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QUINQUEVALENT GOLD SALTS

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Contribution to Revue de Chimie Minérale

Quinquevalent Gold Salts

by

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We are honored to be able to dedicate this paper to Professor Wilhelm Klemm. Professor Klemm's pioneering work on high oxidation states of the transition elements and his continuing interest in such work suggested to us that description of the synthesis and properties of Au(V) salts would be an appropriate contribution in his honor.

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ABSTRACT

The preparation and some properties of AuF_6^- salts of each of the following cations is described: $Xe_2F_{11}^+$, XeF_5^+, K^+, Cs^+, NO^+, O_2^+ and IF_6^+. These salts show structural relationships to their noble-metal relatives. The diamagnetism of the AuF_6^- anion, its octahedral symmetry and its vibrational behavior, are in accord with the low-spin electron configuration $\underline{d}t_{2g}^6$ of the Au(V). The AuF_6^- ion is the smallest and most powerfully oxidizing MF_6^- species of the third transition series. From the magnetic susceptibility of $O_2^+AuF_6^-$, which obeys a Curie-Weiss relationship with $\Theta = 3°$, the magnetic moment of O_2^+ has been found to be 1.66 BM.

SbF_5 displaces AuF_5 from AuF_6^- and in IF_5 solution oxidation to IF_6^+ occurs (at 20°C):

$$IF_5 + AuF_5 + SbF_5 \longrightarrow IF_6^+SbF_6^- + AuF_3$$

INTRODUCTION

From a rationalization, several years ago, of the oxidizing properties of the third transition series hexafluorides, Bartlett concluded [1] that AuF_6 should be a superior oxidizer to PtF_6. Attempts to prepare AuF_6 directly from the elements failed, but these efforts [2] resulted in the isolation of material, the analysis of which indicated an oxidation state higher than Au(III). Au(III) was at that time the highest established gold oxidation state. The existence of PtF_6 (ref. [3]), PtF_5 and PtF_6^- salts [4], and Ag(III) complex fluorides [5], taken together with the usual periodic-table trends, also suggested that a higher oxidation state of gold than Au(III) should exist – at least in a fluoroanion.

It is generally true that a given high oxidation state is thermodynamically more stable in an anionic species than in a binary compound. Klemm and Hoppe recognized this when they synthesized [6,7] the alkali hexafluoronickelates(IV) and the hexafluorocobaltates(IV), neither NiF_4 nor CoF_4 being known then, or now! We note also that although PdF_6^{2-} salts have long been known [8] and are of high thermal stability, the corresponding binary fluoride PdF_4 requires strong oxidizing conditions for its synthesis [9] and is easily reduced. All of these observations are compatible with the electronegativity of the metal atom in the complex anion being appreciably lower than in the corresponding binary fluoride.

Our approach to the synthesis of higher oxidation state gold compounds, therefore, emphasized the generation of gold containing fluoroanions. Previously, we had found XeF_6 to be a moderately good fluoride-ion donor [10]. This property of XeF_6, combined with its rather low melting point of

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49.48°C [11] and the evident instability of XeF_8 [ref. 12], recommended it as the base and solvent for our initial AuF_6^- salt synthesis [13]:

$$2\ XeF_6 + AuF_3 + F_2 \longrightarrow Xe_2F_{11}^+AuF_6^-$$

Subsequently we found that a number of other AuF_6^- salts were readily obtainable from their AuF_4^- relatives by direct fluorination:

$$A^+AuF_4^- + F_2 \longrightarrow A^+AuF_6^-$$

This paper describes the preparation and some of the properties of the AuF_6^- salts.

EXPERIMENTAL

1. General Apparatus and Techniques

Most of the compounds used or prepared in this work are spoiled by water and many, including all of the AuF_6^- salts, are exceedingly strong oxidizers. All handling of materials was, therefore, carried out in the dry atmosphere of a Vacuum Atmospheres Corp., DRILAB, all containers and surfaces being either clean aluminum, Monel, Nickel, Kel-F, Teflon or quartz. Vacuum lines were constructed of Autoclave Engineers 30VM6071 Monel valves (rated to 30,000 psi) and the appropriate connectors. Normal working pressures were measured with Monel Helicoid gauges – one for the 0-1500 mm Hg range, and another for the 0-500 psi range. Pressures less than 1 mm Hg were measured with thermocouple and ion gauges which could be isolated from the system to avoid damage from corrosive chemicals.

For general synthetic work reaction vessels and small systems constructed of Kel-F, Teflon-FEP, quartz and Pyrex glass and equipped with Whitey IKS4 brass valves (Kel-F tipped stems) were used. Quartz and Pyrex apparatus was connected to the system using either graded seals and/or Kovar seals, or directly using bored out Swagelok unions (e.g., 10 mm glass was used with a nominal 3/8 in. union). Teflon ferrules were stretched over the glass tubing using gentle heat from a heat gun.

For high pressure and/or high temperature syntheses, reactions were carried out in autoclave bombs fabricated from Monel and provided with thick copper gaskets, capable of withstanding 500 atmospheres pressure at 600°C. These bombs were used with nickel liners to minimize corrosion and to facilitate handling the solid products in the drybox.

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2. Routine Characterization of Materials

Raman Spectroscopy. Routine Raman spectra were obtained on a Cary 83 Raman Spectrometer (488 nm). For higher resolution work, and for compounds sensitive to blue light, a Spex 1401 double monochromator, and a detection system that utilized photon counting techniques was used in conjunction with a variety of laser lines (principally 488, 514.5 and 647.1 nm). The spectrometer was coupled to an on-line computer which allowed the data to be collected, stored, corrected for phototube sensitivity, normalized and plotted. Powdered samples were loaded into 1 mm o.d. quartz capillaries in the DRILAB, sealed temporarily with a plug of Kel-F grease, and the tube drawn down and sealed in a small flame outside the drybox.

Infrared Spectroscopy. Infrared spectra were routinely obtained on a Perkin-Elmer 337 Grating Spectrometer over the range 400-4000 cm^{-1}. A 10 cm path length Monel cell with AgCl windows (1 mm thick) was used for gases. Spectra of solids were obtained as fine powders pressed between AgCl plates in a Kel-F holder.

X-Ray Powder Photography. X-ray powder diffraction patterns of solid samples were obtained with a General Electric Precision camera (Straumanis loading, graphite monochromatized CuK_α radiation). Finely powdered samples were sealed into 0.3-0.5 mm quartz capillaries as described under Raman spectroscopy.

Xenon Analyses. Xenon was determined using a Dumas nitrometer. Samples were loaded in the Drilab into previously dried and weighed thin-walled Pyrex capillary tubes, which were then sealed as described under Raman spectroscopy. The capillaries were cleaned of grease, reweighed,

and then inserted into the combustion tube of the nitrometer. The evolved gas was collected over 50% KOH solution previously saturated with xenon. Samples of XeF_2 were run to check the accuracy of the method. The nitrogen from the DRILAB present in the capillaries exaggerates the xenon content but usually does so by much less than 1%.

3. Reagent

Gold power (200 mesh) was used as supplied 99.9% pure by ROC/RIC Sun Valley, CA, U.S.A. Oxygen gas of reagent grade from the Pacific Oxygen Company, Oakland, CA., U.S.A., was purified by passing it through traps at -183°C. Fluorine gas, bromine trifluoride, bromine pentafluoride and iodine pentafluoride were obtained from the Matheson Company, East Rutherford, NJ., U.S.A. Volatile impurities were removed from the fluorine at pressures up to 2 atmospheres by trapping at -183°C. BrF_3, BrF_5 and IF_5 were purified by treatment with fluorine gas at room temperature followed by trap to trap distillation. Gas phase infrared spectroscopy was used to monitor their purity. Nitric oxide was supplied by the Matheson Company and was purified by fractional distillation. Its purity was checked using infrared spectroscopy. Cesium fluoride (Alfa Inorganic, Beverly, MA., U.S.A.) and potassium fluoride (Allied Chemical, Morristown, NJ., U.S.A.) were dried at 200°C and stored in the DRILAB. X-ray powder photography was used to check for absence of bifluoride and other impurities. Antimony pentafluoride of Spectrograde quality was used as supplied by Cationics, Inc., Cleveland, OH., U.S.A. Xenon difluoride was prepared using a method previously described [14], as were Nitrosyl Chloride (ref. [15]) and IF_5SbF_5 (ref. 15). BrF_3AuF_3 and AuF_3 were prepared using Sharpe's method [16]. The trifluoride was subsequently treated with F at 60 psi and 320° to remove any trace

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of bromide. $\underline{Cs^+AuF_4^-}$ and $\underline{K^+AuF_4^-}$ were prepared by dissolving equimolar amounts of CsF or FK and AuF_3 in BrF_3 solvent in a quartz reactor. $\underline{NO^+AuF_4^-}$ was prepared using a slight modification of Woolf's method [17], in which AuF_3 was used as a starting material instead of Au powder.

4. $\underline{Xe_2F_{11}^+AuF_6^-}$

Typically, 1.5 g AuF_3 (5.9 mmoles) and 3.0 g XeF_2 (17.8 mmoles) were placed in the removable nickel liner of a Monel autoclave. Fluorine gas (45.4 mmoles) was condensed into the 50 ml capacity autoclave which was then heated to 260° for 24 hr. After slowly cooling to room temperature, excess F_2 and XeF_6 were removed under vacuum, and the bomb was opened in the DRILAB, yielding a macrocrystalline yellow-green solid. This solid melted without decomposition in the range 145-150°C. It reacted explosively with water.

Analysis for Xe: Found: Xe, 33.2±0.4%. Required for $Xe_2F_{11}^+AuF_6^-$, Xe, 33.5%. X-ray powder photographs indicated $Xe_2F_{11}^+AuF_6^-$ to be isomorphous with $Xe_2F_{11}^+MF_6^-$, M = Ru, Ir, Pt. (refs. [10],[18]). A full single crystal X-ray structural analysis in space group Pnma confirmed the stoichiometry and provided the detailed structure, which has already been described [19].

5. $\underline{XeF_5^+AuF_6^-}$

$XeF_5^+AuF_6^-$ was prepared from $Xe_2F_{11}^+AuF_6^-$ by heating the 2:1 compound to 110°C under vacuum in a Kel-F trap. The 1:1 compound was purified by sublimation at this temperature, yielding a pale yellow-green solid which melted without decomposition to a clear greenish-yellow liquid at 190-192°C. This compound also reacted explosively with water.

Analysis for Xe gave Xe, 25.2±0.5% required for $XeF_5^+AuF_6^-$, Xe 24.4%

X-ray powder photographs showed that the 1:1 compound was not isomorphous with $XeF_5^+MF_6^-$ salts where M = Os, Ir, Pt, Ru but that it was isomorphous and nearly isodimensional with $XeF_5^+AsF_6^-$. (ref. [20]). Single crystal data [21] showed $XeF_5^+AuF_6^-$ to be monoclinic with a = 5.88(2)Å, b = 16.54(2), c = 8.35(2), β = 90.1(1)°, V = 812.1Å^3, z = 4, D_{calc} = 3.40 g/cm^3. Systematic absences indicated the space group $P2_1/C$. Pyrolysis of $XeF_5^+AuF_6^-$ gave no evidence for a 1:2 product (i.e., $XeF_5^+Au_2F_{11}^-$).

6. $CsAuF_6$, $KAuF_6$, $NO^+AuF_6^-$

Some samples of $CsAuF_6$ were prepared by interaction of CsF with an equimolar quantity of $Xe_2F_{11}^+AuF_6^-$. The intimate mixture was transferred to a small Monel crucible contained in a quartz tube. The mixture was heated to 110° under 1 atm dry nitrogen at which temperature reaction occurred. The evolved XeF_6 was removed under vacuum, leaving a pale yellow solid. $CsAuF_6$, $KAuF_6$ and $NO^+AuF_6^-$ were also prepared by direct fluorination of the respective AuF_4^- salt in a Monel bomb at 350° and 1000 psi F_2. All are pale yellow diamagnetic solids and are rhombohedral with the unit cell dimensions: $CsAuF_6$, a = 5.24(1)Å, α = 96.43(5)°; $KAuF_6$, a = 4.946(5)Å, α = 97.96(3)°; $NOAuF_6$, a = 5.05(1)Å, α = 98.82(5)°. Unit cell data for related salts are given in Table I. The infrared spectrum of solid $CsAuF_6$ showed one band at 640 cm^{-1} (assigned to ν_3 of AuF_6^-). Raman spectra are tabulated in Table II. $NO^+AuF_6^-$ decomposed at 400°C to yield $NO^+AuF_4^-$ and F_2. The reaction was performed in a Monel can, and the evolved F_2 was detected using KI. An IR spectrum of the gases produced showed no ONF or ONF_3 [22]. The $NO^+AuF_4^-$ was identified by its Raman spectrum and powder photograph.

7. Reduction of $NO^+AuF_6^-$ with NO

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The salt $NO^+AuF_6^-$ dissolved easily in IF_5 solution, contained in a quartz bulb, to yield a yellow-green solution from which the original salt could be recovered by removing the IF_5 under vacuum.

A solution of $NO^+AuF_6^-$ in IF_5 was exposed to nitric oxide gas at 0°C. An initial yellow turbidity was quickly transformed into a purple suspension. Removal of IF_5 by vacuum distillation left an almost black solid which X-ray powder photography proved to be a mixture of Au metal and the compound $NO^+IF_6^-$.

8. Preparation of $O_2^+AuF_6^-$

Typically, 0.50 g AuF_3 (1.97 mmoles) was placed in a nickel liner of a 50 ml prefluorinated Monel bomb, oxygen (18 mmoles) and fluorine (49 mmoles) were then condensed into the bomb which was subsequently heated to 500°C for 48 hr., then cooled slowly to room temperature. The product was a pale yellow-green solid. The X-ray powder photographs showed that $O_2^+AuF_6^-$ was rhombohedral, a = 5.00(1)Å, α = 99.95(5)°, and that it is similar to the rhombohedral form of $O_2^+PtF_6^-$ [23]. The data are given in Table III. The Raman spectrum is shown in Figure 1 and the data are included in Table II.

9. The Magnetic Susceptibility of $O_2^+AuF_6^-$

Magnetic measurements were made, with a 0.2265 g sample, over the temperature range 5 to 98.5°K using a Princeton Applied Research Corporation vibrating sample magnetometer. The magnetic standard was $HgCo(NCS)_4$. The data which are given in Table IV depart only slightly (and perhaps not significantly) from the Curie-Weiss relationship, $\chi_M = C/T+\theta$, with the Weiss constant θ = 3° and the magnetic moment μ = 1.66 BM.

10. Interaction of $O_2^+AuF_6^-$ with IF_5 and the preparation of $IF_6^+AuF_6^-$

Carefully purified IF_7-free iodine pentafluoride was melted onto

$O_2^+AuF_6^-$ contained in a quartz bulb. The gold salt dissolved in the IF_5 to yield a bright red solution as oxygen smoothly evolved at 20°C. As the reaction proceeded to completion the red color faded and a yellow precipitate developed. IF_5 was removed by vacuum distillation at ∿ 20°C to leave a yellow solid which was examined by X-ray powder photography and Raman spectroscopy which indicated two phases. The major phase was represented by X-ray powder pattern which closely resembled that of $IF_6^+AsF_6^-$, and indicated $IF_6^+AuF_6^-$. This was indexed on the basis of a cubic unit cell with a_o = 9.573Å, V = 877Å^3, z = 4, space group Pa3. The unit cell data for IF_6AuF_6 and IF_6AsF_6 are compared in Table V . The minor phase was AuF_3. The Raman spectrum confirmed the presence of AuF_3. The other features of the Raman spectrum were entirely consistent with those to be expected for IF_6AuF_6. The assigned spectrum, less the AuF_3 bands, is given in Table II. The relative intensities in the Raman spectrum and the X-ray powder photographs suggested that the IF_6AuF_6 was in much greater molar abundance than the AuF_3. The data are in harmony with the molar ratio required by the equation:

$$3IF_5 + 4O_2AuF_6 \longrightarrow 4O_2 + 3IF_6AuF_6 + AuF_3$$

11. Interaction of $KAuF_6$ and $CsAuF_6$ with IF_5 in the presence of SbF_5

$KAuF_6$ (80 mg, 0.23 mmoles) and $IF_5.SbF_5$ (200 mg, 0.46 mmoles) were agitated with ∿ 10 ml of IF_7-free IF_5 in a quartz bulb at room temperature until thorough mixing had occurred. The IF_5 was colored pale yellow, indicating some solubility of gold species, but a yellow solid remained in suspension. The IF_5 was removed by vacuum distillation and a yellow solid residue remained at 20°C. X-ray and Raman spectra confirmed that this

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solid contained AuF_3, $IF_6^+SbF_6^-$ and $KSbF_6$. These products indicate the following reaction:

$$K^+AuF_6^- + 2SbF_5 + IF_5 \longrightarrow KSbF_6 + IF_6SbF_6 + AuF_3$$

The salt $IF_6^+SbF_6^-$ was characterized by a cesium-chloride-type cubic unit cell for which a = 6.06(1)Å, V = 223Å^3, z = 1 and by the following Raman spectrum (frequencies in cm^{-1}, relative intensities in parentheses): 738(2), $\nu_2 IF_6^+$; 715(10), $\nu_1 IF_6^+$; 659(<10), $\nu_1 SbF_6^-$; 577(<2), $\nu_2 SbF_6^-$; 341(4), $\nu_5 IF_6^+$; 282(<2), $\nu_5 SbF_6^-$ (the intensities of the SbF_6^- relative to those of IF_6^+ are not known precisely because of the presence of $KSbF_6$ in the mixture. These properties are in excellent agreement with those recently given by Stein and his coworkers [24].

A similar reaction was carried out, with $CsAuF_6$ in place of $KAuF_6$, with parallel results.

12. <u>Displacement of AuF_5 from $Xe_2F_{11}^+AuF_6^-$ with SbF_5</u>

$Xe_2F_{11}^+AuF_6^-$, in a quartz container, dissolved in liquid SbF_5, on gentle heating, to give a red solution. A tube packed with potassium iodide was placed in series with the vacuum line to give indication of fluorine evolution. No F_2 gas evolution was observed from these solutions at temperatures up to 60°. Vacuum distillation yielded an orange distillate indicative of a volatile gold species, but attempts to fractionate this mixture failed. The residue remaining in the reactor was an orange solid. This gave an X-ray powder photograph very similar to that of $XeF_5^+Sb_2F_{11}^-$ and Raman spectra were suggestive of a mixed anionic species $[F_5Au\text{-}F\text{-}SbF_5]^-$ being present. The findings are consistent with the residue being a mixture of $XeF_5^+Sb_2F_{11}^-$ and $XeF_5^+AuSb\,F_{11}^-$.

In other experiments it was observed that heating of the mixtures to 100°C or more yielded gaseous fluorine. The residue in the reactor then also contained AuF_3.

13. The Raman spectrum of AuF_3

The Raman spectrum of AuF_3 proved to be valuable in the detection of that compound in reaction products (see 10, 11, 12) as well as in $O_2^+AuF_6^-$ preparations (see 8). The characteristic spectrum (with frequencies in cm^{-1} and relative band intensities in parentheses) is: 655(30), 643(15), 631(100+), 622(12), 538(2), 530(4), 438(16 broad), 253(16 broad), 212(2), 183(30 broad), 163(38), 79(28), 76(16), 73(15), 66(17), 58(15).

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DISCUSSION

Although the synthesis of AuF_6^- salts may be achieved by oxidative addition of F_2 to AuF_4^- at pressures of F_2 as low as 20 atmospheres (S.T.P.) and at a temperature of 250°C:

$$AuF_4^- + F_2 \xrightarrow[250°C]{F_2 \text{ press.}} AuF_6^-$$

it is clear, from the pyrolysis of $NOAuF_6$ at 400°C:

$$NOAuF_6 \xrightarrow{400°C} F_2 + NOAuF_4$$

that the thermodynamic stability of AuF_6^- salts is not great. Strong oxidizing capability is therefore to be expected for AuF_6^-.

The ready reduction by nitric oxide of $NOAuF_6$ dissolved in IF_5:

$$AuF_6^- + 5NO + 5IF_5 \xrightarrow{20°C} Au + 5NO^+ + 5IF_6^-$$

can be compared with the interaction of PtF_6^- with NO under comparable conditions [1]

$$NO + PtF_6^- \xrightarrow{20°C} NO^+ + PtF_6^{2-}$$

Although AuF_6^- is isoelectronic with PtF_6^{2-} the former is readily reduced and the latter is not. Of course, once reduction of AuF_6^- has occurred, it is not surprising that AuF_6^{2-} does not appear, since such a species should be considerably distorted, as a consequence of a low spin d^7 electron configuration. Thus AuF_6^{2-} would either disproportionate:

$$2AuF_6^{2-} \longrightarrow AuF_4^- + AuF_6^- + 2F^-$$

or dissociate:

$$AuF_6^{2-} \longrightarrow AuF_5^- + F^-$$

Indeed if a Au(IV) fluoroanion can be made it will surely be a five coordinate species.

In the salt O_2AuF_6 one has two powerfully oxidizing species, O_2^+ and Au(V), and the interaction of that salt with IF_5 shows both oxidizers at work. The observed stoichiometry of the spontaneous reaction at ambient temperature is:

$$3IF_5 + 4O_2AuF_6 \longrightarrow 3IF_6AuF_6 + 4O_2 + AuF_3$$

Other observations in these laboratories [25] indicate that the salt O_2AsF_6 dissociates in $XeOF_4$ solution ($XeOF_4$ and IF_5 are closely related compounds [12]) to yield a blood red solution of O_2F and AsF_5:

$$O_2AsF_6 \rightleftharpoons O_2F + AsF_5$$

Since neither $XeOF_6$ nor $XeOF_5^+$ is a thermodynamically favorable species [26] there is no further reaction in $XeOF_4$, but in IF_5 solution O_2AsF_6 oxidizes the solvent [25]:

$$2O_2AsF_6 + IF_5 \longrightarrow IF_6^+AsF_6^- + 2O_2 + AsF_5$$

The solution is again red as the reaction proceeds, but the initial reactants and final products are colorless. Again the transient color is attributed to O_2F, which presumably, oxidizes the IF_5 in a two step process:

$$2O_2F + IF_5 \longrightarrow IF_7 + 2O_2$$

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In the related O_2AuF_6 reaction with IF_5, the dissociation of the salt yields not only O_2F but AuF_5:

$$O_2AuF_6 \longrightarrow O_2F + AuF_5$$

and the red color of the solution can be attributed to either or both species. It is evident from the stoichiometry of the reaction that the AuF_5 must oxidize IF_5:

$$AuF_5 + IF_5 \longrightarrow IF_7 + AuF_3$$

This is also supported by our observation that $KAuF_6$ or $CsAuF_6$ oxidize IF_5 to IF_6^+ in the presence of SbF_5 at 20°C:

$$SbF_5 + AuF_6^- \longrightarrow SbF_6^- + AuF_5 ; \; AuF_5 + IF_4^+ \longrightarrow IF_6^+ + AuF_3$$

The Au(V) in this state is therefore comparable to O_2F or KrF_2 as an oxidizer [27]. Since IF_7 is a good fluorobase [28] it readily generates IF_6AuF_6:

$$AuF_5 + IF_7 \longrightarrow IF_6AuF_6$$

$$O_2AuF_6 + IF_7 \longrightarrow O_2F + IF_6AuF_6$$

We know that AuF_6^- is not capable of oxidizing IF_5 since $NOAuF_6$ can be recrystallized quantitatively from it.

Efforts to obtain AuF_5 from the elements or by oxidation of AuF_3 failed. Treatment of $Xe_2F_{11}^+AuF_6^-$ with a large molar excess of liquid SbF_5 did produce a red solution which, on vacuum distillation, yielded an orange-red distillate. No gaseous fluorine accompanied this change hence, it is safe to assume that AuF_5 co-distilled with SbF_5. Unfortunately we were unable to separate the AuF_5 component from SbF_5, and indeed, it is possible that these pentafluorides form μ-fluoro bridged compounds akin to $NbF_5.SbF_5$ (ref. [29]). Gold pentafluoride has, however, been isolated recently by Falconer and his coworkers [30]. They obtained it by collecting

AuF_5 on a cold finger from thermally dissociated O_2AuF_6. This material has physical properties which suggest a tetrameric μ-fluoro bridged structure which will be, presumably [31], like that of RhF_5 tetramer.

The X-ray crystal structure [19] of $Xe_2F_{11}^+AuF_6^-$ and the Mössbauer study of the AuF_6^- salts [32] attest to the octahedral geometry of AuF_6^-. A recent ^{19}F nmr study [26] of $Xe_2F_{11}^+AuF_6^-$ in BrF_5 solution has established a chemical shift, for the F ligands of AuF_6^-, of +109 ppm relative to $CFCl_3$, this is in harmony with a low spin dt_{2g}^6 electron configuration well separated energetically from any paramagnetic excited state.

It is evident from the unit cell volume data for the $CsMF_6$ salts, given in Table 1, that the AuF_6^- ion is smaller than PtF_6^- which is smaller than IrF_6^-. Indeed, Beaton [33] had earlier found that the formula unit volume for the series of $NOMF_6$ salts (in $Å^3$) decreases as follows: Ta, 133.4; Re, 130.8; Os, 129.8; Ir, 129.33; Pt, 129.25. Evidently this trend continues, AuF_6^- being the smallest MF_6^- ion in the third transition series.

The smallness of the AuF_6^- ion is presumably responsible for salts of this ion occasionally being isomorphous with AsF_6^- salts rather than the noble-metal relatives. The latter $A^+MF_6^-$ salts are usually based (except for small cation cases like Li^+ and Na^+) on an 8:8 coordination (CsCl type) whereas $A^+AsF_6^-$ salts commonly [34] adopt 6:6 coordination (NaCl type). From the data in Table V the AuF_6^- ion is seen to be some 5 to 7 $Å^3$ bigger than AsF_6^-.

The decrease in size of MF_6^- across the series parallels the decrease in effective volume of the hexafluorides and the same explanation applies (see ref. [1]). Briefly, as we proceed from TaF_6^- to AuF_6^-, the F ligands

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are subjected to the polarizing influence of an increasingly positive central atom. In step with the increase in nuclear charge there is an increasing population of the π^* molecular orbitals. These orbitals are the molecular-orbital equivalents of the crystal field dt_{2g} orbitals. Electrons in these orbitals, but poorly screen the effective nuclear charge of M. Therefore in crossing the series, from TaF_6^- to AuF_6^-, we pass from a bonding system, in TaF_6^-, of six sigma and three π bonds to one of six sigma bonds in AuF_6^- (the π^* orbitals being fully occupied). This accounts for the observed decrease in stretching frequency for the totally symmetric (A1g) vibration of the following species [35]:

ν_1 MF_6^- (cm^{-1}): Os, 690; Ir, 672; Pt, 647; Au, 595

Of course the increase in oxidizing power across the series is in harmony with the increasing effective nuclear charge of the central atom. Hence, from Ta to Au, the F ligand electrons are increasingly polarized towards the metal atom, particularly along each M-F bond axis. This pulling in of electron density along the M-F bond in the MF_6 series [1] reduces the van der Waals distances by contracting the electron cloud on the F ligand (the bond lengths are essentially constant). One anticipates a similar effect for the MF_6^- ions. Thus the F ligands in AuF_6^- ion should have less charge than in PtF_6^- and should have a smaller van der Waals radius. A suitably precise structural comparison of a AuF_6^- and PtF_6^- salt pair has not yet been made, but it is of interest that the Au-F bond length, of 1.86(1)Å, in $Xe_2F_{11}^+AuF_6^-$ (ref. [19]) is not significantly shorter than that of Pt-F = 1.82(2)Å, in $O_2^+PtF_6^-$ (ref. [36]), in spite of the volume of AuF_6^- being less than that of PtF_6^-.

There is, then, every reason to expect that the ionization potential of AuF_6^- should exceed that of PtF_6^-. The electron affinity of WF_6 has recently been determined from molecular beam experiments [37] to be 104.5 kcal $mole^{-1}$. Recent calorimetric measurements [38] have given $\Delta H°$ for the reaction $O_2^+(g)+PtF_6^-(g) \longrightarrow O_2^+PtF_6^-(c)$ to be -59 kcal $mole^{-1}$. From this the electron affinity of PtF_6 has been deduced to be $\sim$ 215 kcal $mole^{-1}$. The observed oxidizing properties of the hexafluoride series, [39], suggest a monotonic increase; hence we can estimate that the electron affinity increases by $\sim$ 23 kcal per unit increase in nuclear charge on M. If this relationship holds then the ionization potential of AuF_6^- should be $\sim$ 238 kcal $mole^{-1}$. Such an ionization potential would make the transfer of the electron from AuF_6^- to KrF^+ in $KrF^+AuF_6^-$ an energetically unfavorable process [40] and it even suggests that the same could hold true for $ArF^+AuF_6^-$. Unfortunately, however, we do not have an estimate of the stability of these salts towards fluoride ion transfer:

$$GF^+AuF_6^- \longrightarrow [GF_2] + AuF_5 \longrightarrow G + F_2 + AuF_5$$

and such decompositions could well be highly favored even at moderate temperatures. Nevertheless, there is the prospect that at very low temperatures it may be possible to fix argon as the salt $ArF^+AuF_6^-$. Since, however, ArF_2 is unlikely to exist [12] this poses a formidable synthetic problem.

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Bibliography

[1] Neil Bartlett, Angewandte Chemie, Int. ed., t. 7, 1968, p. 433.

[2] N. Bartlett and P. R. Rao, Abstracts, 154th Meeting of The American Chemical Society, 1967, k15, and P. R. Rao, Ph.D. Thesis, University of British Columbia, 1965.

[3] B. Weinstock, H. H. Claassen and J. G. Malm, J. Amer. Chem. Soc., t. 79, 1957, p. 5832.

[4] N. Bartlett and D. H. Lohmann, J. Chem. Soc., 1964, p. 619.

[5] R. Hoppe, Z. anorg. Chem., t. 292, p. 28.

[6] W. Klemm and E. Huss, Z. anorg. Chem., t. 258, 1949, p. 221.

[7] R. Hoppe, Rec. trav. chim., t. 75, 1956, p. 569.

[8] R. Hoppe and W. Klemm, Z. anorg. Chem., t. 268, 1952, p. 364.

[9] N. Bartlett and P. R. Rao, Proc. Chem. Soc., 1964, p. 393, and P. R. Rao, Alain Tressand and N. Bartlett, J. Inorg. Nuclear Chem., in press.

[10] F. O. Sladky and N. Bartlett, J. Amer. Chem. Soc., t. 90, 1968, p. 5316.

[11] F. Schreiner, D. W. Osborne, J. G. Malm and G. N. McDonald, J. Chem. Phys., t. 51, 1969, p. 4838.

[12] N. Bartlett and F. O. Sladky, in "Comprehensive Inorg. Chemistry", J. C. Bailar et al., eds., Pergamon Press, 1973, Vol. 1, pp. 213-330.

[13] K. Leary and N. Bartlett, J. Chem. Soc., Chem. Communs., 1972, p. 903.

[14] S. M. Williamson, Inorg. Syntheses, t. 11, 1968, p. 147.

[15] A. A. Woolf, J. Chem. Soc., 1964, p. 619.

[16] A. G. Sharpe, J. Chem. Soc., 1949, p. 2901.

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[17] A. A. Woolf, J. Chem. Soc., 1950, p. 1053.

[18] N. Bartlett, F. W. B. Einstein, D. F. Stewart and J. Trotter, Chem. Comm., 1966, p. 550.

[19] K. Leary, A. Zalkin and N. Bartlett, Chem. Comms., 1973, p. 131; Inorg. Chem., t. 13, 1974, p. 775.

[20] N. Bartlett, B. DeBoer, F. Hollander, F. O. Sladky, D. H. Templeton and A. Zalkin, Inorg. Chem., t. 13, 1974, p. 780.

[21] N. Bartlett and C. J. Adams, to be published; see also K. Leary and N. Bartlett, Abstracts 7th International Fluorine Symp., Santa Cruz, CA., 1973, paper I-32.

[22] N. Bartlett, J. Passmore and E. J. Wells, Chem. Comms., 1966, p. 214.

[23] N. Bartlett and D. H. Lohmann, J. Chem. Soc., 1962, p. 5253.

[24] F. A. Hohorst, L. Stein and E. Gebert, Hexafluoroiodine(VII) hexafluoroantimonate(V), $IF_6^+SbF_6^-$, to be published; L. Stein personnel communication to N. B.

[25] T. J. Richardson, Ph.D. Thesis, University of California, 1974; Lawrence Berkeley Laboratory Report LBL-3183, December 1974.

[26] K. Seppelt and N. Bartlett unpublished observations.

[27] D. E. McKee, C. J. Adams, A. Zalkin and N. Bartlett, J. Chem. Soc., Chem. Communs., 1973, p. 26. The report of $XeOF_5^+$ in this paper is wrong (ref. 26), but the report of the ability of KrF^+ to oxidize IF_5 to IF_6^+ at ca. -10°C is correct.

[28] F. Seel and O. Detmer, Z. anorg. Chem., t. 301, 1959, p. 113; N. Bartlett, S. P. Beaton and D. D. Gibler to be published.

[29] A. J. Edwards, Chem. Communs., 1970, p. 820.

[30] A. J. Edwards, W. E. Falconer, J. E. Griffiths, W. A. Sunder and M. J. Vasile, J. Chem. Soc., Dalton Trans., 1974, p. 1129; personal communication.

[31] B. K. Morrell, A. Zalkin, A. Tressand, and N. Bartlett, Inorg. Chem., t. 12, 1973, p. 2640.

[32] G. Kaindl, K. Leary and N. Bartlett, J. Chem. Phys., t. 59, 1973, p. 5050.

[33] S. P. Beaton, Ph.D. Thesis, University of British Columbia, 1966.

[34] D. Babel, Structure and Bonding, t. 3, 1967, p. 11.

[35] F. O. Sladky, P. A. Bulliner and N. Bartlett, J. Chem. Soc., A, 1969, p. 2179.

[36] J. A. Ibers and W. C. Hamilton, J. Chem. Phys., t. 44, 1966, p. 1748.

[37] C. D. Cooper and R. N. Compton, Abstracts, American Physical Society Meeting, Atlanta, Georgia, Dec. 5-7, 1975.

[38] P. Barberi and N. Bartlett to be published.

[39] Ref. [1] and N. Bartlett, S. P. Beaton and N. K. Jha, Chem. Communs., 1966, p. 168.

[40] N. Bartlett, Endeavour, t. xxxl, 1972, p. 107. The ionization potentials quoted for Kr and Ar on pp. 110-111 in this article are in error and should be 323 and 363 kcal mole^{-1} respectively. The values quoted for the electron affinities of KrF^+ and ArF^+ should therefore be appropriately modified.

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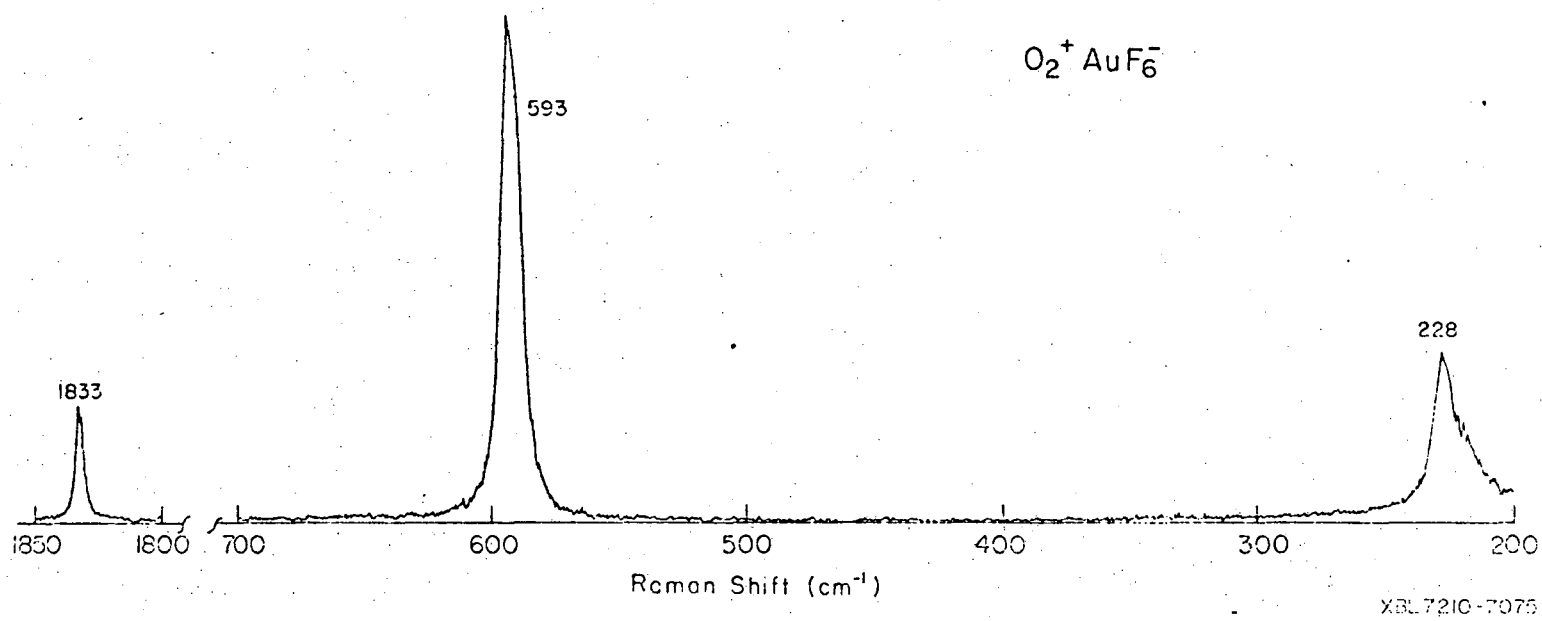

Figure 1. The Raman Spectrum of $O_2^+AuF_6^-$

Table I. Unit cell parameters for some AuF_6^- and related salts.

Compound	Struct Type	a(Å)	α(°)	V(Å^3)	Reference
$CsAsF_6$	R	5.2	96	138.4	1
$CsAuF_6$	R	5.24(1)	96.43(5)	141.3	This work
$CsPtF_6$	R	5.27	96.4	143.4	2
$CsIrF_6$	R	5.27	96.2	143.6	3
$CsOsF_6$	R	5.28	96.1	144.5	3
$CsReF_6$	R	5.28	95.9	144.7	4
$CsRuF_6$	R	5.27	96.4	143.4	5
$KAuF_6$	R	4.946(5)	97.96(3)	117.8	This work
$KPtF_6$	R	4.96	97.4	119.9	6
$KRuF_6$	R	4.97	97.4	119.4	7
O_2AuF_6	R	5.00(1)	99.95(5)	120.1	This work
O_2PtF_6	R	4.96	97.5	119.9	8
"	C	10.032		126.3	8
$NOAuF_6$	R	5.05	98.82(5)	124.5	This work
$NORhF_6$	R	5.02(1)	97.86(5)	123.4	9
$NOPtF_6$	R	5.03	97.6	123.5	10
"	C	10.112		129.5	11

R = Rhombohedral
C = Cubic

1. B. Cox, J. Chem. Soc. 876 (1956).
2. N. Bartlett and N. K. Jha, Noble Gas Compounds, H. H. Hyman, ed (Chicago Univ. Press, 1963), p. 23.
3. M. A. Hepworth, K. H. Jack and G. J. Westland, J. Inorg. Nucl. Chem. 2, 79 (1956).
4. R. D. Peacock, J. Chem. Soc. 467 (1957).
5. J. H. Holloway, P. R. Rao and N. Bartlett, Chem. Comm. 306 (1965).
6. N. Bartlett and D. H. Lohmann, J. Chem. Soc. 619 (1964).
7. R. Hoppe, Rec. Trav. Chim. 75, 569 (1956).
E. Weise and W. Klemm, Z. Anorg. u. Allgem. Chem. 279 74 (1955).
8. N. Bartlett and D. H. Lohmann, J. Chem. Soc. 5253 (1962).
9. N. Bartlett and P. R. Rao, unpublished observation.
10. N. K. Jha, Ph. D. Thesis, Univ. of British Columbia, 1965.
11. S. P. Beaton, " " " " , 1965.

0 0 0 0 4 4 0 0 8 0

Table II. Raman spectra of some AuF_6^- and AuF_4^- salts.
(Frequencies in cm^{-1}, relative intensities in parentheses)

Compound	$\nu_1 AuF_6^-$	$\nu_2 AuF_6^-$	$\nu_5 AuF_6^-$	Other Features
C_sAuF_6	595 (74)	530 (vvw)	225 (26)	ν_3 (IR data) = 640
$KAuF_6$	599 (63)		238 (20)	
			222 (6)	
$NOAuF_6$	597 (70)		230 (17)	V_{NO^+} = 2320 (vvw)
O_2AuF_6	593 (80)		228 (24)	VO_2^+ = 1833 (18)
IF_6AuF_6	595 (100+)		220 (85)	$\nu_1 IF_6^+$ = 750 (49), $\nu_2 IF_6^+$ = 726 (7), $\nu_5 IF_6^+$ = 344 (31), ref. (a)
$Xe_2F_{11}^+AuF_6$	590 (100)		232 (25)	See Ref. (b) for cation features
XeF_5AuF_6	591 (100)		230 (27)	" "
			226 (26)	
			220 (Sh,2)	

Compound	$\nu_1 AuF_4^-$	$\nu_4 AuF_4^-$	$\nu_3 AuF_4^-$	Other Features
$CsAuF_4$	588 (90)	561 (28)	237 (13)	
			230 (14)	
$NOAuF_4$	590 (100+)	555 (54)	270 (w,sh)	ν_{NO^+} = 2305 (12)
			228 (32)	

(a) K. O. Christe and W. Sawodny, Inorg. Chem. 6, 1967, p. 1783 and 9, 1970, p. 2801

(b) C. J. Adams and N. Bartlett, submitted to Inorg. Chem.

Table III.

X-ray powder data for $O_2^+[AuF_6]^-$

(rhombohedral, $\underline{a}$ = 5.00(1) Å, $\underline{\alpha}$ = 99.95(5)°, $\underline{V}$ = 120.1 Å^3, probable space group $R\bar{3}$, $\underline{Z}$ = 1)

h k l	$1/d^2$ Calc.	$1/d^2$ Obs.	Rel. Intensity
100	.0421	.0433	s
10$\bar{1}$	.0666	.0678	s
110	.1018	.1028	m
11$\bar{1}$	.1087	.1099	m
200	.1684	.1690	mw
20$\bar{1}$	.1753	.1776	mw
111	.1791		
2$\bar{1}\bar{1}$	.1998	.2013	mw
21$\bar{1}$	.2350	.2359	s
201	.2457	.2459	m
20$\bar{2}$	.2664	.2670	w
21$\bar{2}$	.3094	.3094	ms
211	.3406	.3402	w
30$\bar{1}$	.3682	.3685	w
22$\bar{1}$, 300	.3789	.3786	mw
220	.4072	.4066	vw
22$\bar{2}$	.4348	.4348	vw
30$\bar{2}$	.4417	.4436	w
31$\bar{1}$	.4455		
3$\bar{1}\bar{2}$	.4662	.4656	vw
310	.4738	.4738	vw
31$\bar{2}$	.5014	.5011	vw
212	.5197	.5186	vvw

0 0 0 0 4 4 0 0 8 0 9

Table IV. Magnetic susceptibility - temperature data for $O_2^+AuF_6^-$

Temp (°K)	5.0	5.0	6.0	9.7	12.0	15.0	15.3
$10^4\chi_M$ (cgs units)	553	576	464	258	208	169	176
Temp °K	19.8	24.0	29.5	29.5	34.8	34.8	40.7
$10^4\chi_M$ (cgs units)	136	114	97	100	84	89	78
Temp °K	50.2	60.6	71.1	83.5	98.5		
$10^4\chi_M$ (cgs units)	64	54	46	39	33		

Table V. A comparison of $XeF_5^+AuF_6^-$ and $IF_6^+AuF_6^-$ salts with related salts

salt	space group		unit cell dimensions (in Å units)	formula unit volume (Å^3)
IF_6AuF_6 [a]	Pa3		a_o = 9.573(1), z = 4	219
IF_6AsF_6 [b]	Pa3		a_o = 9.493(1), z = 4	214
IF_6MF_6 [c] (M = Ru, Ir, Pt)	$P2_1/n$	M = Ru:	a_o = 9.81(1), b_o = 7.61(1), c_o = 5.80(1), β = 107.8(1)°; z = 2	216
XeF_5AuF_6 [d]	$P2_1/c$		a_o = 5.88(2), b_o = 16.54(2), c_o = 8.35(2), β = 90.1(1)°; z = 4	203
XeF_5AsF_6 [e]	$P2_1/c$		a_o = 5.886(3), b_o = 16.564(10), c_o = 8.051(4), β = 91.57(3)°; z = 4	196
XeF_5MF_6 [f] (M = Ru, Ir, Pt)	Pnma	M = Ru:	a_o = 16.77(1), b_o = 8.21(1), c_o = 5.62(1), z = 4	193

0 0 0 0 4 0 0 8 1 0

Table V. (references)

(a) present work

(b) ref. 33 pp. 110-117, gives a structure determination of IF_6AsF_6 from X-ray powder data, from which the bond length I-F = 1.75Å and As-F = 1.67Å, all cis F-I-F angles being 90° and the AsF_6 ion slightly elongated rhombically with cis F-As-F = 86.5°.

(c) D. D. Gibler, Ph.D. Thesis, Princeton University, April 1973, published as Lawrence Berkeley Laboratory Report LBL-1157.

(d) ref. [21]

(e) ref. [20]

(f) N. Bartlett, F. Einstein, D. Stewart and J. Trotter, J. Chem. Soc., A, 1967, p. 478. N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell, and A. Zalkin, Inorg. Chem., 12, 1973, p. 1717.

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