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Silver(I) Undecafluorodiantimonate(V)

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The reaction between $AgBF_4$ and excess of SbF_5 in anhydrous hydrogen fluoride (aHF) yields the white solid $AgSb_2F_{11}$ after the solvent and the excess of SbF_5 have been pumped off. Reaction between equimolar amounts of $AgSb_2F_{11}$ and $AgBF_4$ yields $AgSbF_6$. Meanwhile, oxidation of solvolyzed $AgSb_2F_{11}$ in aHF by elemental fluorine yields a clear blue solution of solvated Ag(II) cations and SbF_6^- anions. $AgSb_2F_{11}$ is orthorhombic, at 250 K, *Pbca*, with $a = 1091.80(7)$ pm, $b = 1246.28(8)$ pm, $c = 3880.2(3)$ pm, $V = 5.2797(6)$ nm^3, and $Z = 24$. The crystal structure of $AgSb_2F_{11}$ is related to the already known crystal structure of $H_3OSb_2F_{11}$. Vibrational spectra of $AgSb_2F_{11}$ entirely match the literature-reported vibrational spectra of β-$Ag(SbF_6)_2$, for which a formulation of a mixed-valence Ag(I)/Ag(III) compound was suggested ($Ag^IAg^{III}(SbF_6)_4$). On the basis of obtained results it can be concluded that previously reported β-$Ag(SbF_6)_2$ is in fact Ag(I) compound with composition $AgSb_2F_{11}$.

Introduction

The investigation of the silver chemistry in superacid media dates to early 1957 when Ag(I) salts ($AgAsF_6$ and $AgSbF_6$) were prepared by dissolution of AgF in anhydrous hydrogen fluoride (aHF) acidified with corresponding Lewis acids.[1] Their crystal structures have been recently determined.[2,3] A great number of Ag(II) compounds have been synthesized and characterized (e.g., $AgFAsF_6$, $Ag(SbF_6)_2$).[4−10] Disproportionation of $AgFAsF_6$ in aHF yields white $AgAsF_6$ and a black mixed-valence pseudotrifluoride $(AgF^+)_2AgF_4^-$-AsF_6^-.[11] Another proposed mixed-valence Ag compound is diamagnetic white "β-$Ag(SbF_6)_2$", where the formulation Ag^I-$Ag^{III}(SbF_6)_4$ is suggested.[10] Even the valence isomerism in the latter is not improbable (i.e., a similar phenomenon was found for AgF_2[11] and the disproportionation of $[Ag(CF_3)_2]^-$ into $[Ag(CF_3)_4]^-$ [12]). In a recent review of silver compounds N. Bartlett remarked that it should not be excluded that the postulated β-$Ag(SbF_6)_2$ is Ag(I) compound ($AgSb_2F_{11}$).[13] There are no available data about $AgSb_2F_{11}$ in the literature except that solid $AgSb_2F_{11}$ is produced after reductive carbonylation of $Ag(SO_3F)_2$ and removal of excess SbF_5 under vacuum at room temperature.[14] Since β-$Ag(SbF_6)_2$ is often given as an example of Ag(I)/Ag(III) compound, we decided to elucidate if this compound really exists. We prepared pure $AgSb_2F_{11}$ and found that its vibrational spectra entirely match the vibrational data previously reported for β-$Ag(SbF_6)_2$. In addition, it is also reported how single crystals of $AgSb_2F_{11}$ can be prepared in aHF, despite its lack of solubility.

Experimental Section

General Experimental Procedures. Volatile materials (BF_3, SbF_5, aHF) were manipulated in an all-PTFE vacuum line equipped with PTFE valves. The manipulation of the nonvolatile solids sensitive to traces of moisture was accomplished in the dry argon

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atmosphere of a drybox (M. Braun). The residual water in the atmosphere within the drybox never exceeded 1 ppm. All reactions were carried out in FEP vessels (height 300 mm, inner diameter 15.5 mm, outer diameter 18.75 mm) equipped with PTFE valves and PTFE-coated stirring bars. Prior to their use all reaction vessels were passivated with elemental fluorine.

Caution! *aHF, BF_3, SbF_5, and elemental fluorine should only be handled in a well-ventilated hood, and protective clothing should be worn at all times!*

Reagents. $AgNO_3$ (Alkaloid Skopje, 99.7%), fluorine (Solvay, 99.98%), and BF_3 (Union Carbide Austria GmbH, 99.5%) were used as supplied. SbF_5 (Merck, >98%) was redistilled in metal−PTFE vacuum lines. Anhydrous HF (Fluka, purum) was treated with K_2NiF_6 for several hours prior to use.

Preparation of $AgBF_4$. $AgBF_4$ was prepared by modified method as described in the literature.[15] A sample of 0.426 g (2.51 mmol) of $AgNO_3$ was loaded into an FEP reaction vessel equipped with a PTFE filter. A volume of 5 mL of aHF was condensed on it at 77 K, and the reaction mixture was warmed to room temperature. In few minutes a clear colorless solution was obtained above the PTFE filter. The bottom part of the reaction vessel was cooled to transfer the solution through the PTFE filter. After the first portion of BF_3 was added at room temperature, a white solid precipitated immediately. Addition of gaseous BF_3 was continued until the pressure in the reaction vessel (2 bar) remained constant. After 12 h the liquid phase was decanted away. Finally, the white sample was dried by pumping the last traces of volatile components away in a dynamic vacuum for 3 h. The product weight was 0.473 g; $AgBF_4$ requires 0.488 g. The X-ray powder diffraction pattern was in agreement with literature data for $AgBF_4$. The Raman spectrum showed only bands that can be assigned to BF_4^-.

Synthesis of $AgSb_2F_{11}$. In a drybox 1.85 mmol (0.361 g) of $AgBF_4$ was loaded into an FEP reaction vessel. Then an excess of SbF_5 (6.23 mmol, 1.350 g) and aHF (2 mL) were condensed on it at 77 K. The reaction mixture was left stirring for few days at room temperature. A clear colorless liquid phase was visible above a nondissolved white solid all the time. Volatiles were slowly pumped off at room temperature for few hours, leaving behind 1.041 g of white solid corresponding to the composition of $AgSb_2F_{11}$ (calcd 1.038 g).

Reaction between $AgSb_2F_{11}$ and $AgBF_4$. A sample of 0.150 g (0.27 mmol) of $AgSb_2F_{11}$ and 0.052 g (0.27 mmol) of $AgBF_4$ was loaded in a drybox into an FEP reaction vessel. Then aHF (2 mL) was condensed on the reaction mixture at 77 K. The reaction was carried out at room temperature for 1 day. Solvent and released BF_3 were pumped off at room temperature. A white solid, 0.194 g, which corresponded to the composition $AgSbF_6$, was obtained (calcd 0.186 g). The vibrational spectrum and X-ray powder diffraction pattern were in agreement with literature data for $AgSbF_6$.

The remaining $AgSbF_6$ (∼100 mg) was redissolved in 7 mL of aHF. Immediately after the addition of elemental fluorine, a dark green solid precipitated. Above it a clear blue solution was observed. After 2 h volatiles were pumped away at room temperature. The X-ray powder diffraction pattern of the isolated black-green solid was of very poor quality. Only a few weak lines were observed that could be tentatively attributed to AgF_2, $Ag(SbF_6)_2$, and $(Ag^{II}F^+)_2Ag^{III}F_4^-SbF_6^-$.[11]

Oxidation of $AgSb_2F_{11}$ by Elemental Fluorine in aHF. A sample of 0.100 g (0.18 mmol) of $AgSb_2F_{11}$ was loaded in a drybox into an FEP reaction vessel, and aHF (2 mL) was condensed on it at 77 K. Fluorine was slowly added at room temperature to the final pressure of 2.1 bar. A clear blue solution formed in a few minutes. Fluorine was added again to the final pressure of 3.2 bar. After 1 day volatiles were pumped off at room temperature. The resulting 0.109 g of blue solid was identified as $Ag(SbF_6)_2$ by material balance (calcd 0.103 g), the Raman spectrum, and the X-ray powder diffraction pattern.

Reduction of $Ag(SbF_6)_2$, Dissolved in aHF, by Elemental Hydrogen. A sample of 0.215 g (1.48 mmol) of AgF_2 was loaded in a drybox into an FEP reaction vessel, and SbF_5 (0.980 g) and aHF (4 mL) were condensed on it at 77 K. The reaction vessel was brought up to 298 K, and a clear blue solution formed in a few minutes. Immediately after the addition of hydrogen at room temperature to the final pressure of 4 bar, the solution changed its color from blue to green. Finally, a white solid precipitated and the solution became colorless. After volatiles were pumped off at room temperature, 0.680 g of white solid was obtained. Raman spectrum showed the mixture of $AgSbF_6$ and $AgSb_2F_{11}$.

Attempt To Prepare Single Crystals of $AgSb_2F_{11}$ from Saturated Solution in aHF. Preparation was carried out in a double T-shaped apparatus made of two FEP tubes (19 mm o.d. and 6 mm o.d.). About 0.300 g of $AgSb_2F_{11}$ was loaded in a drybox into the wider tube. Then aHF (∼7 mL) was condensed on it at 77 K and the mixture was warmed to room temperature. The sample only partly dissolved. The clear solution was poured into the narrower tube. The narrower tube containing saturated solution was kept at room temperature all the time of crystallization. Meanwhile, the wider tube was cooled first by tap water (maintaining temperature gradient of about 10 K for 7 days) and then to 263 K for an additional 1 week, causing the evaporation of solvent from the narrower into the wider tube. Cubic-shaped crystals formed on the walls of the reaction vessel. Volatile components were slowly pumped away. Raman spectra of obtained crystals showed only the bands that can be assigned to $AgSbF_6$.

Preparation of Single Crystals of $AgSb_2F_{11}$. Preparation was carried out in a double T-shaped apparatus made of two FEP tubes of the same size separated by a common valve (19 mm o.d.). A sample of 0.150 g (0.77 mmol) of $AgBF_4$ was loaded in a drybox into one tube. Then 0.500 g (2.31 mmol) of SbF_5 and aHF (∼4 mL) were condensed on it at 77 K and the mixture was warmed to 233 K without stirring. The reaction mixture was slowly allowed to warm to room temperature (1 day) and was left at room temperature without stirring. After 2 days the valve separating both tubes was opened. The tube containing the reaction mixture was kept at room temperature. Meanwhile, the empty tube was first cooled by tap water (maintaining temperature gradient of about 10 K for 1 month), then to 253 K for 1 week, to 223 K for an additional 1 week, and finally to 77 K for 1 day. In that way aHF, released BF_3, and the excess SbF_5 slowly evaporated from one tube into the empty one and colorless crystals were obtained. Crystals were immersed in perfluorinated oil (ABCR, FO5960) in the drybox, selected under the microscope, and transferred into the cold nitrogen stream of the diffractometer. Some of the crystals were also mounted into 0.3 mm quartz capillaries. Raman spectra of selected single crystals were identical to the Raman spectrum of powdered $AgSb_2F_{11}$ prepared by reaction between $AgBF_4$ and excess SbF_5 in aHF.

Elemental Analysis. Silver was determined gravimetrically,[16] and antimony was determined by redox titration.[17] The content of

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Table 1. Crystal Data and Structure Refinement for $AgSb_2F_{11}$[a]

formula	$AgSb_2F_{11}$
fw	560.37
temp (K)	250
a (pm)	1091.80(7)
b (pm)	1246.28(8)
c (pm)	3880.2(3)
V (nm^3)	5.2797(6)
Z	24
D_{calcd} (mg/m^3)	4.230
λ (pm)	71.069
μ (mm^{-1})	8.44
space group	*Pbca* (No. 61)
GOF indicator	1.209
R1; wR2 ($I > 2.00\sigma(I)$)	0.0615; 0.1334

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2/\sum(w(F_o^2)^2]^{1/2}$; GOF $= [\sum(w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$, where N_o = number of reflections and N_p = number of refined parameters.

total fluoride ions was determined after total decomposition with a fluoride ion selective electrode.[18] The chemical analyses are given in mass percents.

X-ray powder diffraction photographs were obtained using the Debye–Scherrer technique with Ni-filtered Cu Kα radiation. Samples were loaded into quartz capillaries (0.3 mm) in a glovebox. Intensities were estimated visually.

X-ray Structure Determination of $AgSb_2F_{11}$. Single crystal data of $AgSb_2F_{11}$ were collected on a Mercury CCD area detector coupled with a Rigaku AFC7S diffractometer using monochromatized Mo Kα radiation. Data were corrected for Lorentz, polarization, and absorption effects and processed using the Rigaku Crystalclear software suite program package. The structure was solved by direct methods (SHELXS) and expanded using Fourier techniques. Some details of the single crystal data collection, data processing, and refinement are given in Table 1.

Infrared and Raman Spectroscopy. The infrared spectra were taken on a Perkin-Elmer FTIR 1710 spectrometer on powdered samples between AgCl windows in a leak-tight brass cell. Raman spectra were recorded on a Renishaw Raman Imaging Microscope System 1000, with the 632.8 nm exciting line of a He–Ne laser.

Results

Elemental Analysis. Calcd for $AgSb_2$F11: Ag, 19.2%; Sb, 43.5%; F, 37.3%. Found: Ag, 19.8%; Sb, 42.0; F, 36.3%.

Raman and IR spectra of the bulk of $AgSb_2F_{11}$ are shown in Figure 1 and given in Table 2.

Discussion

Syntheses. In highly acidic aHF the strong Lewis acid SbF_5 displaces the weaker acid BF_3 from $AgBF_4$, yielding $AgSb_2F_{11}$:

$$AgBF_4 + 2SbF_5 \xrightarrow[298\ K]{aHF,SbF_5} AgSb_2F_{11} + BF_3 \tag{1}$$

If the excess of SbF_5 in aHF is too low or pumping off of the volatiles is too fast, then mainly $AgSbF_6$ is obtained as the final product. This explains why only $AgSbF_6$ was observed in the isolated solids of reactions of AgF with excess of SbF_5.[1,3] However, in the Raman spectra of isolated products a weak broad peak at 680 cm^{-1} was sometimes observed, indicating that some $AgSb_2F_{11}$ was also present (see Vibrational Spectra).[3] In the Raman spectrum of $AgSbF_6$ taken on a single crystal, no such band could be observed. The main driving forces for the $AgSbF_6$ ($AgSb_2F_{11}$) formation are the fluoride ion affinities (FIA) of SbF_5 ($2SbF_5$) and the lattice energy differences between the AgF and the complex fluoroanion salts $AgSbF_6$ ($AgSb_2F_{11}$). The lattice potential energy of $AgSbF_6$ is estimated to be 580 kJ/mol.[19] Using Jenkins et al.'s generalized volume-based Kapustinskii equation,[20] and using the crystal data for $AgSb_2F_{11}$, the lattice potential energy of $AgSb_2F_{11}$ was estimated to be 493 kJ/mol. However, the FIA of $2SbF_5$ is higher than that of SbF_5 (about 165 kJ/mol higher for gaseus SbF_5).[19] These data imply that $AgSb_2F_{11}$ is presumably the result of thermodynamic control, whereas $AgSbF_6$ is the more likely kinetic product.

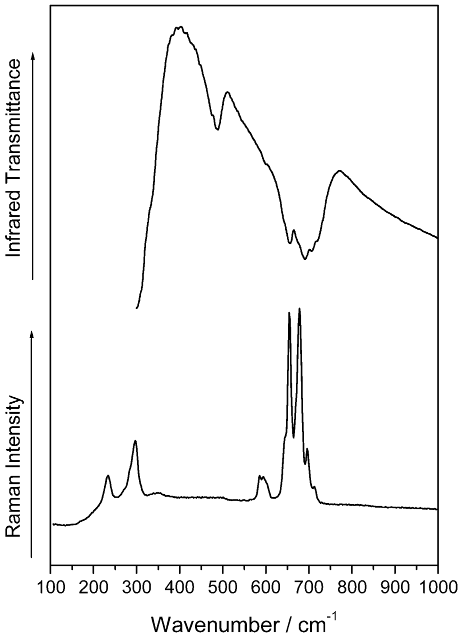

Figure 1. Infrared and Raman spectra of $AgSb_2F_{11}$.

To confirm the composition $AgSb_2F_{11}$, two additional experiments were performed. In the first experiment equimolar amounts of $AgSb_2F_{11}$ and $AgBF_4$ reacted according to the equation

$$AgBF_4 + AgSb_2F_{11} \xrightarrow[298\ K]{aHF} 2AgSbF_6 + BF_3 \tag{2}$$

The solvolysis of $AgSb_2F_{11}$ in aHF to $AgSbF_6$ and SbF_5 is in accordance with previous findings that washing with aHF is an effective way to eliminate SbF_5 from $Sb_2F_{11}^-$ salts.[21] Released SbF_5 displaces BF_3 from $AgBF_4$, yielding $AgSbF_6$.

Oxidation of solvolyzed $AgSb_2F_{11}$ by elemental fluorine yields a clear solution with a blue color typical for solvated

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Table 2. Comparison of Literature Data for β-$Ag(SbF_6)_2$[17] with Obseved Vibrational Wavenumbers for $AgSb_2F_{11}$ and Description of Vibrational Modes for Sb_2F_{11} on the Basis of Literature Data for $Pd(CO)_4(Sb_2F_{11})_2$[41]

β-$Ag(SbF_6)_2$		$AgSb_2F_{11}$		$Pd(CO)_4(Sb_2F_{11})_2$		
IR[a]	Raman[a]	IR	Raman	IR	Raman	assignment[b]
719 (s, sh)	720 (12, sh)	722 (m,sh)	713 (10)	718 (sh)	714 (w)	$\nu(SbF_{ax})$
		706 (s)		708 (vs)	709 (sh)	$\nu(SbF_{ax})$
	700 (33, sh)		697 (30)		697 (w)	$\nu(SbF_{ax})$
692 (vs)		692 (vs)		690 (vs)		$\nu(SbF_{4eq})$
	682 (100)		678 (100)		686 (m)	$\nu(SbF_{4eq})$
673 (s)		674 (m,sh)	672 (sh)	675 (s)	668 (s)	$\nu(SbF_{4eq})$
654 (s)	659 (93)	656 (s)	655 (95)	662 (s)	656 (s)	$\nu(SbF_{4eq})$
	651 (30, sh)	640 (sh)	645 (30, sh)	648 (sh)	649 (m)	$\nu(SbF_{4eq})$
602 (m)	600 (16)	602 (m)	594 (15)	604 (vw)	598 (w)	$\nu(SbF_{4eq})$
	590 (14)		585 (15)	596 (w)	585 (w)	$\nu(SbF_{4eq})$
515 (vw)	526 (4)	490 (ms)		503 (m)		$\nu(SbFSb)$
490 (ms)		475 (sh)		484 (m)		$\nu(SbFSb)$
368 (mw)	365 (1)					
357 (w, sh)			349 (2)			
	312 (13, sh)			315 (s)		$\delta(SbF_{ax})$
301 (sh)	303 (32)		298 (40)	305 (s)	305 (m)	$\delta(SbF_{ax})$
283 (s)	290 (18)		285 (20, sh)	267 (vs)	275 (w)	$\delta(SbF_{4eq})$
278 (s)			272 (2, sh)	250 (sh)		$\delta(SbF_{4eq})$
			233 (15)	228 (sh)	230 (m)	$\delta(SbF_{4eq})$
				196 (vw)	201 (vw)	$\delta(SbF_{4eq})$
				136 (vw)	153 (m)	$\delta(FSbF)$

[a] Intensities are given in parentheses; vw = very weak, w = weak, m = medium, ms = medium strong, s = strong, vs = very strong, sh = shoulder. [b] ν = stretching mode, δ = deformation mode.

Ag(II) in superacid media. The final product of isolation was blue α-$Ag(SbF_6)_2$.[8]

$$AgSb_2F_{11} + (1/2)F_2 \xrightarrow[298\ K]{aHF} Ag(SbF_6)_2 \tag{3}$$

In contrast, the fluorination of $AgSbF_6$ in aHF proceeded in a completely different manner. Addition of fluorine first converts $AgSbF_6$ to $AgFSbF_6$.[4] Further course of reaction depends on the amount of aHF. In a small amount of aHF (concentration of SbF_5 is high), $AgFSbF_6$ disproportionates to $AgSbF_6$ and black insoluble $(AgF^+)_2AgF_4^-SbF_6^-$.[11] The interaction of $AgFSbF_6$ with a large amount of aHF leads to simple solvolysis and AgF_2 and $Ag(SbF_6)_2$ production.[11] Since the fluorination of the product obtained in the $AgBF_4$/SbF_5/aHF system yields a clear blue solution, it can be concluded that $AgSb_2F_{11}$ is not contaminated with $AgSbF_6$. Otherwise, also some precipitation of black $(AgF^+)_2AgF_4^-SbF_6$ or dark green AgF_2 should occur.

Additionally, it was found that the presence of hydrogen in the solvent (aHF) can cause the reduction of solvated cationic Ag(II) to Ag(I), yielding $AgSbF_6$ and/or $AgSb_2F_{11}$ depending on the conditions of isolation.

The mass balance, chemical analysis, and chemical behavior of isolated solid confirm the composition $AgSb_2F_{11}$. The final proof comes from the structure determination.

Structure. The preparation of single crystals of $AgSb_2F_{11}$ from saturated solution in aHF failed because of its solvolysis in aHF. Only single crystals of $AgSbF_6$ were obtained. However, if the starting Ag^I compound is treated with a large excess of SbF_5 in a small amount of aHF at low temperature and then volatiles are slowly removed, single crystals of $AgSb_2F_{11}$ suitable for crystal structure determination can be grown.

Comparing the effective molar volumes of Ag^+ and H_3O^+, it is not so surprising that $AgSb_2F_{11}$ is structurally related to $H_3OSb_2F_{11}$.[22] The calculated effective volume of the Ag^+ cation is 0.00604 nm^3, using Goldschmidt's radius for Ag^+ (0.113 nm)[23] and taking the volume of the cation to be equal to $(4/3)\pi r^3$.[20,24] The average effective volume of H_3O^+ can be calculated by $V_{eff}(H_3O^+) = [(V_{unit\ cell}/Z) - V_{anion}]$. Using the values of $V_{unit\ cell}$ and Z known from the crystal structures of H_3OAsF_6[25] and H_3OSbF_6[26] and using the average effective volumes for the anions AsF_6^- (0.110 nm^3) and SbF_6^- (0.121 nm^3) obtained by the method of Jenkins et al.,[20] the average effective volume of H_3O^+ (0.00758 nm^3) can be estimated.

The complex structure of $AgSb_2F_{11}$ reveals three crystallographically nonequivalent $Sb_2F_{11}^-$ anions (Figure 2). In the ideal case the Sb_2F_{11} unit has a linear Sb−F−Sb moiety, together with eclipsed $SbF_{4,eq}$ groups. Then the dioctahedral anion is centrosymmetrical (point group D_{4h}).[27] The eclipsed conformation is rare but has been previously observed in $H_3F_2Sb_2F_{11}$,[28] $N_5Sb_2F_{11}$,[29] and $Au(CO)_2Sb_2F_{11}$.[30] Because of their flexibility, Sb_2F_{11} anions are usually distorted from D_{4h} symmetry, depending upon the counterions in the crystal

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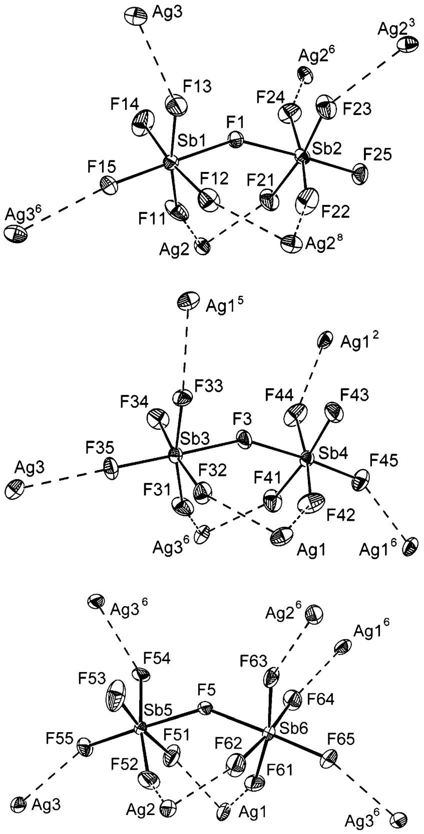

Figure 2. Three crystallographically nonequivalent Sb_2F_{11} units and their interactions with Ag^+ cations in the crystal structure of $AgSb_2F_{11}$ (thermal ellipsoids are drawn at 40% probability level).

lattice. They exhibit a wide range of Sb–F–Sb bridging angles in a staggered conformation. There are two primarily distortional processes involved. First is bending of two SbF_5 groups about F_b (bridging fluorine) which is expressed in terms of the bridge angle α, and second is torsion of two planar $SbF_{4,eq}$ groups from eclipsed to staggered conformation expressed in the torsion angle (ψ).[31] In $AgSb_2F_{11}$ three different bridge (143.5°, 148.3°, and 151.8°) and three corresponding dihedral (37.1°, 22.5°, 18.0°) angles for three crystallographically nonequivalent Sb_2F_{11} units are found. The bridging angles in $AgSb_2F_{11}$ are close to the values found for the anions in structurally related $H_3OSb_2F_{11}$ ($\alpha = 145.9°$, 148.3°, and 149.4°). Meanwhile, dihedral angles found in $AgSb_2F_{11}$ show a larger distinction in comparison with $H_3OSb_2F_{11}$ ($\psi = 29.5°$, 21.2°, and 24.2°).[22] In the literature an explanation can be often found that an increase in ψ serves to minimize steric repulsions between the nearest neighbor F atoms on each octahedron as α decreases below 180°. For example, $\psi = 0°$ when α approaches 180°, and $\psi = 45°$ when α increases to $\sim$145°.[32] However, the values of α and corresponding ψ for Sb_2F_{11} units found in the crystal structure of $AgSb_2F_{11}$ and $H_3OSb_2F_{11}$[22] show that the correlation between α and ψ is not generally valid and consequently has no practical value since deformation of Sb_2F_{11} units depends not only on the nature of the cations but also on packing effects. Another well-known example is $N_5Sb_2F_{11}$ ($\alpha = 155°$, $\psi = 0°$) where the eclipsed conformation results from N_5^+ acting as a spacer between two $SbF_{4,eq}$ units of Sb_2F_{11}.[29] As found for many other Sb_2F_{11} compounds,[22,29,33–36] a slight asymmetry of the $Sb-F_b-Sb$ bridge in Sb_2F_{11} units of $AgSb_2F_{11}$ was observed (Table 3). $Sb-F_t$ bonds are as expected shorter (182.7–186.7 pm) and show a wider spread than $Sb-F_b$ bonds (201.7–204.2 pm). A slight lengthening of some terminal $Sb-F_t$ bonds appears to involve F_t engaged in interionic contacts with Ag cations (Table 3, Figure 2). Bond angles $F_{eq}-Sb-F_{ax}$ are slightly wider than 90°, while $F_{eq}-Sb-F_b$ angles are acute by about 3–6° (Table 4). A slight lean of fluorine atoms in equatorial positions toward the weakly bonded $Sb-F_b-Sb$ moiety is in agreement with the VSEPR theory of molecular structure.[37,38] As for $H_3OSb_2F_{11}$,[22] $Sb-F_t$ distances in $AgSb_2F_{11}$ are in general slightly shorter than distances in corresponding SbF_6^- salts, showing that Sb_2F_{11} is a weaker nucleophile than SbF_6^-.

There are also three crystallographically nonequivalent Ag^+ cations in the crystal structure of $AgSb_2F_{11}$ (figures in Supporting Information). Ag–F bond distances cover a wide range and can be divided into two groups (247.2–263.4 and 269.1–294.7 pm). The Ag–F distances of the second group are a little larger than that based on the sum of the Shanon radii (261 pm)[39] of fluorine and silver, taking into account the coordination number (CN) 8 but still quite below the sum of their respective van der Waals radii (315(8) pm).[40,41] They can be compared to Ag–F distances found in $AgPdZr_2F_{11}$,[42,43] Ag_2CuFeF_7,[42,44] and AgF (type II).[42,45] In the first two compounds the Ag atoms are 8-fold coordinated by four shorter ($AgPdZr_2F_{11}$: 235.5 pm (4×); Ag_2CuFeF_7: 242.1 pm (2×) and 254.0 pm (2×)) and four longer contacts ($AgPdZr_2F_{11}$: 279.8 pm (4×); Ag_2CuFeF_7: 278.8 pm (2×) and 290.7 pm (2×)) that are similar to the distances found in $AgSb_2F_{11}$. In AgF (type II) silver atoms are 8-fold coordinated with equal Ag–F distances (255 pm).[42,8,45] The coordination of silver atoms in $AgSb_2F_{11}$ can be approximately written as 5 + 3 for Ag1 (CN = 8), 6 + 3 for Ag2 (CN = 9), and 6 + 2 for Ag3 (CN = 8).

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Table 3. Selected Bond Lengths (pm) in $AgSb_2F_{11}$[a]

Sb1−F1	202.0(7)	Sb2−F1	203.4(7)	Sb3−F3	204.2(7)	Sb4−F3	201.7(7)
Sb1−F11	184.3(8)	Sb2−F21	185.1(8)	Sb3−F31	184.9(8)	Sb4−F41	186.2(8)
Sb1−F12	183.8(8)	Sb2−F22	185.5(9)	Sb3−F32	186.1(8)	Sb4−F42	185.7(8)
Sb1−F13	186.7(9)	Sb2−F23	184.4(8)	Sb3−F33	185.9(7)	Sb4−F43	182.9(8)
Sb1−F14	183.4(9)	Sb2−F24	185.0(8)	Sb3−F34	183.4(8)	Sb4−F44	185.4(8)
Sb1−F15	185.7(7)	Sb2−F25	184.5(7)	Sb3−F35	185.0(7)	Sb4−F45	185.2(8)
Sb5−F5	204.2(7)	Sb5−F53	182.7(9)	Sb6−F5	201.7(7)	Sb6−F63	185.4(8)
Sb5−F51	184.8(8)	Sb5−F54	184.1(7)	Sb6−F61	186.1(8)	Sb6−F64	185.1(8)
Sb5−F52	184.1(8)	Sb5−F55	185.4(7)	Sb6−F62	184.9(8)	Sb6−F65	185.7(7)
Ag1−F32	252.1(8)	Ag2−F11	257.9(8)	Ag3−F13	254.5(10)		
Ag1^{5}−F33	260.0(7)	Ag2^{8}−F12	257.1(8)	Ag3^{6}−F15	271.4(7)		
Ag1−F42	253.4(9)	Ag2−F21	258.7(8)	Ag3^{6}−F31	261.2(8)		
Ag1^{2}−F44	272.8(9)	Ag2^{8}−F22	255.0(9)	Ag3−F35	273.2(7)		
Ag1^{6}−F45	252.9(8)	Ag2^{3}−F23	281.3(9)	Ag3^{6}−F41	262.2(8)		
Ag1−F51	249.4(8)	Ag2^{6}−F24	261.3(8)	Ag3^{6}−F54	255.1(8)		
Ag1−F61	269.1(8)	Ag2−F52	294.7(10)	Ag3−F55	263.4(8)		
Ag1^{6}−F64	286.4(8)	Ag2−F62	247.2(8)	Ag3^{6}−F65	257.2(8)		
		Ag2^{6}−F63	271.6(7)				

[a] Symmetry operations used for generation of equivalent atoms: (1) x, y, z; (2) $x + 1/2$, $-y + 1/2$, $-z$; (3) $-x$, $y + 1/2$, $-z + 1/2$; (4) $-x + 1/2$, $-y$, $z + 1/2$; (5) $-x$, $-y$, $-z$; (6) $-x + 1/2$, $y + 1/2$, z; (7) x, $-y + 1/2$, $z + 1/2$; (8) $x + 1/2$, y, $-z + 1/2$.

Table 4. Selected Bond Angles (deg) in $AgSb_2F_{11}$

F11−Sb1−F1	84.3(3)	F21−Sb2−F1	84.3(4)	F31−Sb3−F3	84.7(3)
F12−Sb1−F1	86.1(4)	F22−Sb2−F1	85.8(4)	F32−Sb3−F3	86.9(4)
F13−Sb1−F1	84.4(4)	F23−Sb2−F1	85.6(4)	F33−Sb3−F3	82.7(3)
F14−Sb1−F1	86.5(4)	F24−Sb2−F1	86.5(4)	F34−Sb3−F3	86.1(4)
F11−Sb1−F15	95.2(4)	F21−Sb2−F25	94.0(4)	F31−Sb3−F35	96.0(4)
F12−Sb1−F15	93.1(4)	F22−Sb2−F25	92.5(4)	F32−Sb3−F35	93.8(4)
F13−Sb1−F15	96.1(4)	F23−Sb2−F25	96.2(4)	F33−Sb3−F35	96.6(4)
F14−Sb1−F15	94.3(4)	F24−Sb2−F25	95.2(4)	F34−Sb3−F35	93.3(4)
		Sb1−F1−Sb2	148.3(4)		
F41−Sb4−F3	85.3(4)	F51−Sb5−F5	85.0(4)	F61−Sb6−F5	85.0(3)
F42−Sb4−F3	85.7(4)	F52−Sb5−F5	84.8(4)	F62−Sb6−F5	86.5(4)
F43−Sb4−F3	86.1(4)	F53−Sb5−F5	86.7(4)	F63−Sb6−F5	84.7(3)
F44−Sb4−F3	86.5(4)	F54−Sb5−F5	85.9(3)	F64−Sb6−F5	86.5(4)
F41−Sb4−F45	91.1(4)	F51−Sb5−F55	92.4(4)	F61−Sb6−F65	93.1(4)
F42−Sb4−F45	92.1(4)	F52−Sb5−F55	94.7(4)	F62−Sb6−F65	92.7(4)
F43−Sb4−F45	97.5(4)	F53−Sb5−F55	95.8(4)	F63−Sb6−F65	97.1(3)
F44−Sb4−F45	95.7(4)	F54−Sb5−F55	94.6(4)	F64−Sb6−F65	94.3(4)
Sb3−F3−Sb4	151.8(4)			Sb5−F5−Sb6	143.5(4)

Vibrational Spectra. Vibrational spectra of $AgSb_2F_{11}$ are the same as for "β-$Ag(SbF_6)_2$" ($Ag^IAg^{III}(SbF_6)_4$),[10] demonstrating that $AgSb_2F_{11}$ and "β-$Ag(SbF_6)_2$" are one and the same compound. $Sb_2F_{11}^-$ anions strongly deviate from D_{4h} symmetry and have no symmetry (point group C_1). Partial assignment of $Sb_2F_{11}^-$ anions was made on the basis of comparison with $M(CO)_4(Sb_2F_{11})_2$ (M = Pd, Pt)[35] which contain two crystallographically nonequivalent distorted $Sb_2F_{11}^-$ anions. The bands in the regions 585−692 and 697−722 cm^{-1} are assigned to $Sb-F_{eq}$ and $Sb-F_{ax}$ stretchings, respectively; meanwhile, bands around 500 cm^{-1} are typical for Sb−F−Sb bridging. The rest of the bands were assigned to bending deformations.

Conclusions

On the basis of obtained results it can be concluded that "β-$Ag(SbF_6)_2$" (formulated as mixed-valence Ag(I)/Ag(III) compound) is in fact an Ag(I) compound ($AgSb_2F_{11}$). In the original method of preparation of "β-$Ag(SbF_6)_2$" by solvolysis of $Ag(SO_3F)_2$ in liquid SbF_5, a change of color from black brown to greenish blue and finally to yellow was observed.[10] Additionally, the attempts of the same authors to repeat the synthesis of previously reported α-$Ag(SbF_6)_2$ always gave a fair amount of white insoluble solid (postulated to be "β-$Ag(SbF_6)_2$") and a blue solution from which α-$Ag(SbF_6)_2$ was isolated.[10] All these data suggest that in all cases partial reduction of Ag(II) occurred. The first cause could be the presence of the impurities in starting materials serving as reducers. This is not surprising since cationic solvated Ag(II) in aHF acidified with Lewis acids is known to be a very strong oxidizer and it can be easily reduced.[46] The second reason could be the influence of the acidity of aHF. When an large excess of SbF_5 was added to α-$Ag(SbF_6)_2$, it was irreversibly converted in aHF to a white insoluble solid.[10] From literature data it is well-known that increased acidity of aHF favors a low oxidation state in the cation.[47,48−50]

The preparation and crystal structure determination of other ASb_2F_{11} compounds (A = monovalent cation) are in progress.

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Supporting Information Available: X-ray crystallographic file in CIF format, figures of coordination of silver atoms by Sb_2F_{11} units, figures of the Raman spectrum of $AgBF_4$, Raman spectrum of $AgSbF_6$ taken on single crystal, Raman spectrum of $AgSbF_6$ obtained by reaction between $AgSb_2F_{11}$ and $AgBF_4$ in aHF, Raman and IR spectra of $Ag(SbF_6)_2$ obtained by reaction between $AgSb_2F_{11}$ and F_2 in aHF, Raman and IR spectra of the solid isolated after reaction between $AgSbF_6$ and F_2 in aHF. This material is available free of charge via the Internet at http://pubs.acs.org.

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