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COMPOUNDS OF GOLD IN UNUSUAL OXIDATION STATES

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I. Introduction

Compared to the rich chemistry of the neighboring element platinum, the chemistry of gold has developed very slowly. With the advent of a new interest in the role of noble metals in catalysis, in microelectronics, and in pharmacology, gold and its compounds have become the focus of active research in a large number of laboratories throughout the world. New books (*77*, *84*) and review articles (*85*) witness this recent development and will stimulate further investigations.

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Some of the most exciting developments in gold chemistry were initiated by the discovery of unusual oxidation states. This new domain ranges from the rare −1 state in certain alloys of gold, through the gold clusters with nonintegral values between 0 and +1, through +2 in both mononuclear Au^{2+} and binuclear $[Au_2]^{4+}$ species, to +5 in binary or complex fluorides. Thus within only a very few years, there has emerged a much broader scope of the chemistry of gold, which was formerly represented only by Au metal, gold(I), and gold(III).

In this account, the new oxidation states are introduced in the format of a short, but it is hoped complete, summary covering the literature until late 1980. Some of the topics were reviewed previously, but the articles soon became out-dated because of the rapid growth of the fields. Best known are the discussion of gold(II) compounds (*13*) and the early presentation of gold(V) complexes (*5*). Gold clusters have been included in the leading reference texts on gold chemistry (*77, 85*), and the −1 state appeared in a recent summary on liquid metals and liquid semiconductors (*39*).

II. Compounds of Gold in Oxidation State −1

As a general rule, the chemistry of metal ions in solution is characterized by the ability to form *positive* ions. The stable *negative* metal ions are well characterized only in the gas phase (*43*). Mercury forms a monoatomic vapor and behaves like an inert gas in this respect. The gold atom, on accepting an electron, fills its 6s shell and is expected to be converted to the auride ion Au^-, whose electronic configuration is the same as that of Hg, $5d^{10}6s^2$. Further, the relatively high electron affinity of Au (2.4 eV) also suggests that it could behave like halogen atoms in forming negatively charged ions. This prediction has been realized, and a few alkali metal *aurides*, $[M]^+[Au]^-$, have been characterized.

As early as 1943, Sommer (*101*) reported the existence of a *stoichiometric compound* CsAu, exhibiting *nonmetallic* properties. Later reports (*53, 102, 103, 123*) confirmed its existence and described the crystal structure, as well as the electrical and optical properties of this compound. The lattice constant of its CsCl-type structure is reported (*103*) to be 4.263 ± 0.001 Å. Band structure calculations are consistent with observed experimental results that the material is a semiconductor with a band gap of 2.6 eV (*102*). The phase diagram of the Cs–Au system shows the existence of a discrete CsAu phase (*32*) of melting point 590°C and a very narrow range of homogeneity (*42*).

The conductivity measurements of *molten* CsAu (*42*) confirm the nonmetallic electronic structure. The dramatic drop of the electrical conductivity σ in the 50/50 region is shown in Fig. 1. The measurements of electrical transport properties, conductivity, and thermoelectric power of the *liquid Cs–Au alloy system* as a function of temperature and composition, as well as the electromigration studies, show that this liquid alloy consists essentially of Cs^+ and Au^- *ions* (*38, 56, 94*).

Further support for this ionicity comes from the recent Mössbauer (*122*) and ESCA (*55, 122*) spectroscopic measurements *of the solid.* The ESCA measurements of a series of gold compounds revealed (*55, 79, 89*) a monotonic relationship between binding energies of the Au ($4f\frac{7}{2}$) levels and formal oxidation states, and provided a reliable probe for the oxidation states for Au in its compounds. The photoelectron spectra of Au^-, Au^0 (metal), Au^+, Au^{2+}, and Au^{3+} compounds showed that the $4f\frac{7}{2}$ electron levels progressively shift to higher energy in the sequence Au^0, Au^+, Au^{2+}, and Au^{3+}, indicating the presence of Au^- in CsAu or RbAu (Fig. 2) (*55*). Both Cs and Au are classical metals with an electronegativity difference, according to the Pauling scale (*72*), that is characteristic of typical salts like CsI (*94*). Thus the Cs atoms appear to donate just one valence electron to each Au atom to fill its 6s shell, turning it into the Au^- ion. Similar results are obtained from a correlation of Mössbauer isomeric shifts and the electronegativity difference in a series of metal aurides (*122*).

Ultraviolet photoemission spectra have also been used to investigate the electronic band structure of *solid CsAu.* The apparent spin–orbit

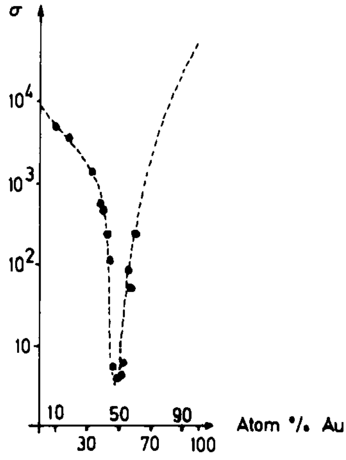


FIG. 1. Electrical conductivity σ [ohm^{-1} cm^{-1}] of liquid CsAu mixtures as a function of the gold content at 600°C (*39*).

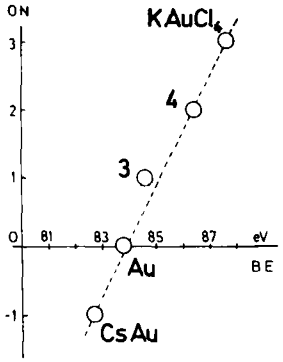


FIG. 2. Binding energy (BE) of the Au(4f $\frac{7}{2}$) level in compounds of different oxydation numbers (ON), from ESCA measurements (*55, 89*). (For compounds **3** and **4**, see Section IV,5).

splitting of the Au 5d orbitals is found to be 2.1 eV, i.e., 40% larger than in the Au atom. The results were correlated with theoretical calculations using the various relativistic methods (*37, 62, 70*).

Evaluation of intensities of X-ray diffraction patterns indicates that the CsCl structure is well ordered in crystalline CsAu. *Excess Cs,* which is the primary source for conduction electrons, is dispersed in the lattice with increase of the cell parameter (*105*). Cesium-133 NMR measurements (line shapes, Knight shifts, and relaxation times) confirm this result (*105*). The interpretation of the data for RbAu is less straightforward, however.

The existence of other alkali metal–gold compounds of the same stoichiometry, MAu, has also been reported. Spicer, *et al.* (*103*) investigated RbAu, KAu, and NaAu systems, and Kienast and Verma (*53*) showed the existence of stable phases at the RbAu and KAu stoichiometries. Other alkali metal–gold compounds of different stoichiometries, such as Li_3Au, Li_4Au_5, Na_2Au, $NaAu_2$, NaAu, K_2Au, KAu_2, KAu, KAu_5, RbAu, $RbAu_2$, and $RbAu_5$ also exist (*53, 78*).

Recent mass spectral studies confirm the presence of CsAu molecules in the *gas phase.* From the appearance potentials and the slope of the ionization curve, a dissociation energy of 460 kJ mol^{-1} was deduced, which agrees well with predicted values for a largely ionic bond. It is also very similar to the value arrived at for CsCl, 444 kJ mol^{-1} (*19a*).

More recently, Peer and Lagowski (*75*) presented spectroscopic and electrochemical evidence for the existence of Au^- ions *in liquid ammonia.* This is the only example of a transition metal *anion* in any solvent. In a simple yet elegant technique, the solutions of auride ion, Au^-, could be prepared by the dissolution of metallic gold in ammonia solutions of Cs, Rb, or K, but not in those of Na, Li, Sr, or Ba. The Au^- was shown to be stable even in the absence of any solvated electron. This work also is enlightening with respect to early unexplained results by Zintl *et al.* (*124*), who showed that *two* equivalents of sodium are required in a titration of AuI in liquid ammonia!

III. Compounds of Gold in Fractional Oxidation States: Gold Clusters

Reports of a strong intermetallic bond in the Au_2 molecule in the gas phase (*65*) and the stability of R_3PAuX compounds, prompted Malatesta (*65*) to attempt the synthesis of compounds of the type $R_3P—Au—Au—PR_3$ by reduction of R_3PAuX with suitable agents, e.g., $NaBH_4$ in EtOH, KOH in MeOH, or $LiAlH_4$ in THF. However, instead of the expected compounds of gold(0), novel clusters of gold were obtained containing Au_6, Au_9, and Au_{11} units, depending on the nature of X and R_3P. These compounds appear to have the metal formally in a nonintegral oxidation state between 0 and +1, and X-ray analysis shows their structures to be closely related to that of the boranes and carboranes (*68*). Most of the cluster molecules or ions are stable to air and water and are easily characterized by modern physical techniques, although yields of most preparations are low.

Application of other synthetic techniques, predominantly metal vapor methods, have added other cluster stoichiometries to this list, which presently includes Au_5, Au_6, Au_8, Au_9, and Au_{11}. The few examples for Au_2 (*3, 69*), Au_3 (*30*), and Au_4 (*36, 76*) will not be considered here, since they do not involve gold in unusual oxidation states. The sections are ordered according to the cluster size, although, historically, the Au_{11} moiety was the first to be detected (*65*).

A. A CLUSTER WITH AN Au_5 CORE

A cluster containing five gold atoms has been prepared by the evaporation of metallic gold into an ethanolic solution of bis(diphenylphosphino)methane (dppmH) and NH_4NO_3. Different mole ratios were used, all of which resulted in the formation of the cation $[Au_5(dppmH)_3(dppm)]^{2+}$. The nitrate forms red crystals, which were shown by X-ray diffraction studies to be composed of NO_3^- anions and cations of the structure shown in Fig. 3 (*108*).

Although the crystals are sensitive to X-ray irradiation, the structure could be refined to satisfactory *R* values. The Au_5 skeleton can be described as a tetrahedron of four Au atoms with the fifth Au atom

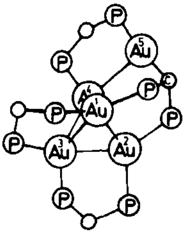


FIG. 3. Cluster structure of the cation in $[Au_5(dppmH)_3(dppm)]^{2+}(NO_3^-)_2$, as determined by X-ray diffraction. Hydrogen atoms and phenyl groups are omitted (*108*).

being attached to Au(4). A dppmH and a dppm ligand bridge Au(2) and Au(4) with Au(5). The dppm ligand has lost a proton from the CH_2 bridge and is attached to Au(5) through its carbon atom. A similar metal–ligand interaction of dppm is known from only very few other examples (*91*). The compound with its formal oxidation state +0.60 for Au is diamagnetic. Mössbauer spectra and ^{31}P NMR are also available but as yet unpublished (*108*). The structure has not yet been related to existing theoretical models.

B. A CLUSTER WITH AN Au_6 CORE

Reduction of $(4\text{-}CH_3{-}C_6H_4)_3PAuNO_3$ by $NaBH_4$ in ethanol (molar ratio 4 : 1) yields a red solution from which a tetraphenylborate salt of the cation $\{[(4\text{-}CH_3{-}C_6H_4)_3PAu]_6\}^{2+}$ can be precipitated in the form of yellow crystals as a small by-product. [The main product appears in the form of red crystals, originally not further specified (*10, 12*).] The X-ray diffraction analysis gave the cation structure shown in Fig. 4.

The core of the cation is an octahedron of gold atoms (formal oxidation state +0.33) with a crystallographic center of symmetry. The six independent edges of the polyhedron can be divided into two classes: two opposite faces, related by the inversion center, have long edges, while the remaining edges are shorter (3.073 and 2.965 Å, respectively). Each of the Au atoms bears one phosphine ligand (*10, 12*). It is

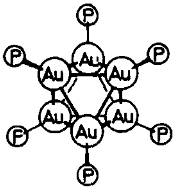


FIG. 4. Cluster structure of the cation in $[Au_6(P(C_6H_4\text{-}CH_3)_3)_6]^{2+}[B(C_6H_5)_4^-]_2$, as determined by X-ray diffraction; p-tolyl groups are omitted (*10*).

important to point out that the presence of hydrido ligands at or even in the cluster cannot be ruled out completely. However, this is rather improbable in view of the crystal stability: the samples were completely stable in air. The only other coinage metal cluster of six atoms has the composition $[HCuP(C_6H_5)_3]_6$ (*17*).

Au_6 clusters with chelating ligands were also synthesized, but are not yet structurally characterized (*68a,b*).

A molecular orbital scheme has been proposed for the $[L_6Au_6]^{2+}$ clusters, which shows that the gold 6s orbitals make the dominant contribution to the bonding. Coordination of ligands to the metal clusters encourages a more favorable hydridization of the metal orbitals and results in stronger radial metal–metal bonding (*8, 68*). The distortion of the octahedron is believed to remove orbital degeneracy in the highest occupied molecular orbital (HOMO) and to give rise to a singlet ground state and diamagnetic properties. Unfortunately, the magnetic properties have not yet been studied, because of insufficient sample quantities.

C. CLUSTERS WITH AN Au_8 CORE

A complex of the type $[(C_6H_5)_3PAu]_8^{2+}\ 2NO_3^-$ is prepared on treatment of $[[(C_6H_5)_3P]_8Au_9](NO_3)_3$ (see Section III,D) with an excess of $P(C_6H_5)_3$ in methanol. The octahydrate can be precipitated in 80% yield by addition of diethyl ether. The red product is recrystallized from CH_2Cl_2 and diethyl ether, and the corresponding picrate, alizarinsulfonate (aliz), hexafluorophosphate, perchlorate, and tetraphenylborate were obtained by metathetical exchange. The compounds were formulated as $[L_8Au_8]Y_2$ on the basis of analysis, conductivity measurements, ^{1}H-NMR spectroscopy, and crystallographic determination of molecular structure (*66*).

In an independent and probably simultaneous study, the above reaction of excess ligand with the Au_9 cluster was carried out in CH_2Cl_2 and followed by ^{31}P-NMR spectroscopy. The equation

$$[L_8Au_9]^{3+} + 2L \rightarrow [L_8Au_8]^{2+} + [LAuL]^+ \qquad (1)$$

was found to account for both product distribution and yields. The product composition $[L_{10}Au_9]^{3+}$ suggested earlier (*117*) was thus ruled out and discarded (*66, 107*).

The crystal structures of $\{[(C_6H_5)_3P]_8Au_8\}(aliz)_2$ (*66*) and of $\{[(C_6H_5)_3P]_8Au_8\}(PF_6)_2 \cdot 2CH_2Cl_2$ (*118*) were determined and the results are in excellent agreement. The structures of the cations are shown in Figs. 5 and 6. The core is a gold-centered cluster with one ligand bonded

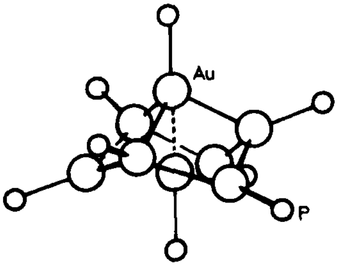


Fig. 5. Cluster structure of the cation $[Au_8(PPh_3)_8]^{2+}$ in the alizarinsulfonate, as determined by X-ray diffraction. Phenyl groups are omitted (*66*).

to each metal atom. It is related to the Au_{11} cluster by the removal of the three gold atoms of the basal triangle (see Section III,E).

D. The Two Types of Au_9 Clusters

A first set of $[(R_3P)_8Au_9]X_3$ cluster compounds, with R = C_6H_5 and 4-CH_3—C_6H_5 and X = NO_3, PF_6, BF_4, or picrate, was synthesized by $NaBH_4$ reduction of R_3PAuNO_3 complexes in ethanol, with metathesis to introduce other anions where necessary. The compounds are green, diamagnetic, crystalline solids, and are best obtained when X has very poor coordinating properties, if any (*9, 23, 65*). Seven members of this series have been prepared, and the species with R = 4-CH_3—C_6H_4 and X = PF_6 has been investigated by X-ray diffraction. The structure of the cation is shown in Fig. 7. In this cluster, a central gold atom is bound to eight peripheral gold atoms, each attached to a phosphine ligand. The center–periphery distances fall in the ranges 2.689(3) and 2.729(3) Å; peripheral distances are around 2.752(3) and 2.868(3) Å, all being shorter than in gold metal (2.884 Å). The geometry may be con-

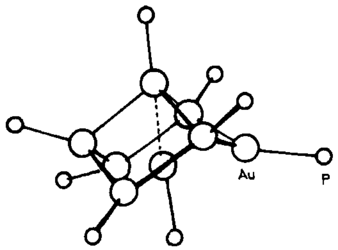


Fig. 6. Cluster structure of the cation in $[Au_8(PPh_3)_8]^{2+}(PF_6^-)_2 \cdot 2CH_2Cl_2$, as determined by X-ray diffraction. Phenyl groups are omitted (*118*).

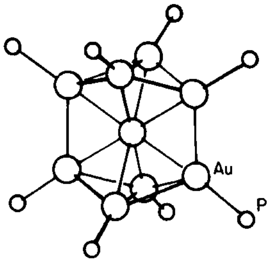


FIG. 7. Cluster structure of the cation in $\{Au_9[P(C_6H_4{-}CH_3)_3]_8\}^{3+}(PF_6^-)_3$, as determined by X-ray diffraction (*9*).

sidered as that of a centered icosahedron from which an equatorial rectangle (two pairs of adjacent vertices from opposite sides) has been removed (*65*).

Extended Hückel molecular orbital calculations give a diamagnetic closed-shell electronic ground state (^1A_g) with a HOMO/LUMO (lowest unoccupied molecular orbital) gap of 1.7 eV. Computer limitations prevented a full calculation, but the dominant role of the Au 6s orbitals for cluster bonding suggests a simpler and computationally less demanding model (*68*). In X-ray photoelectron (*8*) and Mössbauer spectra (*116*), there is only limited evidence for gold in different coordination sites. $\{[(C_6H_5)_3P]_8Au_9\}(NO_3)_3$ reacts with Cl^-, Br^-, I^-, SCN^-, and CN^- in methanol at −50°C to form the metathesis products, which were characterized by ^{31}P-NMR and Mössbauer spectroscopy (*115, 117*). Surprisingly, no separate Mössbauer line is observed for the central gold atom. The isomer shift and quadrupole splitting for the peripheral atoms are similar to those in Au_{11} clusters (see Section III,E).

Solutions of the halides and pseudohalides in CH_2Cl_2 are unstable, and the complexes are transformed into Au_{11} clusters or—in the presence of excess ligand—to Au_8 clusters (see Section III,C) (*66, 107, 117*).

The first *neutral* Au_9 cluster was prepared by reduction of tri(cyclohexyl)phosphinogold(I) thiocyanate, $(c\text{-}C_6H_{11})_3PAuSCN$, with $NaBH_4$, and crystallization from heptane/CH_2Cl_2 as red crystals, dec. 129°C. Its ^{31}P-NMR spectrum shows only one signal at $\delta = 73$ ppm. The structure was determined by X-ray diffraction, and the result is shown in Fig. 8 (*26*). The formula is thus $[(c\text{-}C_6H_{11})_3P]_5Au_9(SCN)_3$. Gold atoms Au(2), Au(6), and Au(8) are attached to sulfur; Au(1), Au(3), Au(4), Au(5), Au(8), and Au(9) to phosphorus; and the central atom Au(7) bears no ligand. The structure can be derived from the icosahedral framework by removing a triangular set of vertices and one of the opposite gold atoms.

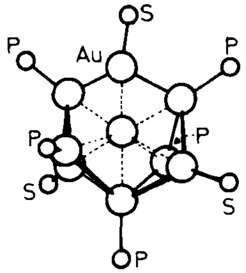


FIG. 8. Cluster structure of the molecule $\{Au_9[P(c\text{-}C_6H_{11})_3]_5\}(SCN)_3$, as determined by X-ray diffraction. Cyclohexyl and CN groups are omitted (*26*).

E. CLUSTERS WITH AN Au_{11} CORE

Compounds of the composition $L_7Au_{11}X_3$ were the first gold clusters to be discovered (in 1966) (*65*). They are obtained by reduction of LAuX complexes, where X = I, CN, or SCN. Seven members of the series with L = $P(C_6H_5)_3$, $P(C_6H_4\text{-4-}CH_3)_3$, $P(C_6H_4\text{-4-}Cl)_3$, or $P(C_6H_4\text{-4-}F)_3$, and X = SCN or CN, were fully characterized, and the structures of $\{[(C_6H_5)_3P]_7\text{-}Au_{11}\}(SCN)_3$ and $[(4\text{-}Cl\text{—}C_6H_4)_3P]_7Au_7I_3$ have been determined. The common feature of the two structures, a gold-centered Au_{11} core, is shown in Fig. 9 (*2, 11, 22, 67*). The center–periphery distances are 2.68 Å and the peripheral distances 2.98 Å. Each peripheral Au atom bears one L or X ligand. The cluster geometry is derived from an icosahedron through replacement of three atoms at the vertices of a triangular face by one atom at the center of the missing face. Space group and unit cell data are available for three other crystalline compounds (*2*).

Cluster compounds with an Au_{11} core can also be synthesized by the metal vaporization technique. Ethanol films containing L and LAuX at

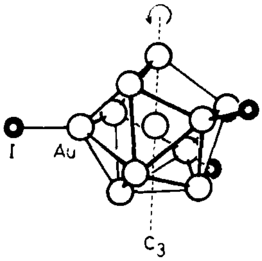


FIG. 9. Cluster structure of the molecule $\{Au_{11}[P(C_6H_4\text{—}Cl)_3]_7I_3\}$, as determined by X-ray diffraction. Phosphine ligands are omitted (*2*).

$-100°C$ give good yields of the products when exposed to Au vapor at 10^{-2} torr (*116*). Mössbauer spectra of the Au_{11} clusters exhibit a set of resonance doublets in agreement with the above structure, though assignments are not straightforward (*116*). X-Ray photoelectron spectroscopy failed to give direct evidence for metal atoms in different coordination sites, however.

The Au($4f_{\frac{7}{2}}$) binding energies of ~ 83.7 eV may be correlated with the low oxidation state of +0.27 (*8*). The values for the $L_8Au_9X_3$ compounds are similar (84.4 eV).

Molecular orbital calculations (*68*) give a closed-shell electronic ground-state configuration ($^1A_1$) for an idealized C_{3v} geometry. Other geometrical approaches give slightly modified results. The calculated charge densities show significant differences for the five different sites of the cluster.

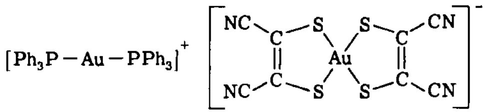
IV. Compounds of Gold in Oxidation State +2

A. INTRODUCTION

A critical examination of the ionization potentials of the members of group IB—i.e., Cu, Ag, Au—shows that, to attain tervalency, less energy is required for Au than for Cu and Ag. However, more energy is required to reach the Au^{2+} ion starting from the uncharged atom than for either Cu or Ag. In addition, the ligand field factors are significant. In d^9 metal complexes with either a tetragonally distorted octahedral or square planar structure, the odd electron is in the $d_{x^2-y^2}$ orbital, and because of greater ligand field splitting (~80% greater) in the case of Au as compared to Cu, this orbital has a much higher energy so that the odd electron in Au^{2+} can be easily ionized. It is not surprising, therefore, to observe that divalent Au compounds readily disproportionate to species in monovalent and trivalent states.

B. PSEUDO-GOLD(II) COMPOUNDS

A large number of complexes originally believed to contain Au(II) were later proved to be mixed-valence systems containing equal proportions of linear two-coordinate Au(I) and square-planar tetracoordinate Au(III) species. Thus, $CsAuCl_3$ (*33*), $(PhCH_2)_2SAuCl_2$ (*18, 25, 40*), AuCl(dmg) (dmg = dimethylglyoxime) (*81*), and AuBr(n-Bu_2NCS_2) (*16*) are all mixed-valence gold compounds. Also, typically, $Ph_3P \cdot Au(S_2C_2(CN)_2)$ is an Au(I)/Au(III) salt (**1**) with a linear Au(I) cation and a square-planar complex Au(III) anion (*14*). The situation is analogous with the related "mnt" complex:



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$[(Ph_3P)_2Au]^+[(mnt)_2Au]^-$, mnt = maleonitriledithiolate)

A similar situation probably exists in the following cases: $AuSO_4$ (*95*), AuO (*57*), AuS (*13*), $(PhCH_2)_2SAuX_2$ (X = Br, I) (*99*), $(nb)_x \cdot Au_2Cl_4$ (nb = norbornadiene; x = 1, 2, or 3) (*44*). See the accompanying tabulation.

Stoichiometry	Mixed-valence formula
AuO	$Au(I)/Au(III)O_2$
AuS	$Au(I)/Au(III)S_2$
$AuSO_4$	$Au(I)/Au(III)(SO_4)_2$
$CsAuX_3$ (X = Cl, Br, I)	$Cs_2(AuX_2)(AuX_4)$
$(PhCH_2)_2SAuX_2$ (X = Cl, Br)	$(PhCH_2)_2SAuX/(PhCH_2)_2SAuX_3$
$(n\text{-}Bu_2NCS_2)AuCl$	$[(n\text{-}Bu_2NCS_2)_2Au]^+[AuCl_2]^-$
(dmg)AuCl	$[(dmg)_2Au]^+[AuCl_2]^-$

Much debate has centered around a compound $AuCl_2$ reported by Thomson (*104*) and disputed by Krüss and Schmidt (*58*) in the late 19th century. Though Brewer (*19*) cited evidence for $AuCl_2(g)$ at high temperatures, the phase diagram and powder-pattern studies (*27*) of the solid did not support this. Finally the reaction of $AuCl_3$ and Au(CO)Cl in an inert atmosphere was reported (*28*) to form black crystalline $AuCl_2$, which was diamagnetic and had a powder pattern different from both AuCl and $AuCl_3$ (*48*). The X-ray structure analysis (*21, 29*) of this compound shows it to be a Au(I)–Au(III) mixed-valence compound with the tetranuclear formula Au_4Cl_8 and adopting a chair-like arrangement, in which the Au(I) is almost linearly coordinated and the Au(III) has a slightly distorted planar four-coordinate structure (Fig. 10). The distance between two Au(I) centers is 3.095 Å, as compared to 2.884 Å in the metal (*74*) and to the Au–Au mean distances (2.98 and 3.02 Å) between peripherial gold atoms in some clusters (*11, 12*).

The electrical conductivity and conductivity activation energy was

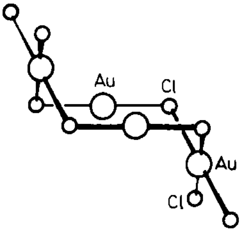


FIG. 10. Molecular structure of Au_4Cl_8, as determined by X-ray diffraction (*29*).

measured for the mixed-valence compounds $(PhCH_2)_2SAuCl_2$ and $(PhCH_2)_2SAuBr_2$ at pressures up to 360 kbar. The results indicate an enhancement of the conductivity in the range of 100–250 kbar attributed to the compression along the metal–halogen chains leading to nearly equivalent coordination environments for the metal atoms. Similar observations have previously been made with $Cs_2Au_2Cl_6$ (*45, 52*).

C. GOLD(II) SPECIES AS REACTION INTERMEDIATES

Evidence for the existence of a true mononuclear Au(II) complex was first provided in 1954 by Rich and Taube (*79*), who, on the basis of kinetic evidence, proved the transient existence of $[AuCl_4]^{2-}$ in aqueous solution, as a reaction intermediate in the Fe(II)-catalyzed exchange of a radioactive Cl^- with $[AuCl_4]^-$ [Eq. (2)].

$$Fe^{2+} + [AuCl_4]^- \rightarrow Fe^{3+} + [AuCl_4]^{2-} \qquad (2)$$

The $[AuCl_4]^{2-}$ is destroyed by disproportionation. It should be noted that kinetic data do not establish the formula of the unstable species; however, $[AuCl_3]^-$ is a possible alternative.

Some reactions involving oxidation of Au(I) to Au(III) complexes are thought to occur by free-radical mechanisms, and Au(II) intermediates are proposed. Thus, oxidation of $MeAu(PMe_3)$ (*97*) by CF_3I to give $MeAuI(CF_3)(PMe_3)$ proceeds through the formation of $MeAu(CF_3)(PMe_3)$ (*49*), and the reaction of $MeAuPMe_3$ with PhSH perhaps involves the Au(II) intermediate $MeAu(SPh)(PMe_3)$ (*50*). In all these cases, Au(II) species are not sufficiently long-lived to be detected directly. However, the oxidation of $[Au(S_2CNEt_2]_2$ by $(Et_2NCS_2)_2$ to form $Au(S_2CNEt_2)_3$ involves the Au(II) species $Au(S_2CNEt_2)_2$, which is sufficiently stable to be detected by ESR methods (*106*) (Section IV,4).

D. MONONUCLEAR GOLD(II) COMPOUNDS

1. *Phthalocyanine Complex of* Au(II)

Phthalocyanine is a divalent ligand with a geometry appropriate for forming a four-coordinated square-planar complex and was thought ideal for generating an Au(II) species. The action of AuBr on molten 1,3-diiminoisoindoline in the absence of solvent indeed yields a neutral gold phthalocyanine (*63*). The EPR spectra of the complex in 1-chloronaphthalene at 77 K clearly showed the presence of Au(II), a d^9 ion. The g value is 2.065, comparable to 2.042 for copper and 2.093 for silver phthalocyanine (*64, 80*).

2. *Carborane Complex of* Au(II)

A sandwich-bonded complex of Au(II) using the (3)-1,2-dicarbollide ligand, $B_9C_2H_{11}^{2-}$, has been prepared (*119*) by the sodium amalgam reduction of $(Et_4N)\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Au\}$ in THF. The isolated complex $(Et_4N)_2\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Au\}$ is deep blue-green and paramagnetic ($\mu_{eff} = 1.79\ \mu_B$) consistent with a d^9 ($s = \frac{1}{2}$) formulation. Its structure was proposed as in Fig. 11, in analogy to that of the Cu(II) complex, for which an X-ray analysis is available.

3. *Dithiolate and Related Complexes of* Au(II)

The reaction between the gold(I) *N,N*-dialkyldithiocarbamates and the corresponding thiuram disulfides [Eq. (3)] is a slow process (*1*).

$$[Au(S_2CNR_2)]_2 + 2(R_2NCS_2)_2 \rightarrow 2\ Au(S_2CNR_2)_3 \tag{3}$$

However, ESR experiments showed that, while the above reactants dissolved separately in C_6H_6 gave no signals, on mixing them four lines

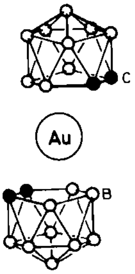
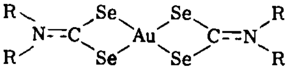


FIG. 11. Proposed structure of the anion in $[(C_2H_5)_4N]_2[Au(B_9C_2H_{11})_2]$. Hydrogen atoms are omitted (*119*).

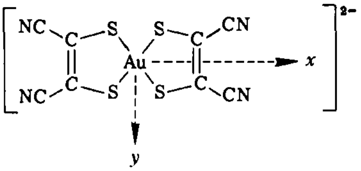
of equal intensity appeared (*106*). The observed *g* value of 2.040 is close to those of Cu(II) and Ag(II) compounds, providing strong evidence for the existence of a Au(II) complex. The hyperfine structure is consistent with the nuclear spin of ^{197}Au ($I = \frac{3}{2}$). The same spectrum is also obtained by dissolving $Au(S_2CNR_2)_3$, due to the equilibrium

$$Au(S_2CNR_2)_3 \rightleftharpoons Au(S_2CNR_2)_2 + 0.5(S_2CNR_2)_2 \qquad R = C_2H_5, i\text{-}C_3H_7 \tag{4}$$

A similar reaction involving the *n*-butyldithiocarbamate ligand, $n\text{-}Bu_2NCS_2$ (*15*), was studied, and a four-line ESR spectrum with a *g* value of 2.039 was again obtained, indicating the presence of Au(II) in the reaction mixture. The existence of a corresponding dialkyldiseleno carbamate derivative $Au(Se_2CNEt_2)_2$, as a product of disproportionation of $Au(Se_2CNEt_2)_3$, has been confirmed by ESR spectroscopic methods (*54*):



Waters and Gray (*120*) prepared a monomeric and paramagnetic Au(II) complex, $(n\text{-}Bu_4N)_2[Au(mnt)_2]$ (**2**) by the borohydride reduction of the corresponding Au(III) complex.



2

The solid is not affected in the presence of air for short periods, but the solution is easily oxidized. However, in the absence of air, the solution is stable indefinitely. The observed magnetic moment ($\mu_{eff} = 1.85\ \mu_B$) and four equally spaced, equally intense lines in the ESR spectrum clearly establish the divalent state for Au. The conductivity, electronic spectra, and cyclovoltammetry results corroborate this conclusion. The structure is suggested to be square planar (**2**). The same compound is also formed (*121*) by reacting equimolar amounts of Au(I) and Au(III) with the ligand $(mnt)^{2-}$ [Eq. (5)].

$$Au(I) + Au(III) \rightarrow 2\ Au(II) \tag{5}$$

As reactants, the Au(I)–Au(III) mixed-valence compounds $(PhCH_2)_2SAuX \cdot (PhCH_2)_2SAuX_3$ (X = Cl, Br), $n\text{-}Bu_4NBr$, and $Li_2(mnt)$ were employed. This reaction, however, does not take place with a variety of other sulfur ligands and appears to be typical for the $(mnt)^{2-}$ ligand.

Some Au(II) complexes of dithiocarbamate ligands are easily cocrystallized with the stable, diamagnetic nickel(II) complexes $[Ni(S_2CNR_2)_2]$, and the EPR spectra of an oriented magnetically dilute sample can be obtained (*109–111*). In some cases, the spectra showed the anomalous feature of having weak satellites outside the main four-line pattern, which was unequally spaced. However, the results of intensive ESR spectral investigations of the square-planar complex $[Au(mnt)_2]^{2-}$ in magnetically dilute single crystals of $[Ni(mnt)_2][n\text{-}Bu_4N]_2 \cdot 2CH_3CN$ and $[M(mnt)_2][n\text{-}Bu_4N]_2$ (M = Ni, Pd, Pt) over a range of temperature (*82*) are consistent with a ground-state hole configuration $(B_{1g})^2(A_{1g})^1$ in D_{2h} symmetry, where A_{1g} is primarily a ligand-based orbital with 15% 6s and smaller 5d admixtures, and B_{1g} is the normally half-filled antibonding orbital in square-planar d^9 complexes. Thus, this complex is best described as an Au(III) complex with a radical-anion ligand. Possibly, the inability of most ligands to form such a structure explains the rarity of formal Au(II) complexes.

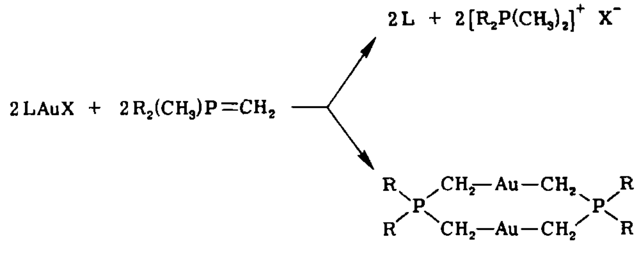
In addition to the $[Au(S_2CNR_2)_2]$ and $[Au(mnt)_2]^{2-}$ complexes discussed above, good chemical and structural evidence is also provided for the formation of the mixed complex $[(S_2CNEt_2)Au(mnt)]^-$ in solution, by electrochemical reduction of $[Au(S_2CNEt_2)(mnt)]$ (*107*). The pseudo-Au(II) complexes $[(Ph_3E)Au(mnt)]$(E = P, As) have been reported by Bergendahl and Waters (*14*), who pointed out their relationship to the authentic $[Au(mnt)_2]^{2-}$ system. They have been, however, reassigned as $[(Ph_3P)_2Au]^+[Au(mnt)_2]^-$, a mixed Au(I)–Au(III) complex (**1**, see Section IV,B). The magnetic susceptibility and ESR measurements on the π-donor–acceptor compound $(TTF) \cdot Au[S_2C_2(CF_3)_2]_2$ (TTF = tetrathiafulvalene) exhibit (*46, 47*) spin Peierls transitions (which is a progressive spin–lattice dimerization occurring below a transition temperature in a system of one-dimensional antiferromagnetic Heisenberg chains) in agreement with a mean-field theory.

In certain gold-containing arsenopyrite ores, FeAsS, a narrow isotropic singlet with a *g* value of 2.001 has been observed in the ESR spectrum (*114*). The signal was reduced on lowering the temperature and was absent in samples not containing Au. The reason for the appearance of the EPR signal seems to be the isomorphic admixture of Au(0) and ions of Au(II) in the lattice. Thus, it appears that Au(II) is stabilized by S-donor ligands.

E. BINUCLEAR GOLD(II) COMPOUNDS CONTAINING A METAL–METAL BOND

In addition to the complexes containing a single Au(II) center, a number of binuclear gold(II) complexes have been synthesized by

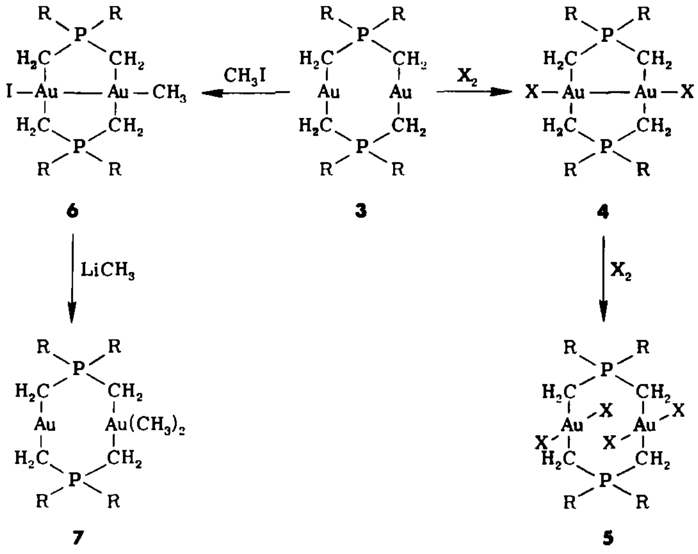
Schmidbaur and co-workers (*83–90a, 92, 93*). In cyclic gold–ylide complexes (**3**), formed by a transylidation reaction (*87*), the two Au atoms have a parallel two-coordinate linear arrangement of ligands [Eq. (6)].



(R = alkyl; X = halogen;
L = phosphine)

(6)

On reaction with halogens, compound (**3**) affords bicyclic derivatives (**4**) having a *transannular Au–Au bond* (*87*). On treatment with CH_3I, oxidative addition proceeds to give the product (**6**), which on methylation yields (**7**) (*71, 88*).



(X = Cl, Br, I;
R = Me, Et, *t*-Bu)

(7)

Further halogenation of the dihalides (**4**) finally results in the rupture of the Au–Au bond to give the Au(III) metallocycles (**5**).

The Mössbauer and ESCA spectra (*89*) confirm the different valence states of the gold atoms in the products (**4**) and (**5**) (see also *8, 24, 34, 35, 116*). The PMR as well as the mass spectra also favor the structure

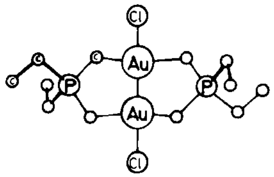
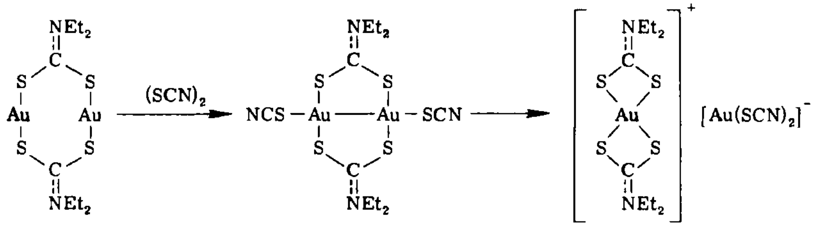


FIG. 12. Molecular structure of $(C_2H_5)_2P[CH_2Au(Cl)CH_2]_2P(C_2H_5)_2$, by X-ray diffraction; see (4) in Eq. (7). Hydrogen atoms are omitted (*90*).

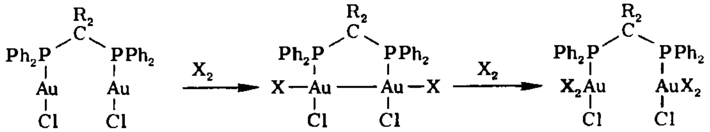
(4). Four X-ray crystal structure analyses (*71, 90, 90a, 91a*) afforded final proof for the proposed formulas. In (4), the two metals of formal oxidation state +2 are separated by a very short distance of 259.7 pm for X = Cl and R = C_2H_5, or 2.67 pm for X = I and R = CH_3 (Figs. 12 and 13). A related sulfur compound is obtained from **3** and thiuramdisulfide (**4**, X = S_2CNR_2) (*88a*).

Another example of an eight-membered metallocycle containing Au(II) centers is the dithiocarbamate complex (**9**) (*20*), obtained from the gold(I) dithiocarbamate complex (**8**) with halogens or pseudohalogens at −78° in CS_2. However, these compounds disproportionate to form mixed-valence salts (**10**). It was shown that the ν_{CN} band of the coordinated dithiocarbamate is sensitive to the oxidation state of the gold, increasing in the order 1495, 1523, and 1547 cm^{-1} for the Au(I), Au(II), and Au(III) complexes, respectively (*20*).



8 **9** **10** (8)

Oxidative addition of halogens to the 1:2 complexes of bis(diphenylphosphino)methane or -propane with gold(I) chloride (**11**) forms the Au(II) complexes (**12**) (*93*).



11 **12** **13**

(X = Cl, Br; R = H, CH_3) (9)

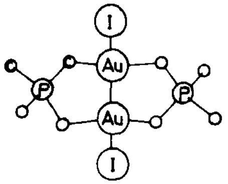
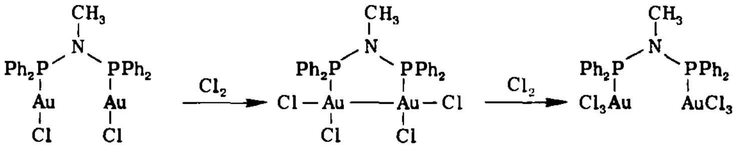


FIG. 13. Molecular structure, by X-ray diffraction, of $(CH_3)_2P[CH_2Au(I)CH_2]_2P(CH_3)_2$; see (4) in Eq. (7). Hydrogen atoms are omitted (*71, 84*).

A compound of bis(diphenylphosphino)methylamine (**15**) (*92*) is prepared similarly. The compound (**15**) adds one more mole of Cl_2 and is oxidized to the Au(III) complex (**16**) (*92*). The ^{197}Au Mössbauer spectra and ESCA measurements indicate that the complexes (**12**) and (**15**) are not mixed Au(I)–Au(III) complexes. The Au(II) appears to be present again as the Au_2^{4+} moiety. Because of the insolubility of the compounds (**12**) and (**15**), no molecular mass could be determined. Oligomeric formulas are therefore possible (*92, 93*).



14 **15** **16** (10)

V. Compounds of Gold in Oxidation State +5

The chemistry of gold in this oxidation state is limited to the binary fluoride AuF_5 and salts or complexes of the hexafluoroaurate(V) anion AuF_6^-. Until the end of the 1960s, the highest established oxidation state of gold was the trivalent state. The existence of PtF_6 and salts of PtF_6^- with the usual predictable periodic trends did suggest, however, the possibility of the synthesis of gold(V) compounds (*4, 5*). Attempts to prepare AuF_5 or AuF_6 directly from the elements failed (*5, 6*), but these efforts resulted in the isolation of a material, the analysis of which indicated at least an oxidation state higher than gold(III).

It is generally true that a given high oxidation state is thermodynamically more stable in an anionic species than in a binary compound (*4*). Many of the experimental observations are compatible with the electronegativity of the metal atom in the complex anion being appreciably lower than in the corresponding binary compound (*73*). The first successful approach to the synthesis of gold compounds of higher oxidation state by Bartlett (*5, 6, 59*) therefore emphasized the generation of gold-containing fluoroanions.

A. HEXAFLUOROAURATES(V)

In a pioneering experiment (*59*), AuF_3 was shown to react with XeF_2 at 400°C in an atmosphere of gaseous fluorine at 1000 p.s.i. to form pale yellow crystals of the empirical formula $AuXe_2F_{17}$, later identified as $[Xe_2F_{11}]^+[AuF_6]^-$. XeF_6 is probably formed as an intermediate, and is known to offer excellent conditions for the generation and complexation of metals in high oxidation states (*7, 59, 96, 98*).

$$2XeF_2 + 5F_2 + AuF_3 \rightarrow Xe_2F_{11}^+AuF_6^- \qquad (11)$$

The Raman spectrum of the product is similar to that of $[Xe_2F_{11}]^+[AsF_6]^-$, implying the existence of an $[AuF_6]^-$ salt. The crystal structure of the compound was determined by X-ray diffraction, and the result is shown in Fig. 14. The analysis clearly defines an AuF_6 and a Xe_2F_{11} group, the latter consisting of two XeF_5 moieties linked by an additional fluorine atom. All three components possess mirror symmetry. The AuF_6 group is approximately octahedral, with only one Au—F distance (of 1.90 Å) departing significantly from the average value of 1.86(1) Å. The F—Au—F angles are close to 90° (*60, 61*).

The pentafluoroxenyl(VI) salt $XeF_5^+AuF_6^-$ is obtained from the $Xe_2F_{11}^+AuF_6^-$ compound on heating to 110°C under vacuum. It is easily purified by sublimation, yielding a pale yellow-green solid, m.p. 190–192°C, reacting explosively with water. The crystals are monoclinic, space group $P2_1/c$ (*5*). The ^{19}F NMR spectra of $XeF_5^+AuF_6^-$ in HF and of $Xe_2F_{11}^+AuF_6^-$ in BrF_5 establish a chemical shift of the anion at $\delta = 109$ ppm (rel. $CFCl_3$). No coupling to the ^{197}Au nucleus is observed (*5, 41*). The spectra also prove the diamagnetism of the material, in harmony with a low-spin d^6 (t_{2g}^6) configuration for Au(V), well separated energetically from any paramagnetic excited state.

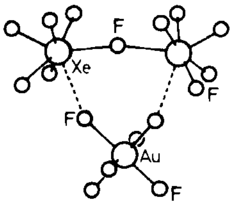


FIG. 14. Molecular structure of $Xe_2F_{11}^+AuF_6^-$, as determined by X-ray diffraction (*61*).

A cesium salt $Cs[AuF_6]$ is obtained if a slight deficiency of CsF is mixed with the above $Xe_2F_{11}^+$ salt and heated to 110°C, when XeF_6 is evolved.

$$[Xe_2F_{11}]^+[AuF_6]^- + CsF \rightarrow Cs[AuF_6] + 2XeF_6 \tag{12}$$

The resulting pale-yellow product has an X-ray powder pattern virtually identical with those of other complex fluorometallates $Cs[MF_6]$ (*59*). Its rhombohedral cell (a = 5.24 Å, α = 96.5°) is isomorphous with that of noble metal congeners. The same material was later also prepared from $Cs[AuF_4]$ and elemental fluorine at 250–350°C under 1000 p.s.i. pressure (*5, 61*). The Raman spectra have been assigned on the basis of an octahedral structure of the anion (*5*). The ^{197}Au Mössbauer spectra of the cesium salt, of $Xe_2F_{11}^+AuF_6^-$, and of $XeF_5^+AuF_6^-$ show only a singlet absorption without quadrupole splitting as expected for an octahedral environment of the metal. The isomeric shift of about 2.30 mm sec^{-1} suggests a high oxidation state (*51*).

The related potassium salt, $K[AuF_6]$, was prepared similarly from $K[AuF_4]$ and has very similar X-ray and Raman characteristics (*5*). A sodium salt is mentioned in a paper on AuF_5. Addition of NaF to this binary fluoride yields $Na[AuF_6]$, which was characterized by its vibrational frequencies (*100*). CsF gives the same reaction.

Salts of the nitrosyl cation NO^+ and the dioxygenyl cation O_2^+ are also accessible through fluorination of $NO[AuF_4]$, or from AuF_3, oxygen, and fluorine, under pressure at 350 and 500°C, respectively (*5*). The nitrosyl salt decomposes at 400°C to yield the starting materials, $NO^+[AuF_4]^-$ and F_2. The powerful oxidizing properties of the O_2^+ salt are shown in the reaction with IF_5, which leads to the new hexafluoroaurate(V) $IF_6^+AuF_6^-$, with AuF_3 and molecular oxygen. With the fluorobase IF_7, the same salt is generated, with O_2F as the byproduct (*5*):

$$3IF_5 + 4O_2^+AuF_6^- \rightarrow 3IF_6^+AuF_6^- + 4O_2 + AuF_3 \tag{13}$$

$$IF_7 + O_2^+AuF_6^- \rightarrow IF_6^+AuF_6^- + O_2F \tag{14}$$

The magnetic moment of $O_2^+AuF_6^-$, $\mu = 1.66\ \mu_B$, indicates the presence of one unpaired electron. The susceptibility data depart only slightly from the Curie–Weiss relationship. X-Ray powder and Raman data are also available (*5*), and molecular-beam mass spectra have been recorded (*31*).

$NO^+AuF_6^-$ is also the product of the addition of NOF to the binary AuF_5 to be described in Section V,C (*41*). The O_2^+ salt is obtained from $KrF^+AuF_6^-$ (see Section V,B) and molecular oxygen (*41*). A series of other complex fluoroaurates(V) of Kr, Xe, and Br is again derived from AuF_5.

B. FLUOROKRYPTYL(II) HEXAFLUOROAURATE(V)

The compound FKr—AuF_6 is treated separately because it appears to be a hexafluoroaurate less ionic in nature than the salts considered in the preceding section. It also plays a key role in the synthesis of many other Au(V) species, in particular the pure binary AuF_5. The compound was prepared by three independent groups in the U.S.A., the United Kingdom, and the U.S.S.R.

On the basis of theoretical considerations, Bartlett postulated the existence of $FKr^+AuF_6^-$ and even of $FAr^+AuF_6^-$, for which an electron transfer from anion to cation should be an energetically unfavorable process (*5*). Holloway and Schrobilgen carried out the reaction of KrF_2 with gold powder in liquid HF at 20°C and obtained a light yellow solid after removal of excess KrF_2 and HF *in vacuo.* The Raman spectrum of the product (under HF at −80°C) is consistent with a formulation in which a KrF group is fluorine bridged to an AuF_6 group (of approximate C_{4v} symmetry).

$$7KrF_2 + 2Au \rightarrow 2F\text{-}Kr\cdots FAuF_5 + 5\ Kr \qquad (15)$$

The compound reacts rapidly with molecular oxygen to yield $O_2^+AuF_6^-$. Gaseous xenon is converted into $XeF_5^+AuF_6^-$ and an unidentified red-orange product. Pyrolysis at 60–65°C yields pure AuF_5 (*41*).

Sokolov *et al.* (*100*) treated gold foil with KrF_2 dissolved in anhydrous HF at 0–20°C. Again, bright yellow crystals of $KrF_2 \cdot AuF_5$ were obtained, stable to 50°C. At 65–67°C, rapid decomposition is observed into gaseous fluorine and krypton, and solid AuF_5. With a large excess of KrF_2 and at low temperature, a compound of the composition $2\ KrF_2 \cdot AuF_5$ is observed, which is unstable even at 0°C, decomposing rapidly into $KrF_2 \cdot AuF_5$ (*100*).

Infrared absorptions for $KrF_2 \cdot AuF_5$ and $2KrF_2 \cdot AuF_5$ have been reported. They suggest reduction of the octahedral symmetry of the AuF_6 group to C_{4v} of C_{2v}, probably caused by fluorine bridging. The oxidation state +5 of gold was confirmed by Mössbauer spectra (*100*). $FXe\cdots FAuF_5$ and $Xe_2F_3^+AuF_6^-$ are obtained from AuF_5 and XeF_2.

C. GOLD PENTAFLUORIDE

AuF_5 is displaced from $Xe_2F_{11}^+AuF_6^-$ by SbF_5 (in liquid SbF_5). A mixture of $XeF_5^+Sb_2F_{11}^-$ and $XeF_5^+AuSbF_{11}^-$ is obtained, but no separation is possible (*5*). (SbF_5 and AuF_5 appear to undergo codistillation.) Pure AuF_5 is easily obtained, however, from the pyrolysis of $KrF_2 \cdot AuF_5$ at 60–65°C as a dark red-brown solid (orange when powdered). Its X-ray powder patterns show that no AuF_3 is present, and suggest similarities to the structure of the (tetrameric) RuF_5. Three bands are observed in the room-temperature Raman spectrum (658, 598, and 228 cm^{-1}). The compound reacts with excess XeF_2 in HF or BrF_5 to give $Xe_2F_{11}^+AuF_6^-$. Addition of NOF yields $NO^+AuF_6^-$ (*41*).

Sokolov *et al.* (*100*), who also obtained pure AuF_5 from the pyrolysis of $KrF_2 \cdot AuF_5$ at 65–67°C, describe the product as a red-brownish crystalline material, vigorously hydrolyzed in moist air. It is reported to sublime at 80°C, to undergo a polymorphic transformation at 120–125°C, and to decompose quantitatively above 200°C into AuF_3 and F_2 without melting. Organic compounds are fluorinated explosively (*100*). The infrared spectrum was presented in a figure, showing bands at positions similar to those given above. A structure resembling that of α-UF_5 was deduced. Nonequivalence of the fluorine atoms is confirmed by the presence of quadrupole splitting in the Mössbauer spectrum (*100*).

AuF_5 forms a complex acid $HAuF_6$ of m.p. 88°C. The species $KrF_2 \cdot AuF_5$, $2KrF_2 \cdot AuF_5$, $XeF_2 \cdot AuF_5$, $2XeF_2 \cdot AuF_5$, and $XeF_6 \cdot AuF_5$ are obtained with KrF_2, XeF_2, and XeF_6, respectively. Br_2 yields $AuF_3 \cdot BrF_3$, and BrF_5 yields $BrF_5 \cdot AuF_5$, from which $BrF_7 \cdot AuF_5$ is generated with KrF_2 in BrF_5 (*100*).

In a third independent study (*112, 113*), amorphous AuF_5 was synthesized by thermal decomposition of $O_2^+AuF_6^-$ *in vacuo* at 160–200°C. A dark red sublimate, formed at a cold finger, melts over the range 75–78°C. (Note the difference from the above reports.) The magnetic susceptibility of $-73 \pm 15 \times 10^{-6}$ emu mol^{-1} agrees well with the value expected for the diamagnetic species. Raman lines were observed at 654, 595, and 219 cm^{-1}. Mass spectra of AuF_5 show Au/F clusters with up to three Au atoms, but no molecular ion AuF_5^+ is detected. The material used in this study also reacts with XeF_2 in liquid HF to form $Xe_2F_3^+AuF_6^-$, isomorphous with $Xe_2F_3^+IrF_6^-$ according to X-ray powder photographs (*112*), and probably resembling the above-mentioned $2XeF_2 \cdot AuF_5$ (*100*).

Note added in proof. Since the submission of this review, the chemistry of gold clusters has developed very rapidly. A new type of hexatomic gold cluster with a structure consisting of two tetrahedra sharing a common edge was discovered: $Au_6(P(C_6H_5)_3)_4 \cdot (Co(CO)_4)_2$ (*107b*). An octatomic gold cluster derived from an icosahedron by selecting a set of apices different from those found in previous examples was detected in the cation $Au_8(P(C_6H_5)_3)_7^{2+}$ (*107a*). Degradation reactions of the $Au_9L_8^{3+}$ clusters by other ligands L, SCN^-, or CN^- to form $Au_8L_8^{2+}$, $Au_{11}L_8(SCN)_2^+$, or $Au_{11}L_8Cl_2^+$ cations have been studied in some detail. An intermediate $Au_8L_7^{2+}$ is postulated (*117a*). Most interesting, however, is the synthesis and structural characterization of examples with an Au_{13} cluster in the form of a gold-centered closed icosahedron of gold atoms. The individual species are $Au_{13}(P(CH_3)_2C_6H_5)_{10}Cl_2^{3+}$ (*19b*) and $Au_{13}(P(C_6H_5)_2CH_2P(C_6H_5)_2)_6^{4+}$ (*108a*). An even larger section of the gold metal lattice is preserved in the present record cluster of the formula $Au_{55}(P(C_6H_5)_3)_{12}Cl_6$ (*82a*). Gold clusters were also found in the ternary phase $Rb_4Au_7Sn_2$ (*97a*). Theoretical work on metal clusters including gold appears in two recent reviews (*35a, 67a*).

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