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Preparation and Structural and Magnetic Properties of $AgF^+MF_6^-$ (M = Ir, Ru, Sb, Bi) and $Ag^{2+}(BiF_6^-)_2$[†]

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$AgFMF_6$ salts (M = Ir, Ru, Sb, Bi) have been prepared by the action of elemental F_2 in AHF on $AgMF_6$, and for $AgFBiF_6$, also by interaction of $Ag(BiF_6)_2$ with KBF_4 or KPF_6 in AHF. Three structure types have been identified. $AgFIrF_6$ {orthorhombic *Pnma*, $a = 7.628(2)$ Å, $b = 7.067(2)$ Å, $c = 10.253(4)$ Å, $V = 552.7(3)$ Å^3, and $Z = 4$, with $R = 0.026$ and $R_w = 0.030$ for 531 observed reflections and 50 parameters refined by full-matrix least squares, Mo Kα radiation at 298 K} is isostructural with $AgFAsF_6$ and $AgFAuF_6$, the one dimensional cation $(Ag-F)_n^{n+}$, showing Ag(II) linearly coordinated to two F ligands with Ag−F = 1.977(9) and 2.014(9) Å and Ag−F−Ag = 146.0(5)°. In $AgFRuF_6$ {monoclinic $P2_1/n$, $a = 8.3432(13)$ Å, $b = 5.4933(8)$ Å, $c = 11.9286(22)$ Å, $\beta = 108.36(1)°$, $V = 518.9(3)$ Å^3, and $Z = 4$, with $R = 0.027$ and $R_w = 0.028$ for 1511 observed reflections and 83 parameters refined by full matrix least squares, Mo Kα radiation at 298 K} the Ag(II) is nearly square coordinated by four F; two *cis* F, each shared nearly equally with another Ag(II) {Ag−F = 2.007(3) and 2.018(2) Å, Ag−F−Ag = 155.9(2)°} give the cation a ribbonlike polymeric character. The other two F ligands of the square array {Ag−F = 2.140(3) and 2.158(3) Å} are each associated with a different RuF_6^-, each of which is so linked to two Ag(II) moieties. $AgFMF_6$ (M = Sb, Bi) belong to a third structure type. The cation chains of the $AgF^+MF_6^-$ salts have approximate temperature independence of magnetic susceptibility, akin to that of metallic systems. In contrast, $Ag(BiF_6)_2$ {triclinic $P\bar{1}$, $a = 5.218(2)$ Å, $b = 5.579(1)$ Å, $c = 8.934(2)$ Å, $\alpha = 76.08(2)°$, $\beta = 88.93(2)°$, $\gamma = 65.08(2)°$, $V = 228.0(1)$ Å^3, and $Z = 1$, with $R = 0.055$ and $R_w = 0.067$ for 1327 observed reflections and 41 parameters refined by full-matrix least squares, Mo Kα radiation at 298 K}, which is isostructural with $Ag(SbF_6)_2$, shows approximate obedience to the Curie−Weiss law. $AgRuF_6BiF_6$ appears to be similar. In the structure of $Ag(BiF_6)_2$, each Ag(II) is linked in nearly square array to four F ligands of four surrounding BiF_6^- ions {Ag−F = 2.096(9) Å × 2 and 2.122(9) Å × 2}, two other anions making contact normal to that plane, with Ag---F = 2.440(10) Å.

Introduction

The Ag(II) salts $AgFAsF_6$ and $Ag(SbF_6)_2$ were first prepared by Frlec and Holloway and their co-workers,[1,2] each salt being structurally characterized by them.[2,3] In addition, Müller, has prepared[4] and structurally characterized, $Ag(MF_6)_2$ (M = Nb, Ta) which are structural relatives of $Ag(SbF_6)_2$.

In the course of investigations of the chemistry of AgF_3, it was discovered in these laboratories[5] that the trifluoride interacted with AsF_5, at ~20 °C, in liquid anhydrous hydrogen fluoride (AHF) to liberate F_2 and yield $AgFAsF_6$ ($AgF_3 + AsF_5 \rightarrow AgFAsF_6 + {}^1/_2F_2$). In searching for evidence of an intermediate Ag(III) solution species in that reaction, it was found that cationic Ag(II) in AHF (Ag^{2+}(solv)) was a sufficiently powerful oxidizer to oxidize xenon at room temperatures. The cation AgF^+ has also been shown to be a strong oxidizer[6] but less potent than Ag^{2+}(solv) which will also oxidize O_2 to O_2^+ at −78 °C.

A number of Ag(II) fluoroanion salts have been investigated as part of a systematic investigation of the oxidizing properties of Ag(II) in AHF, and previous papers[5−8] describe some of that work. In this report synthetic approaches are given for the synthesis of novel $AgFMF_6$ salts (M = Ir, Ru, Sb, Bi) and three structure types are identified. The AgF^+ in these salts are all associated with a weak paramagnetism that is approximately temperature-independent from ~50 K up. This contrasts with the magnetic behavior of Ag(II) in $Ag(BiF_6)_2$ and $AgRuF_6BiF_6$ which approximately obey the Curie−Weiss law. In the $Ag(MF_6)_2$ compounds, the structural evidence indicates that the Ag(II) species are consistent with Ag^{2+} in a tetragonally elongated octahedral environment. Reasons for the structural variety in the $AgFMF_6$ salts and their magnetic properties are discussed.

Results and Discussion

The ability of Ag^{2+}(solv) to oxidize[5,6] Xe or O_2 in AHF demonstrates that even the HF- solvated Ag^{2+} must possess a high effective nuclear charge at the metal center. It was expected then that the Ag^{2+} in salts would exert high polarizing power and only be sustainable by anions of great stabililty with respect either to anionic ligand loss (e.g. F^-) or electron transfer.

From conductivity measurements on $EF_5/HSO_3F/SO_3$ systems, Gillespie and his co-workers have shown[9] that the Lewis

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[†] Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

[®] Abstract published in *Advance ACS Abstracts,* April 1, 1995.

(1) Frlec, B.; Gantar, D.; Holloway, J. H. *J. Fluorine Chem.* **1982**, *20*, 385.

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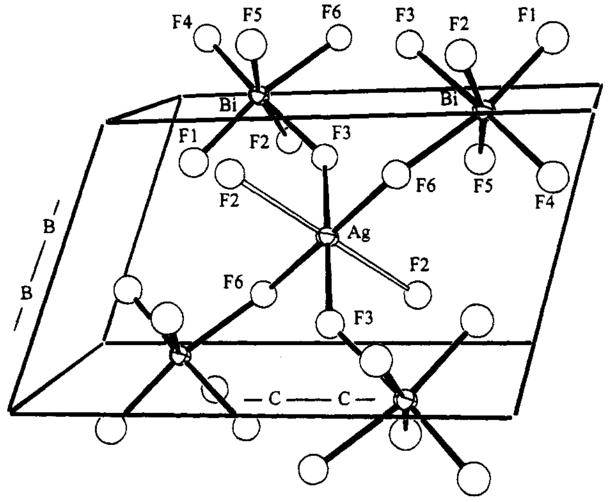

Figure 1. Structure of $Ag(BiF_6)_2$, distances in Å with $\sigma = 0.01$ Å.

acid strength of the group 15 elements increases in the order $PF_5 < AsF_5 < BiF_5 < SbF_5$. This suggests that the failure to prepare $Ag(AsF_6)_2$ (even with removal of AHF and AsF_5 from solutions at −60 °C) is a consequence of the inadequate fluoroacidity of AsF_5. Since the F^- affinity of gaseous AsF_5 has been assessed[10] to be at least 111 kcal·mol^{-1}, the Ag^{2+} is seen to be a very powerful fluoride ion acceptor. The structure of $Ag(SbF_6)_2$ by Gantar *et al.*[2] and those of $Ag(MF_6)_2$ (M = Nb and Ta)[4] are, however, nicely explained by the formulation of $Ag^{2+}(MF_6^-)_2$, so in those instances, the Ag^{2+} fails to abstract F^- from the SbF_6^-, NbF_6^-, or TaF_6^-. To that set can now be added BiF_6^- and RuF_6^-.

Figure 1 shows the essentials of the $Ag(BiF_6)_2$ structure. X-ray powder photographs of this compound had already indicated that it was of the same structure type as $Ag(SbF_6)_2$. Because of this and the less-than-optimal data associated with the need to enclose a powerfully oxidizing, large crystal in a quartz capillary, a lower precision structure was achieved. To avoid artificial anisotropy of fluorine atom positioning, deriving from absorption and capillary scattering effects, these atoms were set isotropic in the refinement. Just as in the $Ag(SbF_6)_2$ case, the Ag^{2+} occupies an elongated octahedral site at a center of symmetry, in an approximately close-packed F ligand array provided by the anions. The approximately square F ligand array {Ag−F = 2.096(9) Å × 2 and 2.122(9) Å × 2} about the Ag^{2+} is not significantly different from that found for $Ag(SbF_6)_2$, nor are the two long bonds {Ag−F = 2.440(10) Å} different from those in $Ag(SbF_6)_2$. The BiF_6^- anions like[2] the SbF_6^- are much distorted by their interaction with the cation. The F ligands of the anion, which make close approach to the cation, are elongated by more than 0.1 Å, relative to those anionic ligands which have no contact with the cation (see Table 1). This and the other departures from O_h symmetry of the anion, point to the strong polarizing influence of the cation. The magnetic susceptibility of $Ag(BiF_6)_2$ obeys the Curie−Weiss law over the temperature range 35−280 K (see Figure 2) and has a room temperature moment, $\mu_{eff} = 2.1\ \mu_B$, in agreement with the structural arrangement, in which discrete Ag(II) species of d^9 configuration are separated by closed-shell BiF_6^- species.

In an experiment designed to check that Ag^{2+}(solv) in AHF was incapable of oxidizing RuF_6^- to RuF_6 {in contrast to cationic Ag(III) which has that capability[6]}, $ARuF_6$ (A = Li or K) dissolved in AHF was added to a solution of $Ag(BiF_6)_2$. Neutral RuF_6 was not generated but a dark green solid precipitated, which, from X-ray powder photography and gravimetry, proved to be $AgRuF_6BiF_6$:

Table 1. Interatomic Distances (Å) and Angles (deg) for $Ag(BiF_6)_2$ at 298 K

	Distances		
Ag−F2	2.440(10)	Bi−F3	2.048(9)
Ag−F3	2.096(9)	Bi−F4	1.939(10)
Ag−F6	2.122(9)	Bi−F5	1.940(11)
Bi−F1	1.944(10)	Bi−F6	2.046(9)
Bi−F2	1.966(9)		
	Angles		
F2−Ag−F2	180	F1−Bi−F6	169.0(4)
F2−Ag−F3	86.3(3)	F2−Bi−F3	83.2(4)
F2−Ag−F6	84.5(3)	F2−Bi−F4	92.1(4)
F3−Ag−F3	180	F2−Bi−F5	165.3(4)
F3−Ag−F6	89.4(3)	F2−Bi−F6	84.3(4)
F6−Ag−F6	180	F3−Bi−F4	174.0(3)
F1−Bi−F2	93.7(4)	F3−Bi−F5	86.2(4)
F1−Bi−F3	85.0(4)	F3−Bi−F6	84.0(4)
F1−Bi−F4	99.1(4)	F4−Bi−F5	97.7(4)
F1−Bi−F5	95.5(4)	F4−Bi−F6	91.8(4)
		F5−Bi−F6	84.6(4)

$$Ag(BiF_6)_2 + ARuF_6 \rightarrow AgRuF_6BiF_6 + ABiF_6 \qquad (1)$$

This salt has a similar powder pattern to those of $Ag(MF_6)_2$ (M = Sb, Bi), although the slightly higher angle positions of the diffraction lines indicate a smaller unit cell. The similarity of the relative line intensities of the patterns of $AgRuF_6BiF_6$ and $Ag(BiF_6)_2$ indicate a close structural similarity, but the magnetic susceptibility dependence upon temperature was less simple for $AgRuF_6BiF_6$ than in the closed-shell anion cases (see Figure 3). The strong bridging interaction of F ligands of the d^3 RuF_6^- with the d^9 Ag^{2+} ion probably gives rise to a ferromagnetic super-exchange coupling via the *sigma* orbital system as discussed, for d^3 with d^5 systems, by Goodenough.[11] Weak coupling of this kind, with an ordered RuF_6^- BiF_6^- anion sequence would account for the field dependence of the susceptibility below 37 K, which is the Curie temperature for the material.

Although several $AgFMF_x$ salts had been reported,[2,5−8] those of the strong-acid anions SbF_6^- and BiF_6^- had not. Fluorination of the appropriate $AgMF_6$ salt in AHF has proved to be effective for the preparation of both of those salts, as well as others:

$$AgMF_6 + {}^1\!/_2F_2 \rightarrow AgFMF_6\ (M = Sb, Bi, Ir, Au, Ru) \qquad (2)$$

(This also proves to be a good approach for the preparation of single crystals suitable for X-ray diffraction structure determination). The $AgFBiF_6$ has also been made by displacement of a weak acid from its alkali salt:

$$Ag(BiF_6)_2 + KBF_4\ (\text{or } KPF_6) \rightarrow$$
$$AgFBiF_6 + KBiF_6 + BF_3\ (\text{or } PF_5) \qquad (3)$$

This synthesis nicely demonstrates the loss of F^- from a weak acid anion to Ag^{2+}. It was not possible to prepare $AgFPF_6$ by fluorination of $AgPF_6$ in AHF, the product being AgF_2 and PF_5. Here, PF_6^- is seen to be an effective F^- donor even to AgF^+. Although the F^- affinity of BF_3(g) is approximately 10 kcal·mol^{-1} less than that of PF_5, the greater lattice energy of small-cation BF_4^- salts more than compensates for that deficiency.[10] This probably accounts for the existence[5,7] of $AgFBF_4$ and the failure to prepare $AgFPF_6$.

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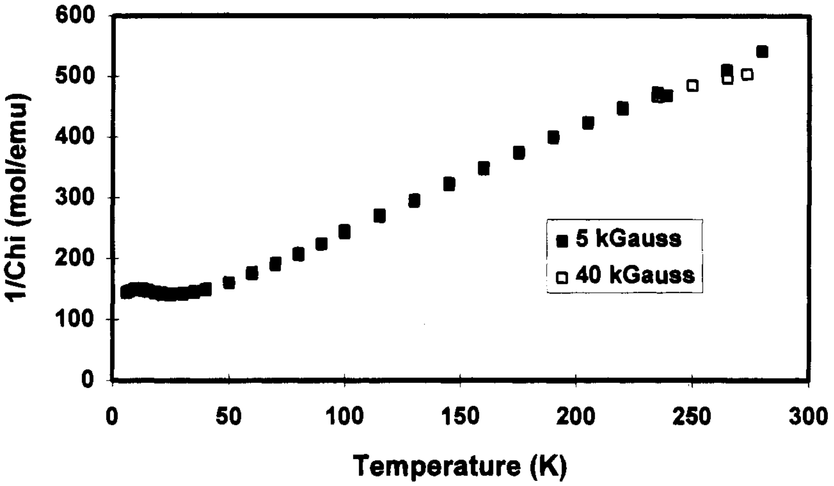

Figure 2. Curie–Weiss plot of the magnetic susceptibility of $Ag(BiF_6)_2$.

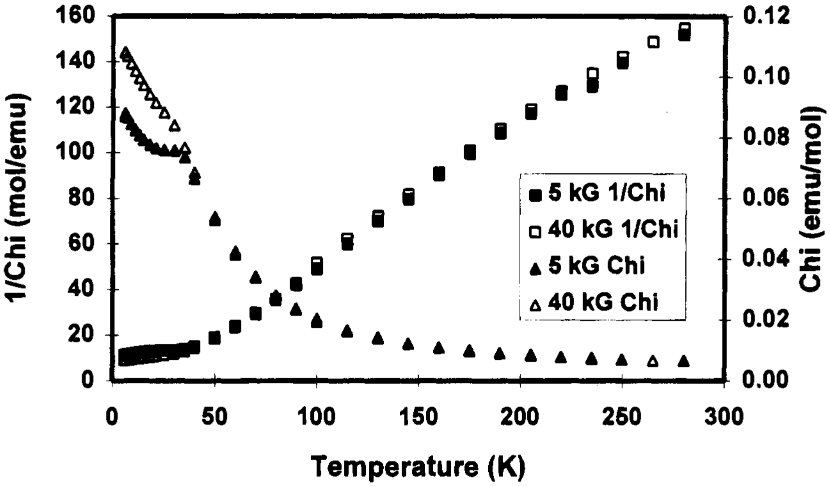

Figure 3. Magnetic susceptibility data for $AgRuF_6BiF_6$.

The liberation of OsF_6 on fluorination of $AgOsF_6$ showed[6] that if the ionization potential of MF_6^- is lower than the 5.7 eV estimated[12] for OsF_6^-, transfer of the anion electron to the cation occurs. In the case of IrF_6^-, the ionization potential is ~1 eV higher than that value, and $AgF^+IrF_6^-$ is stable. The salt has the same structure[3,8] as $AgFAsF_6$ and $AgFAuF_6$. The nature of the $(Ag-F)_n^{n+}$ one dimensional chain is not significantly different[13] from that in $AgFAsF_6$. The important distances and angles are given in Figure 4 and Table 2.

Since the anion RuF_6^- is only ~0.3 Å^3 smaller[14] than IrF_6^-, it was a surprise to find that the $AgFRuF_6$ structure is of a very different type. As may be seen in Figure 5 and Table 3, the Ag(II) species in this salt is approximately square-coordinated by four F ligands as in the $Ag(MF_6)_2$ salts. In contrast to the latter however, neighboring Ag(II) are brought into close proximity with one another by two *cis* related bridging F ligands, each nearly equidistant from two Ag(II). The nearly square F ligand array involves another two ligands, one from each of two RuF_6^-. Each RuF_6^- bridges two Ag(II), and as can be seen from Figure 5, all connected Ag(II) with their four near-neighbor F ligands lie in a common plane. The $(Ag-F)_n^{n+}$ cation is therefore in this case a one-dimensional ribbon.

This ribbon cation shows a striking resemblance to the coordination of Ag(II) in AgF_2. In that structure,[15] each Ag(II) is square-coordinated by F ligands at 2.086(5) Å, which are equidistant from the two linked Ag(II), with Ag–F–Ag = 129.6(1)°. This generates a puckered sheet of stoichiometry AgF_2. These sheets can only be very weakly linked since closest intersheet Ag••F distances (two per silver atom, normal to the square AgF_4 unit) are 2.588(6) Å. The latter distance is similar to the long-bonded contact that the Ag(II) in $AgFRuF_6$ makes to the anions, with Ag••F3 = 2.548(3) Å and Ag••F4 = 2.659(3) Å. The zigzag –Ag–F–Ag–F– chain in this salt has a shorter bridging fluorine distance than in AgF_2, with Ag–F = 2.007(3) and 2.018(2) Å and Ag–F–Ag = 155.9(2)°, but the form of the chain is very like a section of the puckered AgF_2 sheet, defined by tracing adjacent Ag(II) through *cis* F at each Ag. The short Ag–F distances between Ag(II) and the bridging RuF_6^- of $AgFRuF_6$, at 2.158(3) and 2.140(3) Å, complete the square coordination; the Ag–F distances therefore average to

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(12) Thrasher, J. S.; Strauss, S. H., Eds. *Inorganic Fluorine Chemistry: Toward the 21st Century*; ACS Symposium Series; American Chemical Society: Washington, DC, 1994; Chapter 2.

(13) An attempt to obtain a more precise structure by collecting data at 182 K failed. This may have been a consequence of otherwise undetected lowering of symmetry on cooling the crystal but is more likely to be associated with the high background counts from the capillary.

(14) In $LiRuF_6$, $R\bar{3}$, $a_o = 5.369(1)$ Å, $\alpha = 56.34(1)°$, and $V/Z = 100.2$ Å^3, and $LiIrF_6$, $R\bar{3}$, $a_o = 5.397(1)$ Å, $\alpha = 55.88(1)°$, and $V/Z = 100.5$ Å^3 (Botkovitz, P.; Lucier, G. Unpublished data), the Li^+ is in an octahedral-hole site and the formula unit volume must closely represent the anion size in these $A^+MF_6^-$ salts.

(15) Jesih, A.; Lutar, K.; Žemva, B.; Bachmann, B.; Becker, St.; Müller, B. G.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1990**, *588*, 77. Note that in this paper, the orientation designation for the ORTEP is incorrect; the following transformation should be applied, where *a*, *b*, and *c* are the published axes and *a*′, *b*′, and *c*′ are the corrected axes: $a \rightarrow -a'$, $b \rightarrow c'$, $c \rightarrow b'$.

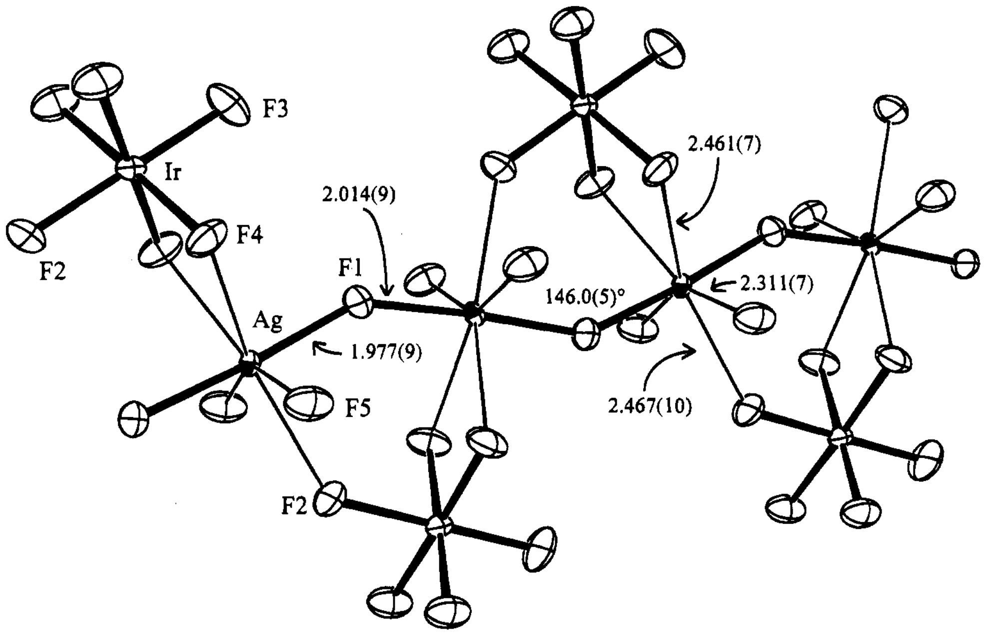

Figure 4. Structure of $AgFIrF_6$, with distances in Å.

Table 2. Interatomic Distances (Å) and Angles (deg) for $AgFIrF_6$ at 298 K[a]

	Distances		
Ag−F1	1.977(9)	Ir−F2	1.886(9)
Ag−F1^{i}	2.014(9)	Ir−F3	1.812(10)
Ag−F2^{i}	2.467(10)	Ir−F4	1.890(7)
Ag−F4	2.461(7)	Ir−F5	1.891(7)
Ag−F5^{ii}	2.311(7)		
	Angles		
F1−Ag−F1^{i}	176.1(4)	Ag−F1−Ag^{v}	146.0(5)
F1−Ag−F2^{i}	95.6(4)	F1^{i}−Ag−F2^{i}	88.4(4)
F1−Ag−F4	86.7(3)	F1^{i}−Ag−F4^{iv}	89.9(3)
F1−Ag−F5^{ii}	88.1(2)	F1^{i}−Ag−F5^{ii}	93.0(2)
F2−Ag−F4^{iv}	148.3(2)	F2^{i}−Ag−F5^{ii}	73.3(2)
F4−Ag−F5^{iv}	138.4(2)	F4^{iv}−Ag−F5^{ii}	75.2(2)
F4−Ag−F4	63.3(2)	F5^{iii}−Ag−F5^{ii}	145.8(2)
F4−Ir−F5	92.4(3)	F4^{iv}−Ir−F5	177.8(3)
F4−Ir−F4	86.2(3)	F5−Ir−F5^{iv}	89.0(3)
F2−Ir−F3	179.3(5)	F3−Ir−F4	90.3(3)
F2−Ir−F4	89.2(3)	F3−Ir−F5	91.4(3)
F2−Ir−F5	89.1(3)	Ag^{v}−F2−Ir	135.5(5)
Ag−F4−Ir	105.1(3)	Ag^{ii}−F5−Ir	147.4(4)

[a] Roman numeral labeling of fluorines corresponds to that designated[3] for $AgFAsF_6$.

2.081 Å, a value similar to that in AgF_2. Evidently the Ru(V) centers attract F ligands more strongly than Ag(II). Withdrawal of 2 *cis* F ligands of the AgF_4 unit, by two Ru(V), shortens the *trans* Ag−F linkages, which are more cationic than in AgF_2 itself.

The square coordination of the Ag(II) in $AgFRuF_6$ can be simply viewed in crystal field theory terminology as a Jahn−Teller distortion of an octahedron, elongated as a consequence of single-electron occupancy of the $d_{x^2-y^2}$ orbital and full occupancy of d_{z^2}. Similarly, the linear coordination of Ag(II) in $AgFMF_6$ (M = As, Ir, Au) and $AgFBF_4$ is attributable to the alternative d^9 configuration orbital occupancy, in which the singly occupied orbital is d_{z^2}.

X-ray powder diffraction photographs show that the salts $AgFMF_6$ (M = Sb or Bi) are isostructural, but the structure is not known. The nearly temperature-independent magnetic susceptibility data (from 50 to 280 K), represented in Figure 6, indicate that the Ag(II) in the cations must again be strongly coupled by Ag−F−Ag−F bridge bonding as in the other AgF salts with diamagnetic anions.[8] The coordination number of the Ag(II) is not known in the $AgFMF_6$ (M = Sb or Bi). The magnetic data for $AgFRuF_6$ and $AgRuF_6$, shown in Figure 7, also indicate that the magnetic susceptibility of the AgF cation in $AgFRuF_6$ is also small and approximately temperature-independent. Thus the change from two coordination (linear) to square coordination does not appear to have a major impact on the magnetic properties.

Table 3. Interatomic Distances (Å) and Angles (deg) for $AgFRuF_6$ at 298 K

	Distances		
Ag−F7	2.007(3)	Ru−F1	1.909(3)
Ag−F7	2.018(2)	Ru−F2	1.895(3)
Ag−F1	2.140(3)	Ru−F3	1.853(3)
Ag−F2	2.158(3)	Ru−F4	1.832(3)
Ag−F3	2.548(3)	Ru−F5	1.818(3)
Ag−F4	2.659(3)	Ru−F6	1.812(3)
Ag−F5	3.068(3)		
	Angles		
F7−Ag−F7	88.64(3)	F1−Ru−F3	89.31(12)
F7−Ag−F1	176.21(11)	F1−Ru−F4	88.71(12)
F7−Ag−F1	90.82(11)	F1−Ru−F5	89.41(13)
F7−Ag−F2	90.65(11)	F1−Ru−F6	178.45(15)
F7−Ag−F2	171.68(12)	F2−Ru−F3	88.81(12)
F1−Ag−F2	89.34(11)	F2−Ru−F4	88.71(13)
F3−Ag−F1	85.29(10)	F2−Ru−F5	177.39(13)
F3−Ag−F2	83.04(10)	F2−Ru−F6	90.28(14)
F3−Ag−F7	90.95(11)	F3−Ru−F4	176.87(13)
F3−Ag−F7	88.68(11)	F3−Ru−F5	90.18(13)
F3−Ag−F4	143.93(9)	F3−Ru−F6	90.71(13)
F3−Ag−F5	158.98(8)	F4−Ru−F5	92.22(14)
F5−Ag−F7	70.39(10)	F4−Ru−F6	91.21(13)
F5−Ag−F7	81.50(10)	F5−Ru−F6	92.14(15)
F4−Ag−F1	75.39(10)	Ru−F1−Ag	139.11(14)
F4−Ag−F2	66.84(10)	Ru−F2−Ag	138.65(14)
F4−Ag−F5	55.15(8)	Ru−F3−Ag	128.92(13)
Ag−F7−Ag	155.90(16)	Ru−F4−Ag	164.54(16)
F1−Ru−F2	88.17(13)	Ru−F5−Ag	134.45(15)

The explanation for the two coordination of Ag(II) in $AgFMF_6$ (M = As, Ir, Au) and $AgFBF_4$ and for the four coordination in $AgFRuF_6$ is uncertain. Two coordination may be associated with larger negative charge on the F ligands of the anion, four coordination being adopted when that charge falls below a critical level. Certainly, that F ligand charge in the BF_4^- (BF_3 is a relatively weak fluoride ion acceptor[10]) must be greater than in any of the MF_6^- considered here (if for no

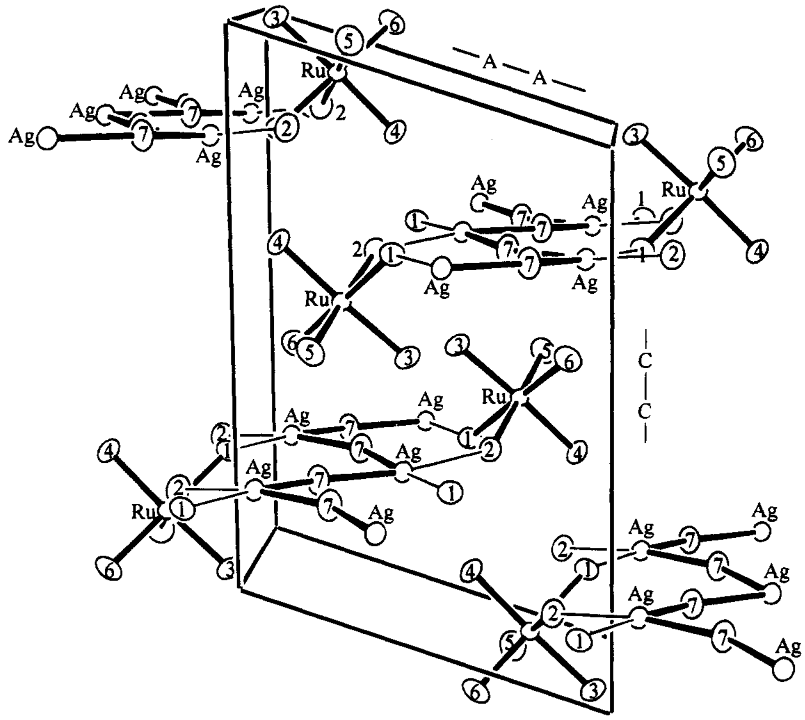

Figure 5. Structure of $AgFRuF_6$.

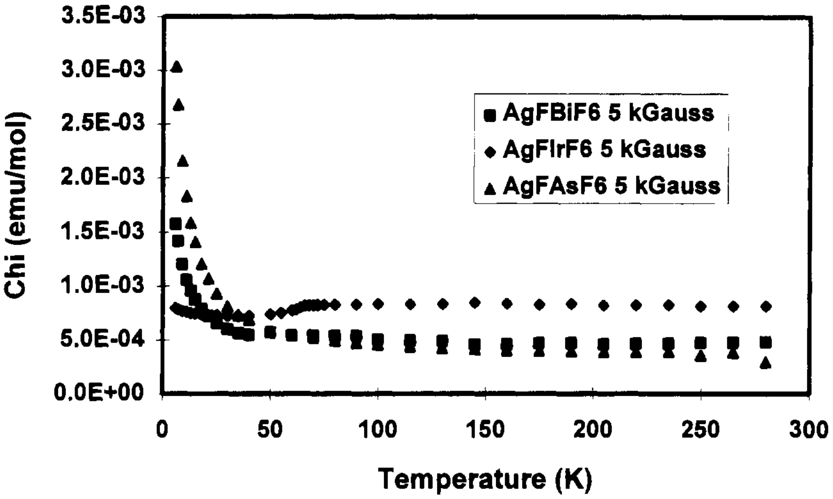

Figure 6. Magnetic susceptibility of $AgFMF_6$ (M = Bi, Ir, and As) which shows temperature-independence above ~50 K.

other reason, than that there are only four F ligands for unit negative charge of the BF_4^-). The Ag(II) in[8] $AgFBF_4$ must therefore have four rather negative F ligands in the xy plane {at 2.330(2) Å} as well as the two linearly coordinated F atoms at 2.002(3) and 2.009(3) Å on z.

If the four coordination of Ag(II) in $AgFRuF_6$ is a consequence of low F ligand charge in the anion, the same would be expected for $AgFMF_6$ (M = Sb or Bi). Perhaps in those cases the anionic F ligands of the AgF_4 unit are placed *trans* rather than *cis* as in $AgFRuF_6$. If so, this would account for the third structure type.

Experimental Section

Apparatus and Technique. A metal vacuum line, fluorine handling equipment, and valves were as previously described.[16] In the experimental work involving anhydrous HF (AHF), the apparatus was constructed from FEP tubing (CHEMPLAST, Inc., Wayne, NJ 07480). The commonly used reactor was constructed from a 3/8 in. o.d. FEP tube sealed at one end and with a Teflon valve (previously described[5]) at the other, a similar tube being joined mid-way by a Teflon Swagelok T compression fitting. This entire T-shaped assembly was connected to the gas handling and vacuum system via ~ 1 ft length of 1/4 in. o.d. FEP tubing. This facilitated the decanting of the AHF solutions from one tube to that at right angles to it, in the T-assembly. The T-reactors were passivated with ~ 2 atm F_2 for several hours, then evacuated before use. All solid starting materials and products were handled in the dry argon atmosphere of a Vacuum Atmospheres DRILAB. X-ray powder photographs and IR and Raman spectra were obtained as previously described.[16] Magnetic measurements were performed as previously described.[8]

Materials. Anhydrous HF (AHF) (Matheson) was condensed from the cylinder into a reservoir FEP tube containing K_2NiF_6 (Ozark-Mahoning Pennwalt, Tulsa, OK) in order to destroy trace quantities of water. AgF (Ozark-Mahoning Pennwalt, Tulsa, OK) and BiF_5 were crystallized from AHF solution prior to use. The pentafluorides of Ru and Ir were prepared by heating the metals in F_2 (5−10 atm, 20 °C) to 300 °C in a nickel can with a Teflon gasket (water-cooled) and a SS-KS4 Whitey valve. BF_3 (Matheson, Newark, CA), PF_5, and AsF_5

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[16] Lutar, K.; Jesih, A.; Leban, I.; Žemva, B.; Bartlett, N. *Inorg. Chem.* **1989**, *28*, 3467.

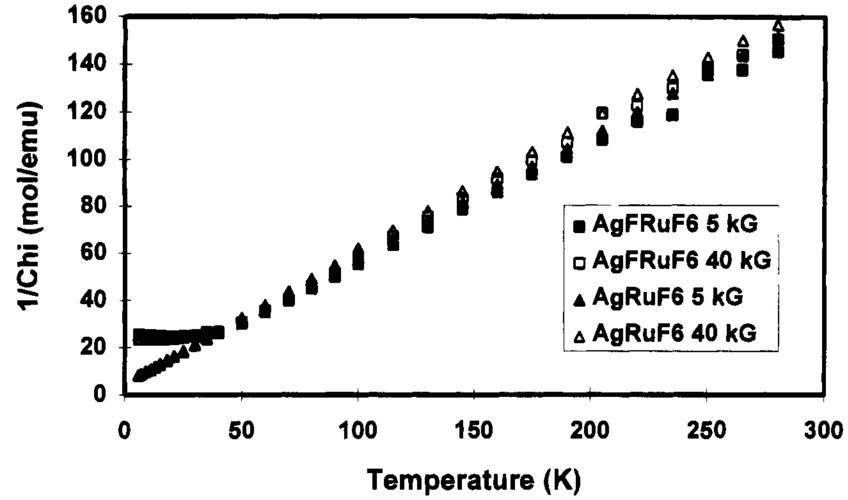

Figure 7. Curie–Weiss plot of the magnetic susceptibility of $AgFRuF_6$ {μ(5 kG) = 3.98, μ(40 kG) = 3.87} and $AgRuF_6$ {μ(5 kG) = 3.91, μ(40 kG) = 3.81}.

Table 4. Atomic Coordinates for $Ag(BiF_6)_2$ at 298 K

	x	*y*	*z*	B_{eq},[a] Å^2
Ag	0.5	0.5	0.5	1.44(2)
Bi	0.72610(7)	0.01872(7)	0.22639(1)	1.401(8)
F1	0.682(2)	−0.236(2)	0.126(1)	2.9(2)
F2	0.134(2)	−0.211(1)	0.286(1)	2.5(1)
F3	0.684(2)	−0.227(1)	0.427(1)	2.3(1)
F4	0.800(2)	0.250(2)	0.048(1)	2.7(1)
F5	0.323(2)	0.245(2)	0.223(1)	3.0(2)
F6	0.771(2)	0.237(1)	0.370(1)	2.3(1)

[a] $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$ where *a*, *b*, and *c* are real cell parameters and $\beta(i,j)$ are anisotropic β's.

Table 5. Atomic Coordinates for $AgFIrF_6$ at 298 K

	x	*y*	*z*	B_{eq},[a] Å^2
Ag	0.1368(1)	0.25	0.2431(1)	1.26(2)
Ir	0.29858(8)	0.25	0.55958(1)	1.49(1)
F1	0.387(1)	0.25	0.1931(9)	2.5(2)
F2	0.523(1)	0.25	0.4821(9)	3.0(2)
F3	0.082(1)	0.25	0.632(1)	4.2(3)
F4	0.2256(9)	0.433(1)	0.4364(6)	2.9(1)
F5	0.3766(9)	0.063(1)	0.6776(6)	3.0(1)

[a] $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$ where *a*, *b*, and *c* are real cell parameters and $\beta(i,j)$ are anisotropic β's.

Table 6. Atomic Coordinates for $AgFRuF_6$ at 298 K

	x	*y*	*z*	B_{eq},[a] Å^2
Ag	0.07248(1)	0.21192(7)	0.22002(1)	1.440(5)
Ru	0.22722(1)	0.28784(7)	−0.06154(1)	1.297(6)
F1	0.0755(3)	0.4622(5)	−0.1900(2)	1.99(5)
F2	0.1559(3)	−0.0026(5)	−0.1487(2)	2.06(5)
F3	0.0544(3)	0.2482(6)	0.0034(2)	2.30(5)
F4	0.3904(3)	0.3208(6)	−0.1335(2)	2.53(6)
F5	0.2867(3)	0.5730(6)	0.0181(2)	2.70(6)
F6	0.3696(3)	0.1148(7)	0.0581(2)	2.81(6)
F7	0.2124(3)	−0.0913(5)	0.2374(2)	2.30(5)

[a] $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$ where *a*, *b*, and *c* are real cell parameters and $\beta(i,j)$ are anisotropic β's.

(Ozark-Mahoning) were checked by IR spectroscopy to ensure absence of major impurities, then used as supplied. SbF_5 (Ozark-Mahoning) was distilled from its cylinder into a reservoir FEP tube. $AgBF_4$ was prepared as previously described.[8] AgF_2 was prepared by the fluorination of AgF in AHF at room temperature.

$AgMF_6$ (M = P, As, Sb, Bi, Ru, Ir) Synthesis. AgF and MF_5 were combined in AHF in a T-shaped FEP reactor at room temperature.

Table 7. Crystallographic Data for $Ag(BiF_6)_2$, $AgFRuF_6$, and $AgFIrF_6$

chem formula	$AgBi_2F_{12}$	$AgRuF_7$	$AgIrF_7$
fw	753.81	341.93	433.08
a_o, Å	5.218 (2)	8.3432(13)	7.628(2)
b_o, Å	5.579 (1)	5.4933(8)	7.067(2)
c_o, Å	8.934(2)	11.9286(22)	10.253(4)
α, deg	76.08(2)		
β, deg	88.93(2)	108.36(1)	
γ, deg	65.08(2)		
V, Å^3	228.0(1)	518.9(3)	552.7(3)
Z	1	4	4
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	*Pnma* (No. 62)
temp, °C	25	25	25
λ(Mo Kα), Å	0.71073	0.71073	0.71073
ϱ_{calc}, g·cm^{-3}	5.49	4.38	5.23
μ, cm^{-1}	406.6	66.7	275.5
R[a]	0.055	0.027	0.026
R_w[b]	0.067	0.028	0.030

[a] $R = \sum(||F_o| - |F_c||)/\sum(|F_o|)$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum(F_o^2)\}^{1/2}$.

In the cases M = Ru or Ir, an excess of AgF was taken, the remaining reagent (in AHF solution) being easily decanted from the insoluble silver salt product. In all other instances, excess pentafluoride reagent was supplied (remaining PF_5, AsF_5, and SbF_5 were removed under vacuum, and BiF_5 which is highly soluble in AHF, was effectively removed by decantation of its AHF solution from the insoluble silver salt product). Purity of the product was checked by X-ray powder diffraction photography against unit cell descriptions previously given.[17,18]

$AgFMF_6$ (M = As, Sb, Bi, Ru, Ir) Synthesis. In a T-shaped FEP reactor, approximately 2–4 mL of AHF was condensed onto $AgMF_6$ (200 to 500 mg). All of these solids have very low solubility in the AHF. The reactor was pressurized to 2 atm with F_2 and agitated continuously. As the F_2 was consumed in reaction, the white (M = As, Sb, Bi) or orange (M = Ru, Ir) reagent was replaced by a blue (M = As, Sb, Bi) or black (M = Ru, Ir) solid. Once the reaction mixture had ceased to take up F_2, either the AHF was decanted into the other arm of the reactor and removed immediately, or the product was first purified of AgF_2 as described below. The product was dried under dynamic vacuum for several hours.

Removing AgF_2 from $AgFMF_6$ (M = Bi, Ru, Ir). Because AgF_2 is ferromagnetic with a Curie temperature of 163 K,[19] it was necessary,

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(17) Kemmitt, R. D. W.; Russell, D. R.; Sharp, D. W. A. *J. Chem. Soc.* **1963**, *844*, 4408.

(18) The combination of AgF and BiF_5 gives a material whose X-ray powder pattern is very similar to that of $AgSbF_6$. Indexing the pattern gives tetragonal unit cell dimensions for $AgBiF_6$: a_o = 5.065 Å, c_o = 9.548 Å, *V* = 244.9 Å^3, *Z* = 2.

for the purpose of magnetic measurements, to strictly ensure its absence from Ag(II) materials made by direct fluorination. When an $AgFMF_6$ salt was obtained, prior to removal of the F_2/AHF solution, the reactor was evacuated to the soda lime to ca. 800 Torr. Then it was pressurized to 2 atm with BF_3 and agitated for a few minutes. Trace amounts of AgF_2 were converted to $AgFBF_4$, which was subsequently dissolved in the BF_3-acidified solution. This solution was decanted, the AHF then back-distilled for one or two more decantations prior to evacuation of the reactor and vacuum-drying of the product.

$Ag(BiF_6)_2$ Synthesis. A T-shaped FEP reactor was loaded with AgF (141 mg, 1.11 mmol) in one arm and BiF_5 (748 mg, 2.46 mmol) in the other. About 3 mL of AHF was condensed onto the AgF, dissolving it completely at room temperature. The reactor was then pressurized to 2 atm with F_2, resulting in the immediate precipitation of AgF_2 from solution. With continuous agitation, fluorine uptake and AgF_2 precipitation were complete within 20 min. Pressure in the reactor was reduced to 1000 Torr. Then the solid BiF_5 was shaken into the AHF and AgF_2, immediately forming a turquoise solid. A small aliquot of AHF was distilled over from one arm to the other in order to wash the remaining BiF_5 reagent into the reaction mixture. The mixture was agitated continuously for 15 h prior to decantation of the pale-blue AHF solution. A turquoise powder was obtained after 3 h of vacuum drying. X-ray powder photography revealed only the powder pattern (indexed by single-crystal based data) characateristic of $Ag(BiF_6)_2$ (835 mg, 99.7% yield).

$AgRuF_6BiF_6$ Synthesis. $Ag(BiF_6)_2$ (158 mg, 0.210 mmol) and $LiRuF_6$ (44 mg, 0.20 mmol) were put into the same tube of a T-shaped FEP reactor. AHF (~1.5 mL) was condensed onto the solids and warmed to room temperature. This mixture was stirred for 40 min as an olive-green solid was formed in a colorless solution. The solution was decanted and the AHF then distilled back onto the olive-green solid, leaving behind a white solid (shown by X-ray powder diffraction to be $LiBiF_6$). Three more decantations followed by distillations were performed prior to removal of the AHF under dynamic vacuum. Powder X-ray photography of the insoluble solid shows a pattern similar to that of $Ag(BiF_6)_2$. The yield of olive-green material (129 mg), based on $AgRuF_6BiF_6$, was 95%.

Crystal Preparation and Structure Determination. Crystals of $Ag(BiF_6)_2$ were grown by slow evaporation of AHF from a saturated solution. Crystals of $AgFMF_6$ (M = Ru, Ir) were obtained by slow fluorination of $AgMF_6$ solid beneath a 2 cm column of liquid AHF. Inside the DRILAB, single crystals were loaded into gradually tapered quartz capillaries which had been thoroughly dried under a vacuum of 10^{-7} Torr at ~ 700 °C for 24 h. Gentle tapping of the capillary was used to firmly fix the crystal into place. The open end of the capillary was temporarily sealed with Kel-F grease as it was removed from the DRILAB and heat-sealed in a microburner flame. Atomic positions are provided in Tables 4–6. Crystal data are given in Table 7.

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Supplementary Material Available: Text discussing the experimental details of the structure determinations and listings of crystal data and thermal parameters (7 pages). Ordering information is given on any current masthead page.

IC9410957

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(19) Gruner, E.; Klemm, W. *Naturwissenschaften* **1937**, *25*, 59. Charpin, P.; Dianoux, A. J.; Marquet-Ellis, H.; Nguyen-Nghi, *C. R. Acad. Sci. Paris* **1967**, *264*, 1108.