

Composition and Molecular Structure of Gaseous Gold Pentafluoride by Electron Diffraction

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Gaseous gold pentafluoride is mostly dimeric at the nozzle temperature of about 220 °C. However, a smaller amount of trimeric molecules is present. In both forms the gold atoms are surrounded by six fluorine atoms in distorted octahedral arrangements. Assuming the two forms to possess D_{2h} and D_{3h} symmetries, respectively, and to have equal Au–F bond distances, and assuming that the estimated root mean-square amplitudes of vibration are correct, least-squares refinements resulted in 81.9(1.0) % of dimers and $R(\text{Au}-\text{F}_{\text{a(axial)}})=1.889(9)$, $R(\text{Au}-\text{F}_{\text{t(terminal)}})=1.822(8)$ and $R(\text{Au}-\text{F}_{\text{b(bridged)}})=2.030(7)$ Å. The angles determined for the dimers and trimers, respectively, were $\angle(\text{F}_a-\text{Au}-\text{F}_a)=181.0(1.1)$ and $193.1(3.2)$, $\angle(\text{F}_t-\text{Au}-\text{F}_t)=92.3(1.7)$ and $75.3(6.5)$ and $\angle(\text{F}_b-\text{Au}-\text{F}_b)=80.1(0.5)$ and $115.7(1.1)^\circ$. The least-squares standard deviations are given in parentheses.

Gold in the oxidation state of +V as AuF_6^- salts¹ and as AuF_5^2 has been known for some years. The gaseous pentafluorides of Nb, Ta and Sb are mostly trimeric at nozzle temperatures in the range 20–60 °C.³ The results of an electron diffraction investigation of gaseous gold pentafluoride at the somewhat higher temperature of about 220 °C are reported in the present paper.

EXPERIMENTAL AND DATA REDUCTION

Gold obtained by reducing Au(III) by formaldehyde in HCl (the Zygmondi method) was oxidized by the stoichiometric quantity of KrF_2 in dry HF. The gold pentafluoride was obtained by distilling off the solvent at 40–50 °C.⁴ According

to chemical analysis the composition was $\text{AuF}_{5.02}$ and the vibrational spectrum agreed with the known one.⁵

The electron diffraction pattern was recorded using the improved apparatus of Moscow State University.⁶ No diffraction pattern could be observed below about 220 °C and the gold pentafluoride started to decompose at 250–300 °C. Vapour pressure measurements of the substance do not exist, the electron diffraction experiment indicates a vapour pressure of the magnitude 0.1 mmHg at the applied temperature. The optical densities of the photographic plates were measured by the Joyce-Loebl digital microphotometer of the University of Oslo. The experimental conditions are summarized in Table 1.

The data were treated in the usual way.⁷ The first backgrounds were determined by fitting a polynomial to the intensities from each single plate and the first average molecular intensities, $s M(s)$, were obtained using these experimental backgrounds. The backgrounds were later adjusted several times according to theoretical molecular intensities.⁸

The atomic scattering factor of F was computed⁹ at 74 kV from an analytical representation of the potential¹⁰ and the scattering factor of Au was obtained by interpolation of numerical tables¹¹ for the same voltage.

ESTIMATES OF u - AND D -VALUES

The root mean-square amplitudes of vibration u and the correction terms between the electron diffraction distances and the distances between the thermal average atomic positions, the D -values,

Table 1. Experimental conditions for the electron diffraction diagrams of gold pentafluoride at about 74 keV.

| | | |
|--|-----------------------|-----------------------|
| Camera distance (mm) | 616.465 | 193.673 |
| Wavelength (Å) ^a | 0.04352(4) | 0.04350(6) |
| Beam current (μA) | 5. | 5. |
| Nozzle temp. (°C) | 225(2) | 215(2) |
| Exposure time (s) | 30 | 80 |
| Blackness interval | 0.2–0.5 | 0.4–0.2 |
| Applied <i>s</i> -range (Å ⁻¹) | 2.0–12.0 ^b | 8.0–29.5 ^c |
| Number of plates | 4 | 4 |

^aFrom zinc oxide diffraction patterns. ^bIntervals of $\Delta s = 0.125 \text{ \AA}^{-1}$. ^cIntervals of $\Delta s = 0.25 \text{ \AA}^{-1}$.

were estimated from simple valence force fields. From the valence force field the symmetry force field and the transformation between symmetry and normal coordinates, the *L* matrix was obtained.¹² Au–F stretching force constants were adjusted to agree with experimental frequencies.^{4,13} The *u*- and *D*-values applied in the final least-squares refinement are given in Table 2. Only the values of the Au–F bond distances have been included.

STRUCTURE INVESTIGATION

The first experimental radial distribution function indicated the presence of dimeric molecules. Least-squares fit of a *D*_{2h} symmetric dimer resulted in a reasonable geometry. To obtain a satisfactory agreement for only this type of molecules, the *u*-values of the nonbonded Au···Au and Au···F distances had to be refined and the obtained values turned out to be much too large compared to the estimated ones. Attempts to increase the estimated *u*-values by reducing the torsional force constants of the ring did not explain the disagreement. However, fixing the *u*-values of the dimer on the originally estimated values, the

Table 2. Estimated *u*- and *D*-values (Å) for the Au–F bond distances of the two forms of gold pentafluoride at 220 °C.

| Distance | Dimer <i>D</i> _{2h} | | Trimer <i>D</i> _{3h} | |
|-------------------|------------------------------|----------|-------------------------------|----------|
| | <i>u</i> | <i>D</i> | <i>u</i> | <i>D</i> |
| Au–F _a | 0.0464 | –0.0125 | 0.0464 | –0.0175 |
| Au–F _t | 0.0443 | –0.0132 | 0.0443 | –0.0178 |
| Au–F _b | 0.0610 | –0.0032 | 0.0618 | –0.0027 |

experimental and theoretical functions showed large discrepancies in the range 3.0 to 3.7 Å. The theoretical function seemed to be missing a peak at about 3.6 Å. As this distance was somewhat longer than the Au···Au distance of the dimer, the missing peak might be due to the Au···Au distance of a smaller amount of trimeric molecules.

Least-squares refinements of a mixture of dimer and trimer readily converged to about 20% of trimeric molecules and the agreement improved very much. The *u*- and *D*-values of a *D*_{3h} symmetric trimer were then estimated. The backgrounds were adjusted, and further least-squares refinements showed that the initial constraint of equal Au–F bond distances of the two forms could not be relaxed. Refinement of the *u*-values of the Au···Au and the nonbonded Au···F distances of the dimer did not improve the agreement significantly and the changes from the estimated *u*-values were now small.

Results of the final least-squares refinement are given in Table 3 and illustrated in Fig. 1. The *D*_{2h} and *D*_{3h} symmetric models were satisfied by the thermal average atomic positions by correcting the

Table 3. Least-squares results and standard deviations for the composition and the parameters of the thermal average atomic positions of the two forms of gaseous gold pentafluoride at about 220 °C. The axial, terminal and bridged fluorine atoms are denoted F_a, F_t and F_b, respectively.

| Parameter ^a | Dimer <i>D</i> _{2h} ^b | Trimer <i>D</i> _{3h} ^b |
|--|---|--|
| Percentage | 81.9(1.0) | 18.1(1.0) ^c |
| $\Delta R \equiv R(\text{Au}-\text{F}_a)$ | | |
| – <i>R</i> (Au–F _t) | 0.067(16) | |
| <i>R</i> (Au–F _a) ^c | 1.889(9) | |
| <i>R</i> (Au–F _t) | 1.822(8) | |
| <i>R</i> (Au–F _b) | 2.030(7) | |
| $\angle(\text{F}_a-\text{Au}-\text{F}_a)$ ^d | 181.0(1.1) | 193.1(3.2) |
| $\angle(\text{F}_t-\text{Au}-\text{F}_t)$ | 93.3(1.7) | 75.3(6.5) |
| $\angle(\text{F}_b-\text{Au}-\text{F}_b)$ | 80.1(0.5) | 115.7(1.1) |
| $\angle(\text{Au}-\text{F}_b-\text{Au})$ ^c | 99.9(0.5) | 124.3(1.1) |
| <i>K</i> ₁ | 0.620(8) | |
| <i>K</i> ₂ | 0.657(32) | |
| <i>R</i> _f | 4.08 | |

^aDistances (Å) and angles (°). *K*₁ and *K*₂ are scale factors for the data of the long and short camera distance, respectively, and *R*_f (%) is a weighted agreement factor (eqn. 16 of Ref. 14). ^bThe Au–F bond distances had to be assumed equal in the two forms. ^cDependent parameters. ^dThe angles are defined in Fig. 1.

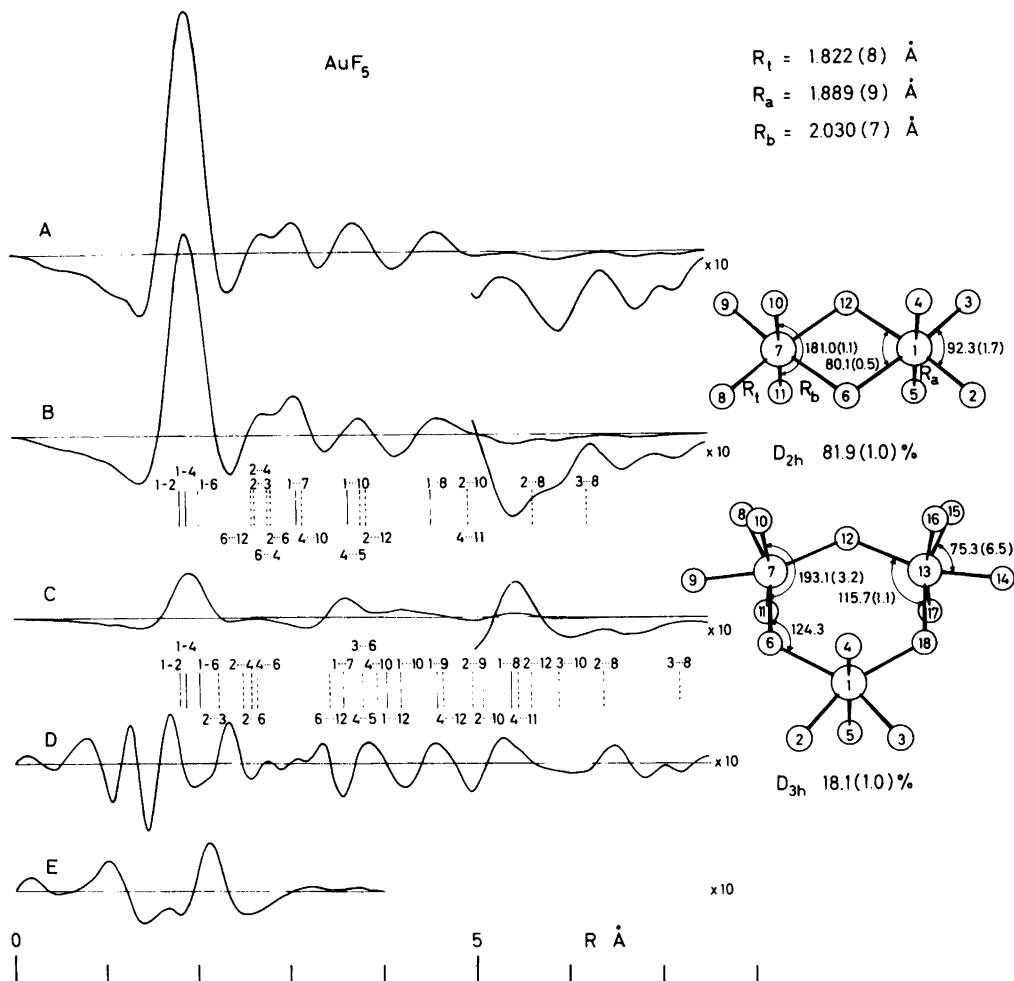


Fig. 1. A, B, C and E are radial distribution functions for gold pentafluoride for a damping function of $\exp(-0.006s^2)$. Theoretical intensities were added inside $s=2 \text{ \AA}^{-1}$ for the experimental function A. B and C are theoretical functions for 81.9 and 18.1 % of the dimer and trimer, respectively, according to the parameters of Table 3. The outer parts of the functions multiplied by a factor of 10 are also illustrated. D is the differences between the experimental and theoretical functions, $D=10(A-B-C)$, and E is the contribution from three atomic scattering from the dimer multiplied by 10. The different distances of the two forms are indicated with the F...F distances as broken lines.

electron diffraction distances according to the estimated D -values. The u -values were fixed on the estimated values, and a non-diagonal weighting matrix was applied.¹⁴ The three elements of the correlation matrix with absolute values greater than 0.70 were the elements $\Delta R/R(\text{Au}-\text{F}_j)$ of -0.94 , $R(\text{Au}-\text{F}_b)/\angle(\text{F}_b-\text{Au}-\text{F}_b)_{\text{dimer}}$ of 0.91 and $R(\text{Au}-\text{F}_b)/\angle(\text{F}_b-\text{Au}-\text{F}_b)_{\text{trimer}}$ of 0.73.

The theoretical intensities of the final least-squares refinement included contributions of three atomic scattering from the dimer according to the ITP₂ approximation,¹⁵ and the Fourier sine transformation of only these intensities is illustrated in Fig. 1. Leaving out these intensities, R_f increased to 4.85 % for the final parameters.

DISCUSSION

The agreement with the experimental data for the final least-squares refinement is satisfactory as shown by the *R*-factor of Table 3 and the difference curve D of Fig. 1. In the refinement the twelve independent parameters are determined from 168 points and the agreement should to some extent justify the different assumptions of the final refinement.

This agreement could not be obtained without including also a smaller amount of the trimeric form. An additional indication of the presence of this species is the small peak at about 5.4 Å of the experimental radial distribution function which is identified as the Au...F8 distance of the trimer. The conclusion that gaseous gold pentafluoride at the applied temperature consists of mostly dimeric and a smaller amount of trimeric molecules should be reliable. However, the composition and structure of the two forms may be less accurately determined than indicated by the standard deviations due to uncertainties in the assumptions of the least-squares refinement.

This result for the composition is in agreement with the mass spectrometric investigation of gaseous gold pentafluoride at 85–90 °C.¹³

The axial distances of AuF₅ seem to be longer than the terminal ones, and the average value of 1.856 Å is the same as the corresponding average of Xe₂F₁₁⁺AuF₆⁻.^{1b} For the trimeric pentafluorides of Nb and Sb no differences between these distances greater than one standard deviation could be determined while the value found in (TaF₅)₃ was 0.023(11) Å.

Assuming that the differences *R*_a–*R*_t really are small in (NbF₅)₃ and (SbF₅)₃, the terminal distances of the four pentafluorides are all in the narrow range from 1.810(2) for NbF₅ to 1.823(5) Å for TaF₅. The bridged distance of 2.030(7) in AuF₅ may be significantly shorter than the (TaF₅)₃ value of 2.062(2) Å while these distances of (NbF₅)₃ and (SbF₅)₃ are in between the two values given.

The metal–metal distances of the three previously investigated trimeric pentafluorides were between 3.95 and 4.04 Å. The Au...Au distances of 3.107(5) Å in the dimer and of 3.589(12) Å of the trimer are significantly shorter. Accordingly, the F_b–Au–F_b angle in the trimer of 115.7(1.1)° is significantly greater than the other four F_b–M–F_b angles with values slightly above 80°.

The axial atoms in (NbF₅)₃, (SbF₅)₃ and (TaF₅)₃

all showed a significant displacement towards the symmetry axis of the ring. This distortion is not observed in the two forms of AuF₅. Here the results indicate that a distortion, if any, is in the opposite direction.

Except for the nonplanar six-membered ring of (SbF₅)₃, the structures of the three previously investigated pentafluorides were all very similar. As shown in this discussion, gold pentafluoride differs from these structures in several ways. The most significant difference, at least from an experimental point of view, is the much shorter metal–metal distance in (AuF₅)₃.

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