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Structural Features of Ag[AuF$_4$] and Ag[AuF$_6$] and the Stuctural Relationship of Ag[AgF$_4$]$_2$ and Au[AuF$_4$]$_2$ to Ag[AuF$_4$]$_2$

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Synchrotron radiation X-ray powder diffraction data (SPDD) have been obtained for Ag[AgF$_4$]$_2$, Au[AuF$_4$]$_2$, Ag[AuF$_4$], and Ag[AuF$_6$]. Ag[AgF$_4$]$_2$ and Au[AuF$_4$]$_2$ are isostructural with Ag[AuF$_4$]$_2$, space group (SG) $P2_1/n$, $Z = 2$, with the following: for Ag[AgF$_4$]$_2$ $a = 5.04664(8)$, $b = 11.0542(2)$, $c = 5.44914(9)$ Å, $\beta = 97.170(2)°$; for Au[AuF$_4$]$_2$ $a = 5.203(2)$, $b = 11.186(3)$, $c = 5.531(2)$ Å, $\beta = 90.55(2)°$. The structure of Ag[AgF$_4$]$_2$ was refined successfully (SPDD) applying the Rietveld method, yielding the following interatomic distances (Å): Ag^{II}−F = 2.056(12), 2.200(13), 2.558(13); Ag^{III}−F = two at 1.846(12), others = 1.887(12), 1.909(13), 2.786(12), 2.796(12), 2.855(12). AgAuF$_4$, like other AA′F$_4$ salts (A = Na−Rb; A′ = Ag, Au), crystallizes in the KBrF$_4$ structure type, SG $I4/mcm$ (140), $Z = 4$ with $a = 5.79109(6)$, $c = 10.81676(7)$ Å. SPDD gave (in Å) four Au^{III}−F = 1.89(1) and eight Ag^{I}−F = 2.577(7). SPDD for AgAuF$_6$ confirmed that it has the LiSbF$_6$ structure, SG $R\bar{3}$, $Z = 3$, with $a = 5.2840(2)$, $c = 15.0451(6)$ Å.

Introduction

Recently, in these laboratories[1] and elsewhere,[2] it was found that metallic gold dissolved at ambient temperatures with F$_2$ in anhydrous HF (aHF) made basic with alkali fluoride[1] or ammonium fluoride[2] to give solutions of AuF$_4^-$. Further work in this laboratory[3] established that when that system was irradiated with sunlight or UV, the AuF$_4^-$ was further oxidized to AuF$_6^-$. It was also found[4] that a solution of AgF in aHF, added to alkali solutions of these salts, quantitatively precipitated AgAuF$_4$[4] or AgAuF$_6$[3]. AgAuF$_4$, the first silver−gold fluoride, was first prepared by Sharpe[5] by dissolving 1:1 silver−gold alloy in liquid BrF$_3$. Its structure has never been described, although recent investigations in these laboratories[4] showed it to be isomorphous with AAuF$_4$ salts[6] (A = K, Rb). Synchrotron X-ray powder diffraction data have provided the structure of AgAuF$_4$ and confirmed that AgAuF$_6$ is of LiSbF$_6$ type.

The Ag^{II} relatives of those two salts AgFAuF$_4$ and AgFAuF$_6$ were structurally defined in our earlier studies,[7] but Ag[AgF$_4$]$_2$, Au[AuF$_4$]$_2$, and Ag[AuF$_4$]$_2$ were not. Synthesis of this last compound had followed the preparation[8] of Ag[AgF$_4$]$_2$, which, in turn, had been made to confirm the nature of the solid formed when the thermodynamically unstable fluoride AgF$_3$ liberated F$_2$ in liquid anhydrous HF. More recently, Au[AuF$_4$]$_2$ was also prepared in these laboratories[9] and was shown to be isomorphous with Ag[AgF$_4$]$_2$ and Ag[AuF$_4$]$_2$. Since then, an X-ray single-crystal structure of the Ag[AuF$_4$]$_2$ has been reported by Fischer and Müller.[10] This has provided the basis for the synchrotron X-ray powder diffraction structure of Ag[AgF$_4$]$_2$, which is described here. Unfortunately, the small particle size of the Au[AuF$_4$]$_2$ resulted in inadequate data for meaningful placement of the F ligands, but structural similarity to the other two compounds seems ensured.

Experimental Section

Materials. Au[AuF$_4$]$_2$,[9] Ag[AgF$_4$]$_2$,[8] Ag[AuF$_4$]$_2$,[7] AgAuF$_4$,[4] and AgAuF$_6$[3] were prepared as previously described. Anhydrous HF (Matheson) was dried in an FEP tube containing K$_2$NiF$_6$ (Ozark-Mahoning Pennwalt, Tulsa, OK). All solids were manipulated in the dry Ar atmosphere of a Vacuum Atmospheres Corp. DRILAB.

Apparatus and Technique. Work involving aHF was carried out in an apparatus constructed entirely from fluorocarbon polymers, T-reactors being made from FEP tubing (CHEMPLAST, Inc., Wayne, NJ 07480) with Teflon valves and Swagelok fittings, as previously described.[11] The metal vacuum and fluorine handling line has also been described.[12]

X-ray Diffraction. X-ray powder samples for X-ray diffraction pattern (XRDP) being recorded on film or for synchrotron radiation X-ray powder diffraction data (SPDD) were prepared in 0.3 mm O.D. quartz capillaries filled to a length of about 1 cm with the sample. The powder was tamped down into a well-packed column with a glass ramrod drawn down to fit the 0.3 mm capillary. Loaded capillaries were

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(1) Lucier, G.; Elder, S. H.; Chacón, L. C.; Bartlett, N. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 809.

(2) Holloway, J. H.; Hope, E. G.; Puxley, C. D. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 821.

(3) Graudejus, O.; Elder, S. H.; Lucier, G. M.; Shen, C.; Bartlett, N. *Inorg. Chem.* **1999**, *38*, 2503.

(4) Shen, C.; Žemva, B.; Lucier, G. M.; Graudejus, O.; Allman, J. A.; Bartlett, N. *Inorg. Chem.* **1999**, *38*, 4570.

(5) Sharpe, A. G. *J. Chem. Soc.* **1949**, 2901.

(6) Engelmann, U.; Müller, B. G. *Z. Anorg. Allg. Chem.* **1991**, *598*, 103.

(7) Casteel, W. J., Jr.; Lucier, G. M.; Hagiwara, R.; Borrmann, H.; Bartlett, N. *J. Solid State Chem.* **1992**, *96*, 84.

(8) Žemva, B.; Lutar, K.; Jesih, A.; Casteel, W. J., Jr.; Wilkinson, P.; Cox, D. E.; Von Dreele, R. B.; Borrmann, H.; Bartlett, N. *J. Am. Chem. Soc.* **1991**, *113*, 4192.

(9) Elder, S. H.; Lucier, G. M.; Hollander, F. J.; Bartlett, N. *J. Am. Chem. Soc.* **1997**, *119*, 1020.

(10) Fischer, R.; Müller, B. G. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1729.

(11) Žemva, B.; Hagiwara, R.; Casteel, W. J., Jr.; Lutar, K.; Jesih, A.; Bartlett, N. *J. Am. Chem. Soc.* **1990**, *112*, 4846.

(12) Lutar, K.; Jesih, A.; Leban, I.; Žemva, B.; Bartlett, N. *Inorg. Chem.* **1989**, *28*, 3467.

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Table 1. Cell Parameters of $Ag[AgF_4]_2$, $Ag[AuF_4]_2$, and $Au[AuF_4]_2$

	a/Å	*b*/Å	*c*/Å	*β*/deg	*V*/Å^3	source
$Ag[AgF_4]_2$	5.04664(8)	11.0542(2)	5.44914(9)	97.170(2)	301.611(8)	synchrotron radiation data
$Ag[AuF_4]_2$	5.229(7)	11.066(11)	5.516(7)	94.63(8)	318.6(1.1)	Debye−Scherrer XRDP[a]
	5.229(3)	11.01(2)	5.515(3)	94.91(5)	316.3(1.0)	single-crystal data[10]
$Au[AuF_4]_2$	5.203(2)	11.186(3)	5.531(2)	90.55(2)	322.0(2)	synchrotron radiation data

[a] Cell parameters have been obtained with the program ERACEL,[13] which refines cell parameters and zero point, applying a Nelson−Riley[14] extrapolation function.

Table 2. Crystallographic Data for the Structure Determination of Ag_3F_8 and $AgAuF_4$

formula	$Ag[AgF_4]_2$	$AgAuF_4$
fw	475.63	381.07
space group, *Z*	$P2_1/n$, 2	$I4/mcm$, 4
a/Å	5.04664(8)	5.79109(6)
b/Å	11.0542(2)	5.79109(6)
c/Å	5.44914(9)	10.8168(2)
β/deg	97.170(2)	90.0
V/Å^3	301.611(8)	362.760(7)
temp/K	299	299
residuals	$R_p{}^a = 5.98$	$R_p{}^a = 6.02$
	$wR_p{}^a = 7.68$	$wR_p{}^a = 8.03$
	$R_{(F^2)}{}^a = 7.13$	$R_{(F^2)}{}^a = 8.47$

[a] As described in the program GSAS.[15]

plugged with Kel-F grease, removed from the DRILAB, and sealed by drawing down in a small flame. The program ERACEL,[13] which incorporates the Nelson−Riley extrapolation function,[14] was used for the refinement of the lattice parameters for $Ag[AgF_4]_2$, $Ag[AuF_4]_2$, and $Au[AuF_4]_2$ from Debye−Scherrer XRDP's, obtained at ~293 K (Tables S1−S3 of Supporting Information). A comparison of lattice parameters is given in Table 1.

Fluorination of $AgAuF_4$ under aHF in Sunlight. $AgAuF_4$ (229.6 mg, 0.6029 mmol) was placed in one arm of an FEP T-reactor, and aHF (~0.8 mL) was condensed on top. On warming to room temperature, the aHF remained colorless, indicating the very low solubility of yellow $AgAuF_4$. The vapor pressure of the aHF was about 500 Torr. The reactor was pressurized with fluorine to a total pressure of 1500 Torr and left in the sunlight without agitation. The reactor was tilted to provide for a maximum surface area for the aHF, the $AgAuF_4$ being always covered with a thin layer of aHF. In 2 days the solid was dark-green, and after four more days the aHF was decanted and the residue washed twice with back-distilled aHF. The XRDP of the dark-green solid (212.7 mg) showed the patterns of both $AgAuF_4$ and $AgFAuF_4$.

Synchrotron Radiation Powder Diffraction. Data were collected on the 2-1 beamline at the Stanford Synchrotron Radiation Laboratory (SSRL) of Stanford University. The data were recorded in Debye−Scherrer geometry, the slit size being 1 mm × 4 mm. The monochromator consists of two Si(111) crystals and the analyzer of one Si(111) crystal. Details of the data collection are given in Table 2. The atom positions of the refined structures of $AgAuF_4$ and $Ag[AgF_4]_2$ are listed in Tables S4 and S5 of Supporting Information.

Structure Refinement. The refinement of the structures of $Ag[AgF_4]_2$, $AgAuF_4$, and $AgAuF_6$ was accomplished using the program GSAS.[15] A Debye−Scherrer absorption correction (part of the program GSAS[15]) was applied to all data sets assuming a packing density of 40−50%. The correction was applied within the program GSAS[15] using an empirical function developed by N. N. Lobanov (personal communication). This function reproduces the required absorption correction within 1% for cylindrical samples with $\mu_r < 30$. Portions of the fitted synchrotron SPDD are shown for each compound {$Ag[AgF_4]_2$ and $AgAuF_4$} in Figure 1.

(a) $Ag[AgF_4]_2$. The starting atom positions for the refinement of $Ag[AgF_4]_2$ were obtained from the single-crystal data of $Ag[AuF_4]_2$.[10] Initial lattice parameters were derived from Debye−Scherrer XRDP. After a background correction had been applied, the lattice parameters and the zero point of the patterns were refined. Afterward the profile and atom positions were obtained. Two minor impurities, AgF_3 and KBF_4, were present in the pattern of $Ag[AgF_4]_2$, and their profiles had to be refined as well. The atomic arrangement derived from the SPDD refinement gave M−F interatomic distances in harmony with Ag^{II}−F and Ag^{III}−F distances observed in AgF_2[16] and salts of[17] $[AgF_4]^-$, indicating the correctness of the $Ag[AgF_4]_2$ refinement (see Table S6) (see Figure 1a).

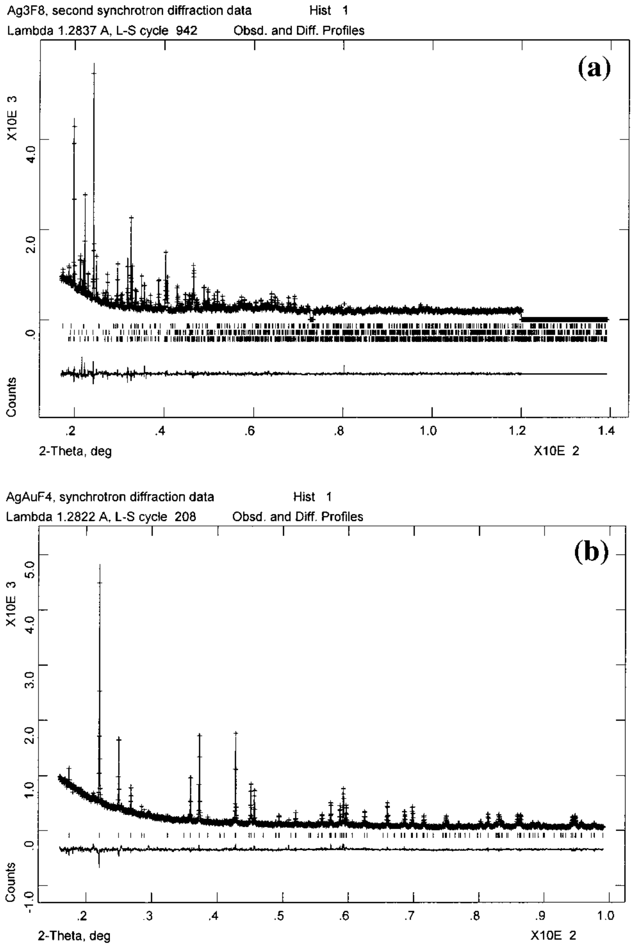

Figure 1. Portions of the fitted synchrotron radiation X-ray diffraction data for $Ag[AgF_4]_2$ and $AgAuF_4$. The observed values are shown as (+), and the calculated values from the best fit are shown as a curve. A difference ($I_{obs} - I_{calc}$) curve and the reflection positions are also shown: (a) $Ag[AgF_4]_2$ (reflection positions from above AgF_3, KBF_4, and $Ag[AgF_4]_2$); (b) $AgAuF_4$.

(b) $AgAuF_4$ and $AgAuF_6$. The structures of $AgAuF_4$ and $AgAuF_6$ were refined similarly. The starting atom positions for the refinements were obtained from the single-crystal data of $RbAuF_4$ [6] and $LiOsF_6$;[18] initial lattice parameters were derived from Debye−Scherrer XRDP's

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(13) Laugier, J.; Filhol, A. Local version of program CELREF, Nantes, 1978.

(14) Nelson, J. B.; Riley, D. P. *Proc. Phys. Soc. (London)* **1945**, *57*, 160.

(15) Larson, A. C.; Von Dreele, R. B. Los Alamos Laboratory Report No. LA-UR-86-748; Los Alamos Laboratories: Los Alamos, NM, 1999.

(16) Jesih, A.; Lutar, K.; Žemva, B.; Bachmann, B.; Becker, S.; Müller, B. G.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1990**, *588*, 77.

(17) Lutar, K.; Milicev, S.; Žemva, B.; Müller, B. G.; Bachmann, B.; Hoppe, R. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 1335.

of the respective compounds. A useful refinement of the data for AgAuF$_6$ did not occur because of contamination with AgAuF$_4$, but the LiSbF$_6$ type was confirmed (see Figure 1b for the AgAuF$_4$ data).

SPDD of Au[AuF$_4$]$_2$ were also obtained. However, the F atom positions could not be satisfactorily derived because of the poor crystallinity of the sample, which caused a heavy background (low signal-to-noise ratio), and the dominance of the gold atom scattering compared to that of the fluorine atoms.

Results and Discussion

Some Chemistry. Since Lucier et al.[19] had discovered that the aHF-insoluble AgIr(or Ru)F$_6$ would interact with F$_2$ in aHF to generate suitable single crystals of the AgFIr(or Ru)F$_6$ salts for structural analysis, it was hoped that such an approach would provide crystals of AgFAuF$_4$ or AgFAuF$_6$, neither structure being known in detail, although from indexing of X-ray powder data,[7] AgFAuF$_4$ was known to be isostructural with[20] CuFAuF$_4$, and AgFAuF$_6$ isostructural with[7,21] AgFAsF$_6$. Fluorination of the AgAuF$_4$, even with sunlight irradiation, was slow (there was deliberately an avoidance of mixing, to maximize opportunities for crystal growth) but the sole fluorination product detected was microcrystalline AgFAuF$_4$. The absence of AgAuF$_6$ (and AgFAuF$_6$) calls for comment.

Since AuF$_4^-$ is converted efficiently by F atoms to AuF$_6^-$, it had been anticipated that the AgAuF$_4$ might be attacked to give AgAuF$_6$ initially, this then being converted to AgFAuF$_6$ in subsequent steps. On the other hand, the previously known[19] conversion of AgIr(or Ru)F$_6$ to AgFIr(or Ru)F$_6$ by F$_2$, in the absence of light, already indicated that the Ag$^+$ *cation* was, in some unknown way, effectively attacked by the highly *electrophilic* F$_2$ species. Of course, even in strong sunlight, the F$_2$ concentration in our experiment must have vastly exceeded that of F atoms. Although F$_2$ oxidizes Ag$^+$, it will not oxidize AuF$_4^-$, F atoms being required for that. Evidently the dominant reaction was the fluorination of Ag$^+$ to AgF$^+$. Since neither AgFAuF$_4$ nor AgAuF$_4$ is soluble in aHF, the opportunity for fluorination of AuF$_4^-$ to AuF$_6^-$ was minimal.

The Lewis acid character of Ag$^+$, its high polarizability associated with its full valence 4d subshell and its tendency to bond to only two ligands (but strongly), perhaps allow even the poor donor F$_2$ to approach and to weakly bond to it. This is probably greatly assisted by the HF solvent, the molecules of which could, in concert with the F$_2$, provide a better donor species, such as HFFF.

Both Ag[AgF$_4$]$_2$ and Ag[AuF$_4$]$_2$ were made, as reported previously from these laboratories,[8,9] by precipitation from aHF solution by mixing solutions of Ag^{II} and Ag(orAu)F$_4^-$. The related compound Au[AuF$_4$]$_2$ was derived from Au[SbF$_6$]$_2$, the latter made[9] by exploiting the effect of strongly acidic aHF, markedly diminishing the prospects for exciting a high oxidation state. XRDP of these compounds showed[9] that they were closely related structurally, and they were indexed on the basis of large hexagonal unit cells. Recently, Fischer and Müller prepared single crystals of Ag[AuF$_4$]$_2$ by a high-temperature route[10] and showed that the true crystal system is monoclinic. The stucture of Ag[AgF$_4$]$_2$ reported here is based on theirs for Ag[AuF$_4$]$_2$.

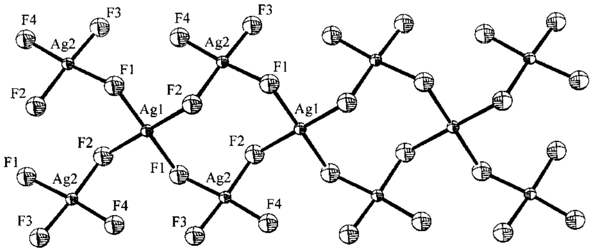

Figure 2. View of a "ribbon" in Ag[AgF$_4$]$_2$.

Structural Features. The Au^{III}−F interatomic distance in RbAuF$_4$ has been reported by Engelmann and Müller,[6] from X-ray single-crystal data, to be 1.915(3) Å. This same value has recently been found[22] for LiAuF$_4$, contrary to the earlier finding.[6] Au^{III}−F = 1.915(3) Å can therefore be confidently associated with AuF$_4^-$. The Au^{III}−F interatomic distance of 1.89(1) Å, found here in AgAuF$_4$, is not significantly different. To a good approximation therefore, the compound can be represented as Ag$^+$AuF$_4^-$. Its lower solubility, compared with that of its alkali relatives[1] in aHF, can be attributed to the lattice energy enhancement provided by the high polarizability[23] of Ag$^+$. A similar effect probably also underlies the very low solubility[3] of AgAuF$_6$ in aHF.

For present purposes it is clear that we can expect Au^{III} to be square-coordinated by F ligands, with the smallest bond distance Au^{III}−F being 1.9 Å. Since AuF$_4^-$ salts are isostructural and nearly isodimensional with their AgF$_4^-$ relatives,[24] much the same set of expectations can be applied to the Ag^{III} compounds. Unfortunately, although a synthesis of the diamagnetic, thermodynamically unstable Ag^{I}Ag^{III}F$_4$ relative of AgAuF$_4$ has been achieved,[4] it has never been obtained in sufficient crystallinity to provide a diffraction pattern. It should be isostructural with AgAuF$_4$.

The close-bonded ribbons (see Figure 2) of the Ag^{II}[Ag^{III}F$_4$]$_2$ structure are not significantly different from those of the Ag^{II}[Au^{III}F$_4$]$_2$ structure.[10] In the Ag^{II}[Ag^{III}F$_4$]$_2$ "ribbon" each Ag^{II} is at the center of a roughly square planar array of F ligands {Ag^{II}−F = 2 × 2.056(12), 2 × 2.200(13) Å}, and the related distances for Ag^{II}[Au^{III}F$_4$]$_2$ are 2 × 2.072(5) and 2 × 2.168(5) Å. Each Ag^{II} is linked by each of its four F ligands (2-fold F1 and F2) via a F bridge to Ag^{III} of a square [Ag^{III}F$_4$] unit. Each of the latter is linked to two adjacent Ag^{II} of the "ribbon" through a cis pair of F ligands (F1 and F2). This arrangement results in all Ag^{II} being lined up along the mid-axis of the ribbon, flanked on each side by rows of [Ag^{III}F$_4$] units, all those on one side sharing a common plane but inclined to the plane of the [Ag^{II}F$_4$] units. This results in a longitudinal creasing of the "ribbon", the cross section of which is that of an opened "Z" (as shown in Figure 3).

The Ag^{II}[Ag^{III}F$_4$]$_2$ structure differs from that[10] of Ag^{II}[Au^{III}F$_4$]$_2$ only in the effective size of the A^{III} atom in its secondary (essentially nonbonding) contacts with the F3 and F4 ligands (which are those on the outer edges of the "ribbons") in the "ribbons" of Ag^{II}[A^{III}F$_4$]$_2$ above and below (see Figure 2). So, in the comparison of the two structures, represented by the data given in Table 3, it is seen that the environment of the Ag^{II} is essentially the same in the two structures, with four close F ligands (in slightly distorted square planar array) at distances ranging from 2.06 to 2.20 Å. There are four more distant ligands (two each of F3 and F4) of the nearest "ribbons" above and below, in a plane roughly at right angles to the close-bonded Ag^{II}F$_4$ unit. The average distance for these Ag^{II}···F interactions

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(18) Graudejus, O.; Wilknson, A. P.; Chacón, L. C.; Bartlett, N. Manuscript in preparation.

(19) Lucier, G.; Münzenberg, J.; Casteel, W. J., Jr.; Bartlett, N. *Inorg. Chem.* **1995**, *34*, 2692.

(20) Müller, B. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1081.

(21) Gantar, D.; Frlec, B.; Russell, D. R.; Holloway, J. H. *Acta Crystallogr.* **1987**, *C43*, 618.

(22) Borrmann, H.; Lucier, G. M.; Bartlett, N. Unpublished results.

(23) Waddington, T. C. *Adv. Inorg. Chem. Radiochem.* **1959**, *1*, 157.

(24) Hoppe, R.; Homann, R. *Z. Anorg. Allg. Chem.* **1970**, *379*, 193.

Table 3. Comparison of the $\mathrm{Ag^{II}}$ and $\mathrm{A^{III}}$ Interatomic Distances (Å) in $\mathrm{Ag[AgF_4]_2}$ and $\mathrm{Ag[AuF_4]_2}$

		$\mathrm{Ag^{II}}$−F(1)	$\mathrm{Ag^{II}}$−F(2)	$\mathrm{Ag^{II}}$−F(3)	$\mathrm{Ag^{II}}$−F(4)
$\mathrm{Ag[AgF_4]_2}$	$\mathrm{Ag^{II}}$−F	2 × 2.056(12)	2 × 2.200(13)	2 × 2.558(13)	2 × 2.900(11)
$\mathrm{Ag[AuF_4]_2}$		2 × 2.072(5)	2 × 2.162(5)	2 × 2.484(5)	2 × 3.028(5)
		$\mathrm{A^{III}}$−F(2)	$\mathrm{A^{III}}$−F(3)	$\mathrm{A^{III}}$−F(4)	$\mathrm{A^{III}}$−F(1)
$\mathrm{Ag[AgF_4]_2}$	$\mathrm{Ag^{III}}$−F	1.846(12)	1.846(13)	1.887(12)	1.909(13)
$\mathrm{Ag[AuF_4]_2}$	$\mathrm{Au^{III}}$−F	1.934(5)	1.899(5)	1.902(5)	1.946(5)
		$\mathrm{A^{III}}$−F(4)	$\mathrm{A^{III}}$−F(3)	$\mathrm{A^{III}}$−F(4)	$\mathrm{A^{III}}$−F(3)
$\mathrm{Ag[AgF_4]_2}$	$\mathrm{Ag^{III}}$−F	2.786(11)	2.796(12)	2.856(12)	3.313(12)
$\mathrm{Ag[AuF_4]_2}$	$\mathrm{Au^{III}}$−F	2.890(5)	2.909(5)	2.926(5)	3.388(5)

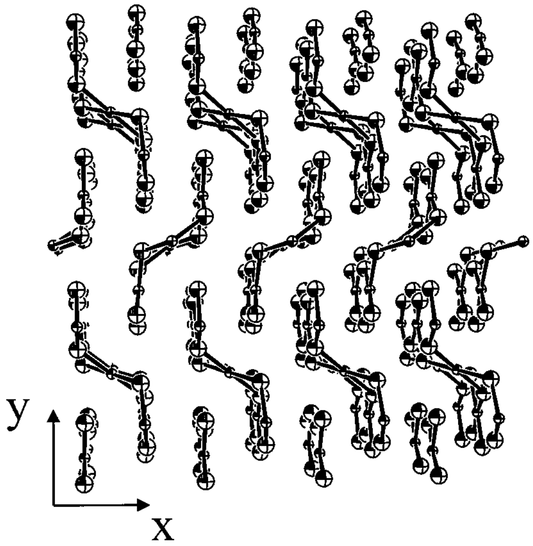

Figure 3. View down *c* in $\mathrm{Ag[AgF_4]_2}$ showing the stacking of the “ribbons”.

in $\mathrm{Ag^{II}[Ag^{III}F_4]_2}$ is 2.73 Å, and in $\mathrm{Ag^{II}[Au^{III}F_4]_2}$ it is 2.76 Å. For the $\mathrm{A^{III}}$ environment, however, there are significant differences, especially for the secondary contacts $\mathrm{A^{III}}$···F.

It can be seen from the data given in Table 3 that the $\mathrm{Ag^{III}}$−F distances of the $\mathrm{[Ag^{III}F_4]}$ units range from 1.846 to 1.909 Å (average, 1.87 Å), whereas the $\mathrm{Au^{III}}$−F distances of the$\mathrm{[Au^{III}F_4]}$ units range from 1.900 to 1.949 Å (average, 1.92 Å). This indicates a slightly greater effective size for the $\mathrm{Au^{III}}$ in the plane of the $\mathrm{[Au^{III}F_4]}$ species. In the case of the secondary $\mathrm{A^{III}}$···F contacts (those between “ribbons”) the $\mathrm{Au^{III}}$ has a much greater effective size than $\mathrm{Ag^{III}}$ on the axis normal to the $\mathrm{[A^{III}F_4]}$ plane. For the four secondary contacts of the $\mathrm{Au^{III}}$ the average distance is 3.029 Å, and for the $\mathrm{Ag^{III}}$ the average is 2.938 Å. This is probably a consequence of the larger effective size of the local d_{z^2} (antibonding σ) electron pair, as previously discussed for the comparison of the $\mathrm{AgF_3}$ and $\mathrm{AuF_3}$ [8] and for other high-valent silver and gold chemistry.[25]

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Supporting Information Available: Listings of indexed Debye−Scherrer powder patterns, positional and thermal parameters, and interatomic distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Bartlett, N. *Gold Bull.* **1998**, *31*, 22.