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Contribution from the Departement de Physicochimie,
Centre d'Etudes Nucléaires de Saclay,
91191 Gif-sur-Yvette Cedex, France,
and Institut Curie, ERA 1006, 75321 Paris Cedex 05, France

Synthesis and Properties of Silver Trifluoride, AgF_3

R. Bougon,[*,†] T. Bui Huy,[†] M. Lance,[†] and H. Abazli[‡]

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Considering that the hexafluoride of platinum and the tetrafluoride of palladium as well as the pentafluoride of gold are known,[1-3] the existence of a fluoride of silver in an oxidation state higher than II had been expected. We effectively succeeded in obtaining a new silver binary fluoride corresponding to the composition AgF_3 and have recently reported[4,5] its synthesis and its characterization. This paper gives more details on the properties of this interesting compound.

Experimental Section

Materials. Commercial anhydrous HF was further treated by shaking with ca. 10 bar of fluorine prior to use. Silver powder and silver fluoride were purchased from Prolabo; silver difluoride was prepared by fluorination of silver metal powder with either fluorine at ca. 300 °C or a mixture of ClF_3 and F_2 in HF solution at room temperature. Krypton difluoride was prepared by photolysis of a mixture of liquid fluorine and solid krypton at ca. −196 °C. The mixture was irradiated by the UV beam of a 2.5-kW Hanovia lamp. The irradiation cell was made of Monel with a 75-mm sapphire window. The UV beam was reflected at 90° and focused at the liquid-fluorine level. This preparation is based on the photochemical method described by others[6,7] but achieved here with the type of irradiation cell described by Christe et al.[8] for the synthesis of NF_4^+ salts. Typical yields of about 200 mg of KrF_2 per hour were so obtained.

Apparatus. The volatile materials were transferred in a vacuum line made for the most part of Monel metal tubing equipped with valves purchased from FW Co. For reactors, depending on the experimental requirements, Monel high-pressure vessels or Teflon-FEP or PFA tubes were used. These vessels were attached to the vacuum line through Monel, Kel-F, or Teflon valves or Autoclave Engineering high-pressure Monel valves. The nonvolatile samples were transferred in a drybox containing P_2O_5 as a desiccant.

X-ray Diffraction Patterns. The Debye–Scherrer powder patterns were taken on a 114-mm diameter Philips instrument with copper Kα radiation (1.5418 Å). The samples were contained in quartz capillaries (~0.5 mm).

Spectra. Infrared spectra were recorded with a Perkin-Elmer Model 457 spectrometer. For these spectra, the powdered samples were pressed between thin plates of AgCl. Attempts to reach lower frequencies with AgBr windows were unsuccessful because of the rapid reaction of AgF_3 with this material.

Raman spectra were recorded with a Coderg Model T800 spectrometer using as exciting light the 647.1-nm line of a Model 165 Spectra Physics laser. Solutions were examined in a Teflon-FEP reaction tube. Owing to its red-brown color, attempts to obtain spectra of AgF_3 with samples in Pyrex capillary tubes were unsatisfactory, even with the capillaries cooled by liquid nitrogen. A Coderg spinning cell, modified to sustain moisture-sensitive materials, had to be used to obtain the Raman spectrum of AgF_3.

The ^{19}F NMR spectra of the solutions were obtained in a Varian NV14 spectrometer operating at 56.4 MHz.

Magnetic Susceptibility. The magnetic susceptibility of a powdered sample was measured by the Faraday method with a value of $H\partial H/\delta x$, the product of the field times its gradient, equal to 14 kG cm^{-1}. The samples, the weights of which ranged from 20 to 100 mg, were encapsulated in gold containers sealed under a pressure of 200 mmHg of dry helium. Three sets of measurements were made, two of them using liquid helium as cooling agent so that the temperature range explored was from 4 to 290 K. Corrections for ferromagnetic impurities were made by the Honda–Owen method,[9] and the diamagnetism of the F^- ions was taken[10] as $3 \times (-9.1 \times 10^{-6}$ emu cgs mol^{-1}).

Table I. X-ray Powder Pattern of AgF_3

d, Å	intens	*d*, Å	intens
5.53	4	2.090	7
4.55	24	2.013	4[a]
3.91	8	1.924	19
3.70	100	1.852	30
3.46	19	1.847	
3.30	39	1.745	15
3.19	11	1.704	4
3.04	81	1.682	8
2.96	14	1.649	12
2.75	4	1.621	30
2.696	19	1.615	
2.619	3	1.546	11
2.496	20[a]	1.520	11
2.427	9[a]	1.485	8
2.330	18	1.464	8
2.279	40	1.432	7[a]
2.271			
2.215	6		
2.174	3		
2.125	13		

[a] Broad.

Thermal Stability. The thermal stability of AgF_3 was determined by using the programmed heating system of an ARION MCB microcalorimeter. The samples were loaded in an evacuable prefluorinated Monel cell, which for the measurements was heated at a rate of 1 K min^{-1} under pumping. The pressure indicated by a vacuum gauge close to the decomposition cell was recorded.

Preparation. Both silver metal and its monofluoride are perfluorinated by KrF_2 in HF solution, but in order to conserve KrF_2, AgF_2 was the preferred starting material. In a typical experiment, 0.247 g (1.69 mmol) of AgF_2 was introduced into a Teflon-PFA tube. After evacuation, about 1.5 cm^3 of liquid HF was distilled in an atmosphere of 200 mmHg of F_2 and condensed onto the AgF_2. Fluorine was removed by pumping at liquid-nitrogen temperature, and an excess of KrF_2 was condensed into the reactor. The mixture was left at room temperature for 2 days, with periodic removal of krypton and fluorine generated by the reaction and/or KrF_2 decomposition. Studies of the reaction media achieved by ^{19}F NMR and Raman spectrocopy did not indicate the formation of krypton fluoride cationic species such as KrF^+ or $Kr_2F_3^+$ peviously observed for the $Au/KrF_2/HF$ system.[11] Only KrF_2 and F_2 were observed as solutes. Owing to the significant amount of HF plasticized into the walls of the reaction tube, no accurate determination of the weight change was possible.

However, the elemental analysis of the red-brown solid residue showed that its composition corresponded to the formulation AgF_3. Anal. Calcd for AgF_3: Ag, 65.43; F, 34.57. Found: Ag, 64.75; F, 34.22.

It should be noted that under similar experimental conditions no fluorides higher than the difluorides were obtained with the elements Cu, Ni, or Hg.

[†] Centre d'Etudes Nucléaires de Saclay.

[‡] Institut Curie.

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Results and Discussion

Stability. Silver trifluoride is stable at room temperature in a dry atmosphere but is readily decomposed by atmospheric moisture. The products of this decomposition were identified as Ag_2O_2 and AgF from their X-ray powder patterns. The thermal stability study showed that AgF_3 starts to decompose at 163 ± 1 °C under pumping. The weight change and the X-ray diffraction pattern of the residue indicated that it decomposes into AgF_2 and F_2.

X-ray Data. The positions and intensities of the lines observed on the X-ray powder pattern of AgF_3 are listed in Table I. This pattern indicates a low symmetry of the lattice and could not be indexed. No similarities with other trifluorides were observed.

Vibrational Spectra. The infrared spectrum of AgF_3 was found to be quite distinct from that of AgF_2. A strong broad band is observed at 600 cm^{-1} with two bands of medium intensity at 535 and 480 cm^{-1}. Superimposed on the fluorescence from the glass part of the spinning cell, the Raman spectrum of AgF_3 displays a strong line at 543 cm^{-1} and two lines of much weaker intensity at 573 and 261 cm^{-1}. Obviously no interpretation of these spectra is yet possible without other sources of structural information.

Chemical Properties. AgF_3 is not significantly soluble in HF or ClF_3. Depending on the reation conditions, it reacts at room temperature with liquid FNO to yield the new silver fluoro complexes $NOAgF_3$ and $NOAgF_4$. The Ag^{2+} complex (Anal. Calcd for $NOAgF_3$: Ag, 55.35; F, 29.25; N, 7.19; O, 8.21. Found: Ag, 55.55; F, 29.18; N, 7.15; O, 8.12 (by difference)) was obtained whenever the reactor contained any metallic parts (Monel, nickel, or stainless steel). The blue color of the excess of FNO recovered after the reaction indicated that nitrogen oxide had been formed, and this was confirmed by infrared analysis of a sample. The formation of $NOAgF_3$ is then easily explained by the reaction of AgF_3 and/or $NOAgF_4$ with these oxides. Only the use of an all-Teflon reactor together with fluorine added to FNO allowed the preparation of a pure sample of $NOAgF_4$. Anal. Calcd for $NOAgF_4$: Ag, 50.44; F, 35.53; N, 6.55; O, 7.48. Found: Ag, 50.70; F, 35.25; N, 6.27; O, 7.78 (by difference). Probably owing to the great reactivity and/or easy decomposition of this compound, its X-ray powder patterns always showed the presence of decomposition products, such as $NOAgF_3$ or AgF_2, and not enough lines were available to fully characterize $NOAgF_4$. On the other hand, the X-ray powder pattern of $NOAgF_3$ clearly indicated that this compound is isostructural with $KAgF_3$.

Magnetic Properties. The measurements show that AgF_3 is paramagnetic and obeys the Curie–Weiss law in the temperature range studied (4–290 K). Three sets of measurements obtained on samples from different preparations gave a magnetic moment of 1.15 ± 0.05 μ_B.

Owing to the great reactivity of AgF_3 and the eventual presence of degradation products, the origin of this paramagnetism has to be discussed. The X-ray powder patterns taken before and after the magnetic measurements did not show the presence of AgF_2; also, contrary to the findings for this compound,[12] no magnetic transition was observed for our sample. An uncontrolled hydrolysis also cannot account for the paramagnetism since the products of the hydrolysis, AgF and Ag_2O_2 (vide supra), are both diamagnetic.

On the other hand, the low value of the magnetic moment, when compared to the expected 2.83 μ_B spin-only value for a $4d^8$ high-spin electronic configuration, deserves some comments. As stated above, no indication for an antiferromagnetic behavior was noticed and no other lines other than those of AgF_3 were observed in the X-ray diffraction patterns. Therefore, neither an antiferromagnetic effect nor some crystalline impurity appears to account for the low value of the magnetic moment. Keeping in mind that the ion Pd^{2+} is isoelectronic with Ag^{3+}, it is interesting to mention the magnetic properties of palladium species. Whereas the difluoride is paramagnetic, only a few other Pd^{2+} fluoro derivatives are paramagnetic.[13] The trifluoride was demonstrated[3,14] to be the mixed-valency compound $Pd^{2+}[PdF_6]^{2-}$, and its paramagnetism was interpreted by the high-spin electronic configuration of Pd^{2+} ($d_{2g}{}^6e_g{}^2$) and the low-spin configuration of Pd^{4+} ($d_{2g}{}^6e_g{}^0$).

In a similar way, AgF_3 may be supposed to be the mixed-valency compound $Ag^{2+}[AgF_6]^{2-}$. With this formulation, the lower magnetic moment is obtained with a low-spin configuration of the ion Ag^{4+} corresponding to only one unpaired electron and the total magnetic moment of "AgF_3" would be 1.73 μ_B for the spin-only value. It is worth mentioning that a Jahn–Teller distortion is to be expected[15] with ions of the electronic structure $t_{2g}{}^6e_g{}^1$ in an octahedral site and that this would be compatible with the low symmetry of the lattice.

So far, attempts were unsuccessful to prepare other $M^{2+}[AgF_6]^{2-}$ salts (with M being a divalent element) that would be isomorphous with "AgF_3". Also, no single-crystal X-ray diffraction study of AgF_3 has so far been possible.

A second tentative explanation, which is less probable than the former one, is that there are Ag^{3+} ions in two different crystals sites, with only one of them leading to a paramagnetic ion. The spin-only value would then be equal to 2.83/2 μ_B per AgF_3 entity.

Conclusions. The use of the strong fluorinating agent KrF_2 in HF solution has allowed us to obtain a new silver fluoride. This compound having the overall composition AgF_3 has been characterized. On the basis of its magnetic properties, AgF_3 might actually be $Ag^{2+}[AgF_6]^{2-}$, but this requires a confirmation by a crystal structure determination.

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Registry No. AgF_2, 7783-95-1; KrF_2, 13773-81-4; AgF_3, 91899-63-7; FNO, 7789-25-5; $NOAgF_3$, 91899-65-9; $NOAgF_4$, 91899-67-1.

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Contribution from Ames Laboratory and the Department of
Chemistry, Iowa State University, Ames, Iowa 50011

Kinetics and Mechanism of the Formation of Alkyl Radicals and Alkylpentaaquochromium(2+) Complexes by the Reaction of Free Radicals Derived from (2-Hydroxy-2-propyl)pentaaquochromium(2+) Ions with Alkyl Iodides

James H. Espenson,* Suzanne L. Bruhn, and Andreja Bakac

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The unimolecular homolysis of organochromium cations[1-4] serves as a source of "stored" free radicals, which can be useful

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