the central chlorine and the fluorine in the ClF$_2^+$ cation which is not present in Cl$_3^+$.

We have not been able to obtain the spectrum of ClClF$^+$ in solution and it appears that it is completely disproportioned even at low temperatures according to 2ClClF$^+$ $\rightarrow$ ClF$_2^+$ + Cl$_3^+$. Thus in a solution of ClF in excess SbF$_5$ and HF at $-76°$ in addition to the rather complicated spectrum attributable to SbF$_5$ and SbF$_6$(SbF$_5$)$_n^-$ the only other band observed was a strong, rather broad peak at 500 cm^{-1} which can be assigned to ν_1 of Cl$_3^+$. No lines that could be attributed to ClClF$^+$ were observed. Unfortunately the spectrum of ClF$_2^+$ was obscured by the solvent spectrum.

It seems reasonable to regard the cations ClClF$^+$ and Cl$_3^+$ as being derived from the coordination of Cl$^+$ with the ClF and Cl$_2$ molecules, respectively. Thus ClF can be displaced from ClClF$^+$ by chlorine to give the Cl$_3^+$ cation. Hence we expect to be able to prepare other cations such as ClBrF$^+$ and ClBrBr$^+$ by displacing the ClF in ClClF$^+$ with BrF or Br$_2$.

Experimental Section

Materials.—All substances were handled in a Monel vacuum line fitted with Whitey valves with Kel-F seats, to which Kel-F traps were attached with Swagelok fittings. The line was well aged by treatment with ClF$_3$ and ClF. Chlorine monofluoride and antimony pentafluoride (Ozark-Mahoning Co.) and bromine trifluoride (Matheson Co., Inc.) were purified by several low-temperature vacuum distillations. Antimony pentafluoride was double-distilled at atmospheric pressure followed by vacuum distillation. Chlorine was bubbled through permanganate solution and concentrated sulfuric acid and distilled at $-78°$.

The compounds Cl$_2$F$^+$AsF$_6^-$ wand Cl$_2$F$^+$BF$_4^-$ were prepared exactly as described by Christe and Sawodny.[1] Samples were obtained in clear, thin-wall, 4-mm Kel-F tubes which were subsequently heat sealed under vacuum.

The compound Cl$_3^+$AsF$_6^-$ was prepared by warming Cl$_2$F$^+$AsF$_6^-$ in the presence of excess chlorine until all the solid had vaporized and then recooling to Dry Ice temperatures and pumping off the excess gases. Treatment of Cl$_2$F$^+$AsF$_6^-$ with Cl$_2$ in excess AsF$_5$ as solvent at $-78°$ resulted in only partial conversion to Cl$_3^+$AsF$_6^-$ as the salts are not appreciably soluble in AsF$_5$.

Cl$_3^+$AsF$_6^-$ is a yellow solid completely dissociated to Cl$_2$, ClF, and AsF$_5$ at 25°. The intensity of the AsF$_5$ absorptions in a 10-cm Monel infrared cell fitted with silver chloride windows and Teflon gaskets had one-third of the intensity of the absorptions for pure AsF$_5$ at the same pressure.

Raman Spectra.—Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing a double monochromator and a phototube detector with a dc electrometer amplifier and recorder. The 6328-Å exciting radiation was from a Spectra Physics Model 125 He–Ne laser giving approximately 30 mW at the sample.

The vertical laser beam was focused on the solids contained in a horizontal Kel-F tube mounted in a quartz tube with an evacuated jacket silvered except at the center. Nitrogen was boiled off from a dewar and passed through the quartz tube and the temperature was recorded with a thermocouple. Light scattered at 90° from the sample was focused on the slits of the monochromator so that the image of the Kel-F tube walls fell well outside the limits of the slit.

Acknowledgment.—We thank the National Research Council of Canada for financial support of this work and the Department of University Affairs, Province of Ontario, for the award of an Ontario Graduate Fellowship to M. J. M.

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Sulfur Hexafluoride. Its Reaction with Ammoniated Electrons and Its Use as a Matrix for Isolated Gold, Silver, and Copper Atoms

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Received September 24, 1969

The reactivity of SF$_6$ with reactive metals was studied to explore the use of SF$_6$ as a matrix material for low-temperature isolation of metallic atoms. At 212°K SF$_6$ rapidly decolorized the blue liquid ammonia solutions of alkali metals to produce white precipitates of alkali fluorides and sulfides. The codeposition of Au vapor with SF$_6$ at 20°K gave well-isolated matrices with very sharp atomic spectra comparable to those obtained with inert-gas matrices, but Cu and Ag spectra in SF$_6$ were very broad. *n*-Perfluoroheptane was also examined as a matrix material, but Ag and Au gave very complex spectra.

Introduction

The rare gases, which have been widely used[1] for matrix isolation of reactive species, are restricted to very low temperatures because of their low melting points. SF$_6$ with a melting point of 218°K is an attractive nonpolar molecule for matrix studies that could be extended to above liquid nitrogen temperatures. It is known to be chemically inert toward aqueous or fused alkali, ammonia, and oxygen and does not react appreciably with sodium metal[2] below 200° or with CF$_3$ or CH$_3$ radicals[3] up to 365°. The high electron affinity[4] and

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(1) B. Meyer in "Low Temperature Spectroscopy; Optical Properties of Molecules in Matrices, Mixed Crystals, and Organic Glasses," Elsevier, Publishing Co., New York, N.Y., 1970, Chapter 9.

(2) H. C. Cowan, F. Reding, and E. Warhurst, *J. Chem. Soc.*, 4168 (1953).

(3) H. F. Le Fevre, J. D. Kale, and R. B. Timmons, *J. Phys. Chem.*, **73**, 1614 (1969).

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ready formation[5] of SF_6^- offer the interesting possibility of the study of charge transfer from one trapped species to another through the intermediary of SF_6^-.

In contrast to the inertness of SF_6 with virtually all reagents, Demitras and MacDiarmid[6] found that SF_6 reacted with solutions of sodium in biphenyl–ethylene glycol dimethyl ether to produce Na_2S and NaF slowly below $-10°$ but within a few minutes at room temperature. They also reported rapid reaction with a solution of sodium in ammonia at $-64°$ but did not identify the products. The reaction of SF_6 with hydrated electrons[7] has also been reported. The proposed mechanisms for the reactions in both the aqueous and ether solutions involve the intermediate SF_6^- followed by formation of SF_5.

The present study was designed to determine if SF_6^- could be a stable species in liquid ammonia or if SF_6^- could be stabilized by precipitation with a stabilizing cation just as unstable O^{2-} can be stabilized in solid MgO by the coulombic interaction with Mg^{2+}. It can be predicted[8] that salts of a large anion such as SF_6^- will be less soluble the larger the cation; therefore ammonia solutions of Cs were largely used for the study of SF_6 with alkali metals. Cu, Ag, and Au atoms were trapped in SF_6 matrices as a test of the use of SF_6 matrices of metal atoms.

Experimental Section

Liquid Ammonia Solutions.—In preliminary experiments, SF_6 gas was bubbled through liquid ammonia solutions of potassium held in dewars open to the atmosphere. A white product precipitated which was found to be paramagnetic in a Gouy balance. This suggested the formation of $K^+SF_6^-$. However diffusion of oxygen to the solution of metal in ammonia could have contaminated the product with paramagnetic peroxides or superoxides. The reaction was repeated in a vacuum line as described below, but the product was still paramagnetic and esr measurements yielded a *g* factor of 2.008. The infrared spectrum of the product in Nujol had absorption frequencies at 870, 1145, 1258, 1360, and 1646 cm^{-1} in addition to those of the Nujol blank. After exposure of the Nujol mixture to air for several minutes, the first four peaks disappeared and the last one became weaker and shifted to 1670 cm^{-1}. A new broad peak, which could be due to reaction with moisture, appeared with the center frequency at 3420 cm^{-1}. Repetition of the preparation with better efforts to clean the metal to reduce oxygen contamination produced a similar product but with reduced paramagnetism.

A more direct test of the stoichiometry of the reaction was devised. Predried ammonia was passed through a vacuum line and condensed into a reaction tube containing a known amount of cesium metal. The ammonia was allowed to melt to dissolve the cesium and form a blue solution which was then immersed into a $-61°$ bath. A known amount of commercial SF_6 (minimum purity 98%) was introduced into the vacuum line and the solution was stirred magnetically until the blue color had disappeared. This was repeated with different ratios of SF_6 to Cs. With $^1/_{16}$ mol of SF_6/mol of Cs, the blue color persisted. With $^1/_8$ mol or more of SF_6/mol of Cs, the blue color disappeared. The quantitative reaction thus corresponded to

$$8Cs + SF_6 = 6CsF + Cs_2S \tag{1}$$

The ratio of the weight of the white precipitate to the weight of cesium metal was found to be 1.14, 1.13, 1.12, and 1.16 compared to 1.14 expected on the basis of reaction 1. Any products other than CsF and Cs_2S which could be responsible for the observed paramagnetism and ir spectra must be produced in low yield.

Since SF_6, as gas or solid, has a very low solubility in liquid NH_3 and it took about 4 hr for enough SF_6 to dissolve to react completely with the metal, the solution contained an excess of metal during the reaction. An experiment was performed to test whether a different reaction might take place if SF_6 were in excess as there would be a large excess of SF_6 over metal if SF_6 were used for matrix isolation of metal atoms.

The high vapor pressure and low solubility of SF_6 make it difficult to provide an excess of SF_6 in the NH_3 solution. The reaction tube was modified to have a side entrance on its wall which was covered with a cap. A known amount of SF_6 was condensed at the bottom of the reaction tube. NH_3 was condensed on top of the SF_6 to completely cover it. The whole vacuum line was then filled with 1 atm of pure nitrogen gas while keeping the condensate at liquid nitrogen temperature using a dewar. The side entrance was opened; a portion of Cs solid was quickly poured in. The entrance was capped and the vacuum line was evacuated immediately to minimize the amount of Cs being oxidized. More NH_3 was condensed into the reaction tube. The dewar was then lowered to just the level to keep the SF_6 condensed while allowing the NH_3 to melt. The reaction tube was swirled to get a uniform solution on top of the condensed SF_6. The dewar was then removed and the SF_6 was allowed to warm up. As soon as SF_6 started bubbling through the upper solution, the reaction tube was quickly swirled. In about 30 sec the blue color disappeared. Everything was then condensed in the reaction tube and covered with another portion of condensed NH_3 and more Cs was added in the same way. Because of the low solubility of SF_6 in NH_3, the rate-determining step was probably the rate of solution of SF_6 and we may not have achieved an excess of SF_6 in solution during the actual reaction, but with this procedure the rough stoichiometric ratio was again found to correspond to reaction 1. In both cases the product was a white precipitate which was completely soluble in water and H_2S was released when dilute HCl was added to the product.

Matrix Isolation.—Although reaction 1 was found to take place quickly in liquid ammonia at $-61°$, there is still the possibility that SF_6 might be useful as a matrix for metal atoms at liquid nitrogen temperatures or lower. With a large excess of SF_6 at very low temperature, it would not be possible for a reaction to proceed beyond SF_5. As a first test of the use of SF_6 as a matrix for metal atoms, Au atoms at 1350°K were isolated in SF_6 matrices at liquid hydrogen temperatures using the apparatus and techniques previously used for isolation of Ag atoms in rare gas matrices.[9] Excellent Au spectra were obtained comparable to those obtained with inert-gas matrices[10] except that the ${}^2P_{3/2} \leftarrow {}^2S_{1/2}$ transition gave a single band in SF_6 and the ${}^2P_{1/2} \leftarrow {}^2S_{1/2}$ band was much sharper than in Kr and Xe with half-widths of 100 and 450 cm^{-1}, respectively. The half-width in SF_6 of the order of 75 cm^{-1} at 20°K increased upon warming and the maxima of the lines shifted to the red, but warm-ups to liquid nitrogen temperatures and back to 20°K could be carried out reversibly. On the other hand, it was not possible to obtain spectra upon initial condensation at liquid nitrogen temperatures. The thermal radiation from the furnace and the high heat of condensation of SF_6 must increase the surface temperature sufficiently to allow diffusion of the gold atoms during the condensation process. For a typical experiment in which 2×10^{-7} mol

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[9] L. Brewer, B. A. King, J. L. Wang, B. Meyer, and G. F. Moore, *J. Chem. Phys.*, **49**, 5209–13 (1968).

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of gold vapor from a furnace at 1336°K was codeposited with 7×10^{-4} mol of SF_6, the radiant heat input from the furnace amounted to 4×10^{-4} cal sec^{-1} mm^{-2} at the center of the sapphire plate compared to 3×10^{-9} cal sec^{-1} mm^{-2} heat input from condensation of the gold atoms and 10^{-6} cal sec^{-1} mm^{-2} due to condensation of SF_6. Under these circumstances, precooling of the SF_6 did not help. For metal vapor which could be generated from a cooler source, the use of precooled SF_6 might allow trapping at liquid nitrogen temperatures.

Gold vapor at 1350°K was also trapped in an n-C_7H_{16} matrix. The matrix gas source was the liquid at room temperature. In contrast to the simple spectrum in SF_6, the spectrum of 0.13 atom % gold in n-C_7H_{16} was surprisingly complex with 13 bands similar to a molecular progression appearing between 268.7 and 232.3 nm with most spacings in the range 480–500 cm^{-1}. A blank run with no gold showed no spectrum.

The absorption spectrum of silver cocondensed with SF_6 at 20°K had a diffuse appearance with no clear bands observable with less than 0.2 atom % Ag and with only two broad, weak continuous bands with maxima at 333.0 and 329.0 nm discernible at high concentrations. At yet higher concentrations of silver, the two bands became still broader with a weak very broad band developing around 315 nm. A broad but strong absorption band centered at about 214.5 nm was also observed.

The spectrum of silver cocondensed with n-C_7F_{16} vapor showed a weak continuum centered at about 310 nm with five weak but discrete bands at 268.7, 258.8, 252.7, 246.9, and 236.8 nm.

At fairly high concentrations (1 atom %) of copper in SF_6, a strong continuum centered at approximately 315 nm extended over a 17 nm wide region. At lower concentrations two poorly resolved, broad components were observed at about 319 and 312.5 nm. Upon warming the more concentrated matrix and recooling to 20°K, the overall intensity diminished but the broad continuun split into a band at 318.5 nm and a weaker shoulder at 310.6 nm. Weaker bands were seen at 242.5 and 237.4 nm.

Discussion

The sharp Au bands can be unambiguously assigned to the $^2P_{1/2,3/2} \leftarrow {}^2S_{1/2}$ transitions of the gaseous atom as shown in Table I. The Ag and Cu bands are too broad and poorly defined for a clear assignment, but a possible assignment is shown in Table I.

TABLE I

BAND PEAKS FOR Au, Ag, AND Cu IN THE SF_6 MATRIX AND FOR GAS (CM^{-1})

	$^2P_{1/2} \leftarrow {}^2S_{1/2}$		$^2P_{3/2} \leftarrow {}^2S_{1/2}$	
Atom	Gas	Matrix	Gas	Matrix
Au	37,359	38,140	41,174	42,050
Ag	29,552	30,000	30,473	30,400
Cu	30,535	31,350	30,783	32,000

Aside from the general difficulty of characterizing the broad Ag and Cu spectra, the assignment to the atoms is made uncertain because of the existence of Ag_2 bands in the same spectral region. Also in view of the reduction of SF_6 by alkali metals observed in liquid ammonia solutions, it is tempting to propose the formation of CuF and AgF to explain the complexity of the spectra of Cu and Ag in SF_6 and n-C_7F_{16}. Clements and Barrow[11] observed the absorption spectrum of gaseous AgF and reported that the strongest feature is a continuum centered at about 303 nm (33,000 cm^{-1}) with two discrete bands to the red and a third band system below 260 nm. However, Timms[12] cocondensed Cu and Ag vapor with SF_6 at liquid nitrogen temperatures and reported that he could recover the SF_6 quantitatively with pure metal left behind. He found that SF_6 is also inert toward other transition metals. The possibility is still open that the broad spectra observed with Cu and Ag might be due in part to charge transfer to the SF_6 or to substitutional and interstitial site occupation by the smaller Cu and Ag atoms. If the assignment of the spectra around 333 nm to Ag atoms is accepted, one could also assign the band observed at 214.5 nm, which has no counterpart in the spectra of Ag trapped in rare gases[9,10] to a red shift of the strong 6p $^2P_{3/2,1/2} \leftarrow {}^2S_{1/2}$ transitions observed in the gas at 207.0 and 206.2 nm.

Additional studies of the more reactive metals isolated in SF_6 will be necessary to define the extent to which SF_6 can be used with strongly reducing species. SF_6 has been shown to be an excellent matrix for Au atoms and it has also been found to be a satisfactory matrix material for molecular species.[13,14] It is hoped that precooling of the gas along with slow deposition rates will make it possible to isolate a wide range of species in SF_6 matrices at liquid nitrogen temperatures.

Acknowledgments.—We wish to thank Professor C. W. Tobias for use of his liquid ammonia apparatus, Professor Joel Hildebrand for a sample of purified n-C_7H_{16}, and Professor Beat Meyer for his helpful suggestions. Gary Masada carried out the initial explorations of the reaction between SF_6 and potassium solutions as a Chemistry 106 project in the spring of 1966. This work was performed under the auspices of the U. S. Atomic Energy Commission.

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