Preparation and Characterization of Gold Pentafluoride

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Gold pentafluoride, AuF_5, has been prepared by the termal decomposition of $[O_2][AuF_5]$ *in vacuo*. Some reformation of $[O_2][AuF_6]$ occurs on the surface, suggesting that vapour transport is *via* AuF_5 and O_2F radicals since no evidence could be found for AuF_6. The sublimate also contains AuF_3, a decomposition product. More pure AuF_5 can be separated from the mixture by a second sublimation leaving AuF_3 as a residue. Each of the species AuF_5, $[O_2][AuF_6]$, and AuF_3 is distinguishable by its mass spectrum and Raman spectrum. AuF_3 and $[O_2][AuF_6]$ are crystalline, whereas AuF_5 prepared by double sublimation is amorphous. It is diamagnetic, and the Rman spectrum indicates that AuF_5 is a fluorine-bridged polymer. AuF_5 reacts with XeF_2 in anhydrous HF solution to form an insoluble adduct isomorphous with $[Xe_2F_3][IrF_6]$.

COMPLEX fluorides containing pentavalent gold as the $[AuF_6]^-$ anion have been prepared by Leary and Bartlett,[1] and characterized by *X*-ray diffraction, Mössbauer, and vibrational spectroscopy.[2,3] Evidence for the binary fluoride AuF_5, obtained from the thermal decomposition of $[O_2][AuF_6]$, has been reported.[4] Mass spectrometric measurements on the vapour phase pyrolysis products of $[O_2][AuF_6]$ showed $[O_2]^+$ ions appearing at oven temperatures of *ca.* 55 °C, and a series of gold fluoride ions with $[O_2]^+$ simultaneously at temperatures of *ca.* 150 °C.[4] The gold fluoride spectra resembled those of transition-metal pentafluorides, with relatively abundant dimer and trimer ions.[5] Vapour transport of the salt $[O_2][RuF_6]$ showed that $[O_2][RuF_6]$ could be recovered on a cold finger maintained at liquid-nitrogen temperature while RuF_5 was obtained if the substrate temperature was 0 °C.[6] These studies indicated a similar approach might provide bulk samples of a stable pentafluoride of gold, particularly since the gold fluoride spectrum could be obtained from a molecular-beam source between temperatures of 150 and 210 °C.

Here we report the preparation of gold pentafluoride by the vacuum decomposition of $[O_2][AuF_6]$, and the chemical and physical characterization of AuF_5.

The compound $[O_2][AuF_6]$ was prepared by heating gold powder with an excess of a 4 : 1 $F_2 : O_2$ mixture in a Monel reactor at 350—380 °C and a total pressure of *ca.* 8 atm for periods of 48—60 h. The dioxygenyl salt was decomposed between 160 to 200 °C, in a fused silica sublimation apparatus with a cold finger which was maintained at either 0 or 25 °C. The initial sublimations of $[O_2][AuF_6]$ were done with the apparatus connected to a molecular-beam source mass spectrometer,[6,7] with the cold finger held at liquid nitrogen temperature or at 0 °C. In experiments with a liquid-nitrogen cooled substrate, oxygen evolution was observed when the bath temperature reached 100 °C, and continued as the temperature was raised in excess of 180 °C. A small amount of dark red sublimate was observed, and no other gases evolved until the cold finger was warmed to room temperature when a relatively small amount of HF evolution occurred. Sublimation to a 0 °C cold finger yielded simultaneous evolution of O_2 and HF with the intensity of the O_2 signal more than ten times that of the HF signal.

Larger scale sublimations using 1—2 g of starting material were done with the fused-silica apparatus on a Monel vacuum line. Gas evolution began at 100 °C; sublimate was perceptible at bath temperatures of *ca.* 160 °C, and it was necessary to raise the temperature to nearly 200 °C to decompose all the $[O_2][AuF_6]$. The sublimation residue was determined to be AuF_3 by *X*-ray powder photography and mass spectrometry. This AuF_3 may be a result of the decomposition of $[O_2][AuF_6]$ or present as an impurity in the starting material.

The decomposition of $[O_2][AuF_6]$ may proceed sequentially *via* reactions (1) and (2) with attack of the vessel walls by the O_2F radical or by AuF_5. No direct evidence for the O_2F radical could be obtained mass spectrometrically. Reaction (3) most likely occurs at

$$[O_2][AuF_6] \longrightarrow AuF_5 + O_2F \qquad (1)$$

$$O_2F \xrightarrow{\text{wall}} O_2 + HF \qquad (2)$$

$$[O_2][AuF_6] \longrightarrow AuF_5 + O_2 + 1/2\ F_2 \qquad (3)$$

temperatures in excess of 180 °C, since both O_2 and F_2 are observed in the mass spectra above that temperature. Decomposition according to reaction (4) was not observed

$$[O_2][AuF_6] \longrightarrow O_2 + MF_6 \qquad (4)$$

for $[O_2][AuF_6]$, while it is the prevalent route[6] for the dioxygenyl salts of Ru, Rh, and Pt.

Recombination to $[O_2][AuF_6]$ can occur on the cold finger, and the extent of recombination depends upon the substrate temperature. The initial preparations of AuF_5 from a single sublimation of $[O_2][AuF_6]$ to a liquid-nitrogen cooled substrate yielded AuF_5 with a considerable amount of $[O_2][AuF_6]$. Sublimation to a 0 °C cold finger produced material which was paramagnetic at room temperature. Re-sublimation to a 0 °C substrate yielded a sample with a significantly

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reduced paramagnetic susceptibility. Although no $[O_2][AuF_6]$ could be detected in either of these last mentioned samples by Raman spectroscopy, a powder *X*-ray pattern for it was obtained; further O_2 was easily detected by mass spectrometry. An anisotropic e.s.r. spectrum was observed near $g = 2$ for both of these samples. This spectrum resembled that previously ascribed [8,9] to $[O_2]^+$ in $[O_2][AsF_6]$, $[O_2][BF_4]$, $[O_2][SbF_6]$, and $[O_2][Sb_2F_{11}]$. No other resonance was observed at *X*-band up to 14 kG. We conclude that the observed paramagnetism is due to $[O_2][AuF_6]$ impurity in diamagnetic AuF_5. The $5d^6$ Au^V in AuF_5 is therefore a low-spin configuration.

Multiple sublimations of AuF_5 to a substrate held between 23 and 27 °C yielded AuF_5 of sufficient purity to determine some of its physical and chemical properties with a high degree of confidence. Gold pentafluoride is a dark red solid which melts over the range 75—78 °C. No powder *X*-ray pattern could be obtained from this sample. It is diamagnetic at room temperature with a susceptibility of $-73 \pm 15 \times 10^{-6}$ e.m.u. mol^{-1}. The tables of diamagnetic core contributions would predict $\chi = -(75—80) \times 10^{-6}$ e.m.u. mol^{-1} in good agreement with the observed value.

Raman spectra were obtained using a Monel rotating cell [10] with a sapphire window and Kr^+ laser excitation at 6 471 Å. The Au–F symmetrical stretch occurs at 595 ± 2 cm^{-1}, an antisymmetrical stretching mode at 654 cm^{-1} and one of the bending modes is observed at 219 cm^{-1}. A broad weak band appears between 370 and 450 cm^{-1}, which is probably due to fluorine bridges. The $[O_2][AuF_6]$ spectrum was taken using Ar^+ laser excitation at 5 145 Å. The Au–F symmetrical stretch occurs at 598 ± 2 cm^{-1}, which is very close to that of AuF_5. The weak band between 370 and 450 cm^{-1} was absent in the $[O_2][AuF_6]$ spectrum.

Elemental analyses for gold were carried out by dissolving a weighed sample of AuF_5 in *aqua regia*, followed by a suitable dilution of the solution for atomic absorption measurements against known standards. Fluorine content was determined by a sodium carbonate fusion (using a large excess of sodium carbonate) followed by dissolution in water. The specific ion electrode was used to determine fluorine with the solution buffered at pH = 5 (Found: Au, 65.0; F, 32.3. Calc. for AuF_5: Au, 67.5; F, 32.5%). The upper and lower limits of the chemical formula calculated on the estimated errors in the analyses yield $AuF_{5.0}$ and $AuF_{5.2}$.

Mass spectra of comparable absolute intensities are given in Table 1 for AuF_3, $[O_2][AuF_6]$, and AuF_5. These spectra have been corrected for mass discrimination effects of the quadrupole mass filter. It is clear that AuF_5 can be distinguished from AuF_3 and the decomposition products of $[O_2][AuF_6]$ on the basis of its volatility and cracking pattern. Note that AuF_5 prepared by sublimation is more highly associated than AuF_5 that results from the effusion source decomposition of $[O_2][AuF_6]$. AuF_5 Is also more highly associated in the vapour phase than other pentafluorides such as PtF_5, IrF_5, or RhF_5. Table 2 gives the relative abundances of the monomer, dimer, and trimer ions for these compounds with mass spectra taken under very similar source conditions. Modulated molecular beam studies [7] of AuF_5 vapour showed that the Au^+ ion and the $Au_2F_7^+$ ion had no significant phase difference ($\Delta\Phi < 2°$) which means that they have a common neutral precursor. Consequently, AuF_5 vapours at 85—90 °C contain very little if any AuF_5 monomer. The ions Au^+, $Au_2F_5^+$, and $Au_2F_7^+$ did not refocus when an inhomogenous electric field was applied to the molecular beam.[7] Neutral precursors to these ions having dipole moments are therefore highly improbable.

TABLE 1

Relative abundance of ions from AuF_5, $[O_2][AuF_6]$, and AuF_3 at the specified temperature

Ion	AuF_5, 89 °C	$[O_2][AuF_6]$, 120 °C (A)	$[O_2][AuF_6]$, 120 °C (B) *	AuF_3, 255 °C
O_2	—	266	100	—
Au	100	100	37.6	100
AuF	8.2	9.6	3.6	7.7
AuF_2	6.3	9.4	3.6	6.3
AuF_3	3.5	11.0	4.1	1.5
AuF_4	1.2	6.5	2.5	—
AuF_5	—	—	—	—
Au_2	31.4	8.8	3.4	36.8
Au_2F	18.0	6.1	2.3	22.2
Au_2F_2	19.3	5.7	2.2	10.5
Au_2F_3	26.6	7.3	2.7	27.9
Au_2F_4	29.1	10.5	4.0	50.3
Au_2F_5	46.7	18.4	6.9	96.0
Au_2F_6	46.9	23.5	8.8	77.4
Au_2F_7	67.1	43.3	16.3	—
Au_2F_8	25.2	17.2	6.4	—
Au_2F_9	67.4	21.2	8.0	—
Au_2F_{10}	4.2	—	—	—
Au_3F_6	2.9	0.8	0.3	0.4
Au_3F_7	4.4	1.6	0.6	0.8
Au_3F_8	4.9	2.0	0.8	1.4
Au_3F_9	3.0	1.2	0.5	—
Au_3F_{10}	4.8	1.7	0.6	—
Au_3F_{11}	8.5	3.0	1.1	—
Au_3F_{12}	11.2	3.1	1.2	—

— Not detected.

* (A) Calculated with the intensity of Au^+ set equal to 100, for comparison with AuF_5 spectra. (B) Calculated with the most intense peak set equal to 100.

Approximately 0.5 ml of anhydrous HF was condensed onto a 2 : 1 solid mixture of XeF_2 and AuF_2 at −196 °C. (There was no apparent reaction between XeF_2 and AuF_5 when mixed in the solid phase.) The HF was allowed to melt under its own vapour pressure in a closed system. The solid phase began to dissolve at *ca.* 0 °C, and as the temperature approached ambient a yellow precipitate formed. The material recovered was

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TABLE 2

Comparison of oligomer ion abundances of the AuF_5 mass spectrum with other pentafluorides ; 70 V electron energy

Pentafluoride	Source temperature (θ_c/°C)	Orifice diameter (cm)	Monomer	Dimer	Trimer
AuF_5	89	0.040	0.31	1.0	0.10
PtF_5 *	93	0.025	1.0	0.14	5×10^{-3}
IrF_5 *	65	0.012	1.0	0.15	0.01
RhF_5 *	90	0.051	1.0	0.51	0.12

* Spectra taken from ref. 5.

a yellow-orange solid, which was found to be isomorphous with $[Xe_2F_3]^+[IrF_6]^-$ by *X*-ray powder photography.[11] Pyrolysis of this adduct in the molecular-beam mass spectrometer yielded only XeF_2 for source temperatures up to 50 °C. Above 60 °C a combination of XeF_2 and XeF_4 evolved, with XeF_4 increasing in relative amounts as the temperature increased. Gas evolution ceased between 145 and 200 °C, whereupon the mass spectrum of AuF_3 was detected. These findings are consistent with the adduct being $[Xe_2F_3]^+[AuF_6]^-$ with the following decomposition scheme:

$$[Xe_2F_3]^+[AuF_6]^- \longrightarrow XeF_2 + [XeF]^+[AuF_6]^- \quad (5)$$

$$[XeF]^+[AuF_6]^- \longrightarrow XeF_4 + AuF_3 \quad (6)$$

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