^- is slightly weaker than in AuF_4^-. It is also notable that the $\nu_1(a_1)$ vibration of AuF_6^- in $XeF_5^+AuF_6^-$[5,10,24] at 582 cm^{-1} is close to that for ν_1 of AuF_4^-. Clearly the addition of two more F ligands to AuF_4^- has very little impact on the Au–F bonding. The repulsive interaction of the additional two ligands must be similar to the repulsive effect of the d_{z^2} pair of electrons of the Au(III). It is possible that the relationship of AgF_6^- to AgF_4^- could be similar to that of AuF_6^- to AuF_4^-. It is evident, however, from the present studies, that the involvement of the Ag(III) d_{z^2} pair in further bonding, by oxidative addition of two ligands, will not be readily achieved.

The greater basicity of AuF_4^- compared with that of AgF_4^- implies that the effective positive charge at Au(III) is lower than at Ag(III). This is a measure of the electronegativity difference between Au(III) and Ag(III) and therefore of the relative ease of oxidation of these centers. Au(III) was already known to be oxidizable to Au(V) in fluoro environments, yet the interaction with KrF_2 carried out in this study proved to be remarkably facile:

$$XeF_5^+AuF_4^- + KrF_2 \xrightarrow{\text{AHF } (\leq 0\ ^\circ\text{C})} XeF_5^+AuF_6^- + Kr$$

In contrast all attempts to carry the oxidation of silver further, by using KrF_2 in liquid AHF, failed.

If $XeF_5^+AgF_6^-$ were to exist, it would probably be structurally similar to $XeF_5^+AuF_6^-$ and $XeF_5^+AsF_6^-$. The last two salts are isostructural,[10,24] and both are highly soluble in AHF, even below 0 °C. The oxidation of AgF_4^- by KrF_2 in AHF must therefore be regarded as highly advantageous toward the synthesis of the AgF_6^-. The failure to form AgF_6^- under such favorable conditions indicates that, if such an anion is to be preparable, electronic excitation of the precursor silver species (e.g. AgF_4^-) may have to be a component of the approach.

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Supplementary Material Available: Table V, listing anisotropic temperature factors for $XeF_5^+AgF_4^-$ (1 page); a listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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