

Preparation and Characterization of Gold Pentafluoride

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Gold pentafluoride, AuF₅, has been prepared by the thermal decomposition of [O₂][AuF₆] *in vacuo*. Some reformation of [O₂][AuF₆] occurs on the surface, suggesting that vapour transport is *via* AuF₅ and O₂F radicals since no evidence could be found for AuF₆. The sublimate also contains AuF₃, a decomposition product. More pure AuF₅ can be separated from the mixture by a second sublimation leaving AuF₃ as a residue. Each of the species AuF₅, [O₂][AuF₆], and AuF₃ is distinguishable by its mass spectrum and Raman spectrum. AuF₃ and [O₂][AuF₆] are crystalline, whereas AuF₅ prepared by double sublimation is amorphous. It is diamagnetic, and the Raman spectrum indicates that AuF₅ is a fluorine-bridged polymer. AuF₅ reacts with XeF₂ in anhydrous HF solution to form an insoluble adduct isomorphous with [Xe₂F₃][IrF₆].

COMPLEX fluorides containing pentavalent gold as the [AuF₆]⁻ 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 AuF₅, obtained from the thermal decomposition of [O₂][AuF₆], has been reported.⁴ Mass spectrometric measurements on the vapour phase pyrolysis products of [O₂][AuF₆] showed [O₂]⁺ ions appearing at oven temperatures of *ca.* 55 °C, and a series of gold fluoride ions with [O₂]⁺ 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 [O₂]-[RuF₆] showed that [O₂][RuF₆] could be recovered on a cold finger maintained at liquid-nitrogen temperature while RuF₅ 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.

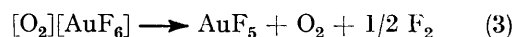
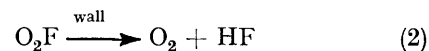
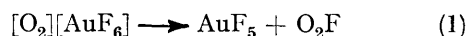
Here we report the preparation of gold pentafluoride by the vacuum decomposition of [O₂][AuF₆], and the chemical and physical characterization of AuF₅.

The compound [O₂][AuF₆] was prepared by heating gold powder with an excess of a 4 : 1 F₂ : O₂ 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 [O₂][AuF₆] 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

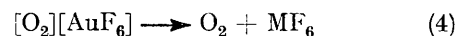
when a relatively small amount of HF evolution occurred. Sublimation to a 0 °C cold finger yielded simultaneous evolution of O₂ and HF with the intensity of the O₂ signal more than ten times that of the HF signal.

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 [O₂][AuF₆]. The sublimation residue was determined to be AuF₃ by X-ray powder photography and mass spectrometry. This AuF₃ may be a result of the decomposition of [O₂][AuF₆] or present as an impurity in the starting material.

The decomposition of [O₂][AuF₆] may proceed sequentially *via* reactions (1) and (2) with attack of the vessel walls by the O₂F radical or by AuF₅. No direct evidence for the O₂F radical could be obtained mass spectrometrically. Reaction (3) most likely occurs at



temperatures in excess of 180 °C, since both O₂ and F₂ are observed in the mass spectra above that temperature. Decomposition according to reaction (4) was not observed



for [O₂][AuF₆], while it is the prevalent route⁶ for the dioxygenyl salts of Ru, Rh, and Pt.

Recombination to [O₂][AuF₆] can occur on the cold finger, and the extent of recombination depends upon the substrate temperature. The initial preparations of AuF₅ from a single sublimation of [O₂][AuF₆] to a liquid-nitrogen cooled substrate yielded AuF₅ with a considerable amount of [O₂][AuF₆]. 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

¹ K. Leary and N. Bartlett, *J.C.S. Chem. Comm.*, 1972, 903.

² K. Leary, A. Zalkin, and N. Bartlett, *J.C.S. Chem. Comm.*, 1973, 131.

³ G. Kaindl, K. Leary, and N. Bartlett, *J. Chem. Phys.*, 1973, 59, 5050.

⁴ A. J. Edwards, W. E. Falconer, J. E. Griffiths, W. A. Sunder, and M. J. Vasile, *J.C.S. Dalton*, 1974, 1129.

⁵ W. E. Falconer, G. R. Jones, W. A. Sunder, M. J. Vasile, A. A. Muentzer, T. R. Dyke, and W. Klemperer, *J. Fluorine Chem.*, 1974, 4, 213.

⁶ M. J. Vasile and W. E. Falconer, *J.C.S. Dalton*, 1975, 316.

⁷ M. J. Vasile, F. A. Stevie, and W. E. Falconer, *Internat. J. Mass Spectrom. Ion Phys.*, 1975, 17, 195.

reduced paramagnetic susceptibility. Although no $[\text{O}_2][\text{AuF}_6]$ 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 $[\text{O}_2]^+$ in $[\text{O}_2][\text{AsF}_6]$, $[\text{O}_2][\text{BF}_4]$, $[\text{O}_2][\text{SbF}_6]$, and $[\text{O}_2][\text{Sb}_2\text{F}_{11}]$. No other resonance was observed at X -band up to 14 kG. We conclude that the observed paramagnetism is due to $[\text{O}_2][\text{AuF}_6]$ impurity in diamagnetic AuF_5 . The $5d^6 \text{Au}^{\text{V}}$ 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 cell¹⁰ with a sapphire window and Kr^+ laser excitation at 6471 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 $[\text{O}_2][\text{AuF}_6]$ spectrum was taken using Ar^+ laser excitation at 5145 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 $[\text{O}_2][\text{AuF}_6]$ 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 $\text{AuF}_{5.0}$ and $\text{AuF}_{5.2}$.

Mass spectra of comparable absolute intensities are given in Table 1 for AuF_3 , $[\text{O}_2][\text{AuF}_6]$, 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 $[\text{O}_2][\text{AuF}_6]$ 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

⁸ I. B. Goldberg, K. O. Christe, and R. D. Wilson, *Inorg. Chem.*, 1975, **14**, 152.

of $[\text{O}_2][\text{AuF}_6]$. 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 studies⁷ of AuF_5 vapour showed that the Au^+ ion and the Au_2F_7^- ion had no significant phase difference ($\Delta\Phi < 2^\circ$) which

TABLE 1

Relative abundance of ions from AuF_5 , $[\text{O}_2][\text{AuF}_6]$, and AuF_3 at the specified temperature

Ion	AuF_5 , 89 °C	$[\text{O}_2][\text{AuF}_6]$, 120 °C		AuF_3 , 255 °C
		(A)	(B) *	
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.

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 inhomogeneous electric field was applied to the molecular beam.⁷ Neutral precursors to these ions having dipole moments are therefore highly improbable.

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

⁹ F. J. Di Salvo, W. E. Falconer, R. S. Hutton, A. Rodriguez, and J. V. Waszczak, *J. Chem. Phys.*, 1975, **62**, 2575.

¹⁰ J. E. Griffiths, W. A. Sunder, and W. E. Falconer, *Spectrochim. Acta*, 1975, **A31**, 1207.

TABLE 2

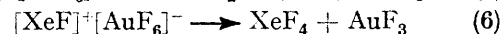
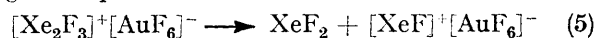
Comparison of oligomer ion abundances of the AuF₅ mass spectrum with other pentafluorides ; 70 V electron energy

Pentafluoride	Source temperature (θ _s /°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 [Xe₂F₃]⁺[IrF₆]⁻ by X-ray powder photography.¹¹ Pyrolysis of this adduct in the molecular-beam mass spectrometer yielded only XeF₂ for source temperatures up to 50 °C. Above 60 °C a combination of XeF₂ and XeF₄ evolved, with XeF₄ increasing in relative amounts as the temperature increased. Gas evolution ceased between 145 and 200 °C, whereupon the mass spectrum of AuF₃ was detected. These findings are consistent

with the adduct being [Xe₂F₃]⁺[AuF₆]⁻ with the following decomposition scheme:



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¹¹ F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. (A)*, 1969, 2179.